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Cincinnati OH 45268

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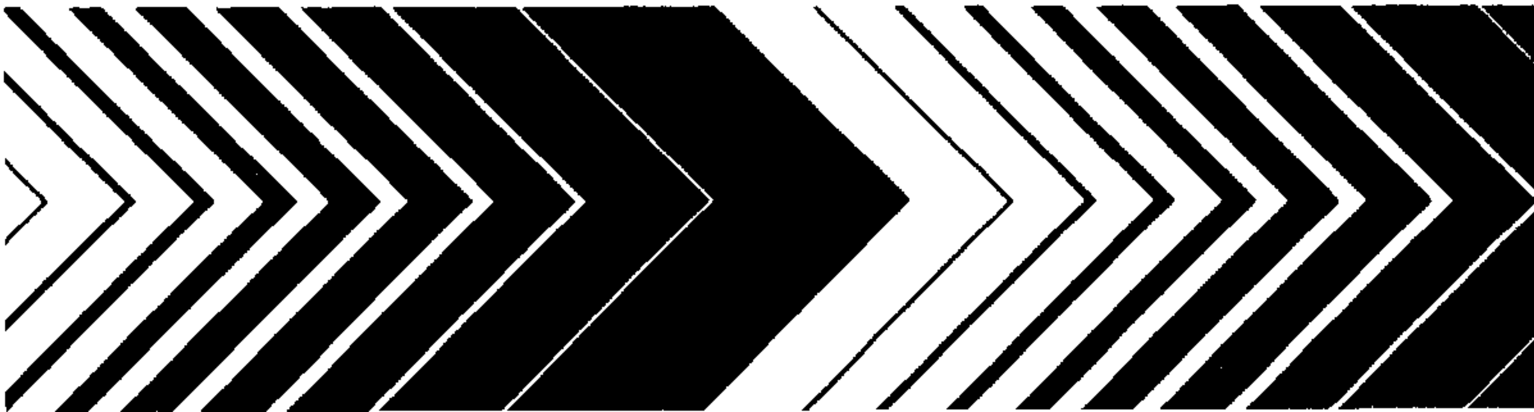
June 1980

Research and Development

EPA

Dioxins

Volume III. Assessment of Dioxin-Forming Chemical Processes



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2. Environmental Protection Technology
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7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

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June 1980

DIOXINS:
VOLUME III.
ASSESSMENT OF DIOXIN-FORMING CHEMICAL PROCESSES

by

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INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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DISCLAIMER

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a three-volume series dealing with a group of hazardous chemical compounds known as dioxins. The extreme toxicity of one of these chemicals, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), has been a concern of both scientific researchers and the public for many years. The sheer mass of published information that has resulted from this concern has created difficulties in assessing the overall scope of the dioxin problem. In this report series the voluminous data on 2,3,7,8-TCDD and other dioxins are summarized and assembled in a manner that allows comparison of related observations from many sources; thus, the series serves as a comprehensive guide in evaluation of the environmental hazards of dioxins.

Volume I is a state-of-the-art review of dioxin literature. Detailed information is presented on the chemistry, sources, degradation, transport, disposal, and health effects of dioxins. Accounts of public and occupational exposure to dioxins are also included. Volume II details the development of a new analytical method for detecting part-per-trillion levels of dioxins in industrial wastes. It also includes a review of the analytical literature on methods of detecting dioxins in various types of environmental samples. Volume III identifies various routes of formation of dioxins in addition to the classical route of the hydrolysis of chlorophenols. The possible presence of dioxins in basic organic chemicals and pesticides is addressed, and production locations for these materials are identified.

For further information, contact Project Officer David R. Watkins, Organic and Inorganic Chemicals Branch, IERL-Ci. Phone (513) 684-4481.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

PREFACE

This report is Volume III in a series of three reports dealing with a group of hazardous chemical compounds known as dioxins. This volume details the chemistry of dioxin formation, and identifies the types of organic chemicals and pesticides which may have dioxins associated with them as impurities or byproducts. Other volumes of this series examine the occurrence, environmental transport, toxicity, and disposal of this class of compounds, analytical techniques used to identify dioxins, and commercial products with potential for containing dioxin contaminants.

An extensive body of published literature has appeared during the past 25 years that has been concerned primarily with one extremely toxic member of this class of compounds, 2,3,7,8-tetrachlorodibenzo-p-dioxin. Often described in both popular and technical literature as "TCDD" or simply "dioxin," this compound is one of the most toxic substances known to science. This report series is concerned not only with this compound, but also with all of its chemical relatives that contain the dioxin nucleus. Throughout these reports, the term "TCDD's" is used to indicate the family of 22 tetrachlorodibenzo-p-dioxin isomers, whereas the term "dioxin" is used to indicate any compound with the basic dioxin nucleus. The most toxic isomer among those that have been assessed is specifically designated as "2,3,7,8-TCDD."

The objective in the use of these terms is to clarify a point of technical confusion that has occasionally hindered comparison of information from various sources. In particular, early laboratory analyses often reported the presence of "TCDD," which may have been the most-toxic 2,3,7,8-isomer or may have been a mixture of several of the tetrachloro isomers, some of which are relatively nontoxic. Throughout this report series, the specific term 2,3,7,8-TCDD is used when it was the intent of the investigator to refer to this most-toxic isomer. Since early analytical methods could not dependably isolate specific isomers from environmental samples, the generic term "TCDD's" is used when this term appears to be most appropriate in light of present technology.

ABSTRACT

Concern about potential contamination of products and wastes by dibenzo-p-dioxins in the production of organic chemicals and pesticides is the reason for this study of products and processes subject to such contamination. In addition, speculative consideration is given to other possible dioxin sources.

Chemical reaction mechanisms by which dioxins may be formed are reviewed, particularly those likely to occur within commercially significant processes. Various routes of formation are identified in addition to the classical route of the hydrolysis of trichlorophenol. Basic organic chemicals and pesticides with a reasonable potential for dioxin byproduct contamination are surveyed as to current and past producers and production locations.

Classifications are presented both for general organic chemicals and for pesticides that indicate likelihood of dioxin formation. Conditions are noted that are most likely to promote dioxin formation in various processes.

This report was submitted in fulfillment of Contract No. 68-03-2579, by Walk, Haydel & Associates, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 31, 1978, to March 16, 1980, and work was completed as of March 16, 1980.

CONTENTS

FIGURES

FIGURES (continued)

TABLES

LIST OF ABBREVIATIONS

DBDCDD's	dibromodichlorodibenzo-p-dioxins
DBDD's	dibromodibenzo-p-dioxins
DCDD's	dichlorodibenzo-p-dioxins
Dioxins	dibenzo-p-dioxins
DFDD's	difluorodibenzo-p-dioxins
DMSO	dimethyl sulfoxide
DNDD's	dinitrodibenzo-p-dioxins
Hexa-CDD's	hexachlorodibenzo-p-dioxins
Hepta-CDD's	heptachlorodibenzo-p-dioxins
OBDD	octabromodibenzo-p-dioxin
OCDD	octachlorodibenzo-p-dioxin
PCP	pentachlorophenol
Penta-CDD's	pentachlorodibenzo-p-dioxins
TBDD's	tetrabromodibenzo-p-dioxins
TCDD's	tetrachlorodibenzo-p-dioxins
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCP	trichlorophenol
Tri-CDD's	trichlorodibenzo-p-dioxins

ACKNOWLEDGMENT

This report was prepared by Walk Haydel & Associates, Inc. under the direction, contribution, and contract management of Forrest E. Dryden. Contributing authors included Harry E. Ensley, Ronald J. Rossi, and E. Jasper Westbrook.

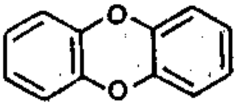
Final compilation of this report for integration into the three-volume dioxin series was done by PEDCo Environmental, Inc., Cincinnati, Ohio, with Mr. R. W. Gerstle as Project Director and Ms. M. Pat Esposito as Project Manager. Information on natural compounds as potential precursors of dioxins was provided by PEDCo Environmental, Inc.

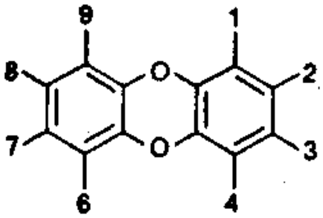
The cooperation of the many organizations and individuals who assisted in the collection, editing, and critiquing of this material is appreciated. Particular thanks to Robert J. Planchet, Jerome F. Pankow, and William J. Kimsey, Jr. for their contributions.

SECTION 1

INTRODUCTION

A dioxin is any of a family of compounds known chemically as dibenzo-para-dioxins. Each of these compounds has as a nucleus a triple-ring structure consisting of two benzene rings interconnected to each other through a pair of oxygen atoms. Shown below are the structural formula of the dioxin nucleus and also the abbreviated structural convention used throughout the report series.





Halogenated dibenzo-p-dioxins (dioxins), and in particular chlorinated dioxins such as 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), are known to be toxic even at low concentrations. Such contaminants have been found in a number of commercial organic chemical products, primarily pesticides of the 2,4,5-T type. For this reason an analysis was undertaken of the chemical products and processes likely to be conducive to the formation of dioxins. This report reviews the chemical mechanisms by which commercial organic processes might produce dioxins as byproducts and tabulates those chemicals likely to be associated with dioxins as a consequence. In addition, it lists known producer locations for such chemicals, indicating potential sources of current and past contaminated wastes.

In approaching this study, the investigators proceeded as follows.

1. Reviewed current theories on mechanisms of the formation of dioxins under various reaction conditions.

2. Tabulated reported laboratory preparations of dibenzo-p-dioxins.

3. Established criteria for structure and reaction conditions conducive to dioxin formation in chemical processing.

4. Postulated conditions under which dioxins might be formed other than in commercial chemical production.

5. Differentiated between pesticide chemicals and all other types of organic chemicals for purposes of this study.

6. Reviewed commercially significant chemicals, using as primary sources the Stanford Research Institute Directory of Chemical Producers, the Merck Index, The Farm Chemicals Handbook, and other reference materials.

7. Designated those products in which the chemical structures might indicate association with dioxins.

8. Further screened the list by consideration of reaction conditions, processing sequence, and intermediates.

9. Categorized general organic chemical products in three classes.

   Class I: strong likelihood of polyhalogenated dibenzo-p-dioxin association

   Class II: strong likelihood of other dioxin association

   Class III: moderate probability of dioxin association

10. Categorized the target pesticide chemicals as belonging in Class I or Class II.

11. Identified the dioxin compounds and formation mechanisms expected to be related to each Class I compound.

12. Listed known locations in the United States in which production occurs or has occurred in the past 10 years. The primary source was the Stanford Research Institute Directory of Chemical Producers covering the years 1968 through 1978.

Some recent regulatory restrictions on the use of some herbicides, such as 2,4,5-T and silvex, may result in curtailed production. This study does not address the effects of any such curtailment (e.g., production shutdowns).

Although there is a substantial range of toxicity among the various substituted dibenzo-p-dioxins, processes indicating potential for generation of the less-toxic forms are included for two reasons:

1. Dioxins other than those that might be hypothesized by straightforward mechanisms have been found in a number of commercial products (Fishbein 1973).

2. Disproportionation and other composition changes may cause shifts in content, possibly from lower to higher toxicity forms (Buser 1976).

Subjective judgement was exercised with respect to inclusion and classification of chemicals and processes. In addition, although every reasonable effort was made to avoid omissions, some are inevitable in view of the number of organic chemical compounds to be dealt with.

SECTION 2

CONCLUSIONS

1. Dibenzo-p-dioxins should be expected as byproduct trace contamination in a number of commercially manufactured organic chemicals. These include not only the frequently cited herbicides of the 2,4,5-T type, but also numerous other ortho halogenated phenols and related structures commonly made or used in organic chemical processing.

2. Processing conditions of elevated temperatures plus either alkalinity or the presence of free halogen--conditions often necessary for dioxin formation--are frequently encountered in the manufacture of these organic compounds.

3. The particular dibenzo-p-dioxins found as trace byproduct materials are often at variance with those anticipated on the basis of straightforward mechanisms. This variance is possibly due to mechanisms more complex than those that have been proposed or to disproportionation (shifting of halogens) of the initially produced halogenated dioxins.

4. Dioxin contamination resulting from the manufacture of many organic chemicals could follow either of two paths. First, it could appear as trace contamination of the finished chemical product; second, it could appear as a component of wastes from leakage, handling, purification, neutralization, and "off-spec" production. This report does not consider the formation of dioxins in subsequent consumptive uses.

5. Plant locations of present and past commercial production of potentially dioxin-associated chemicals are widespread over the United States.

6. Sites of exposure or contamination are not necessarily defined by production locations, because wastes are often dumped at sites remote from the production facility. Exact locations of disposal sites would require investigation of individual plant practices.

7. There is a variety of potential dioxin sources other than commercial production by syntheses of organic chemicals. Among these are laboratory preparation of dioxins in small quantities but high concentrations, and the combustion of mixed wastes containing potential dioxin precursors.

8. Reaction conditions ranging from temperatures as low as 145°C, and the presence of weak to strong bases acting on the organic and pesticide products can result in production of trace quantities of dioxins.

SECTION 3

THE CHEMISTRY OF DIBENZO-p-DIOXINS

Concern has recently arisen about the occurrence of trace quantities of halogenated dibenzo-p-dioxins (hereafter referred to as halogenated dioxins) and in particular 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in the environment. A study of the reported laboratory procedures for preparation of dioxins can serve as a guide to the chemical conditions that are most likely to lead to dioxin formation. This review of the literature is not limited to methods for the preparation of halogenated dioxins; rather it delineates the known procedures for the preparation of dioxins of any substitution pattern.

LABORATORY PREPARATIONS OF DIOXINS

The first report of intentional preparation* of this class of compounds occurred in 1872, when Merz and Weith described the preparation of "perchlorophenylenoxyd" by thermolysis of potassium pentachlorophenate (1).

Hugounenq (1890) reported that the treatment of pentachloroanisole (2) with concentrated sulfuric acid also gives "perchlorophenylenoxyd."

(1) (2)

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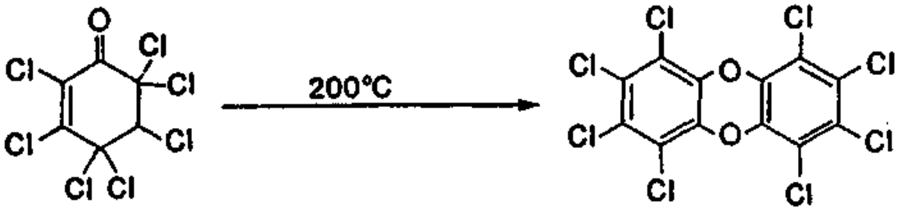
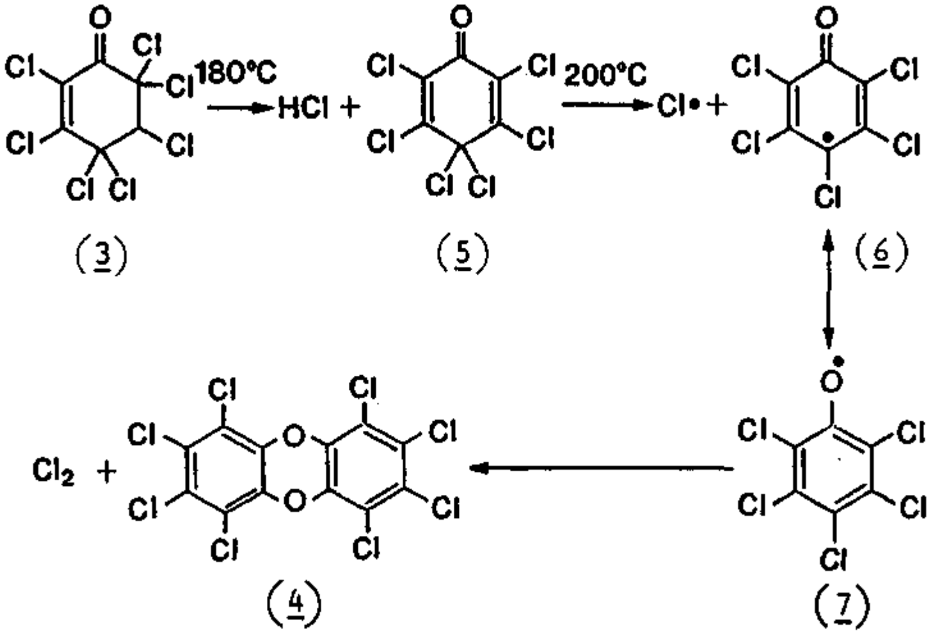
* According to scientists of Dow Chemical (Rawls 1979), dioxins have been prepared since "...Prometheus stole fire from the gods and brought it to mankind...".

Soon after these reports Zinke (1894) and Blitz (1904) showed that heating heptachlorohexenone (3) to 200°C gave "perchlorophenylenoxyd." Not until 1960 was it shown that "perchlorophenylenoxyd" is octachlorodibenzo-p-dioxin (OCDD)(4) (Denivelle 1960).



(3) (4)

The mechanism of the reactions reported by Zinke and Blitz remained unknown for over a half-century. In 1961 Kulka showed that heptachlorocyclohexenone (3) eliminates a molecule of hydrogen chloride at about 180°C to give hexachlorocyclohexadienone (5). Kulka proposed that this compound, on heating to 200°C, loses a chlorine radical to give the pentachlorocyclohexadienone radical (6) (or its resonance isomer, the pentachlorophenoxy radical (7)), which then dimerizes to give (4) and a molecule of chlorine.



(3) (5) (6) (4) (7)

The mechanism that Kulka proposed, supplemented with earlier work by Denivelle (1959, 1960), initiated numerous reports on the preparation of halogenated dibenzo-p-dioxins under neutral or acidic conditions. A number of these reactions are listed in Table 1.

Bayer (1903) patented a process for the preparation of dibenzo-p-dioxin (8) from sodium o-chlorophenylate (9). This procedure, which is an extension of the earlier work reported by Merz and Weith (1872), is based on

TABLE 1. PERHALO DIBENZO-p-DIOXINS VIA FREE RADICAL REACTIONS

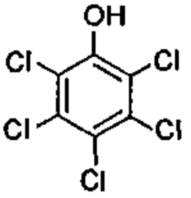
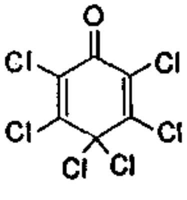
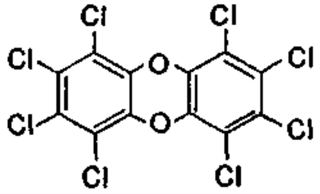
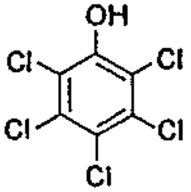
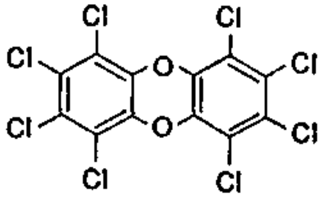
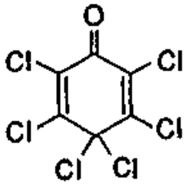
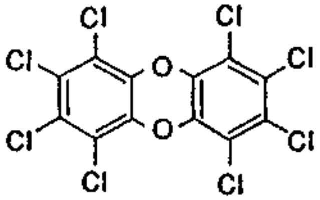
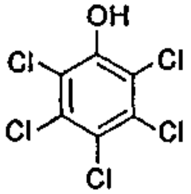
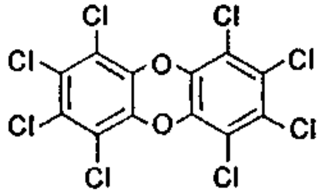
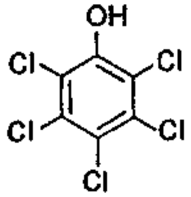
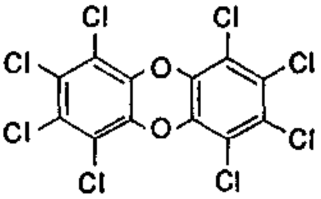
Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
①	 40 g +  10 g	250°-300°C 25 min		(83%)	b
②	 25 g + Cl_2	REFLUXING 1,2,4 TRICHLOROBENZENE 16 h	 18g	(83%)	c
③		270°-280°C 30 min	 11g	(73%)	c
④	 25 g + Br_2	1,2,4 TRICHLOROBENZENE REFLUX 16 h		(52%)	c
	 + I_2	1,2,4 TRICHLOROBENZENE REFLUX 16 h		(23%)	c

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TABLE 1 (continued)

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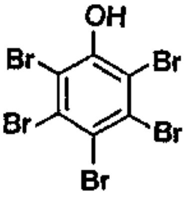
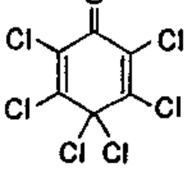
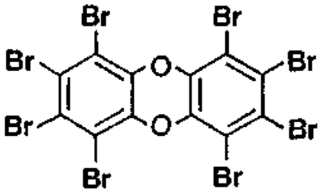
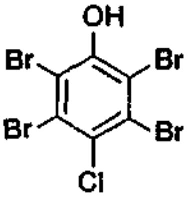
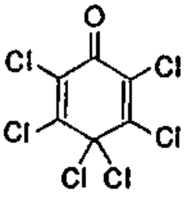
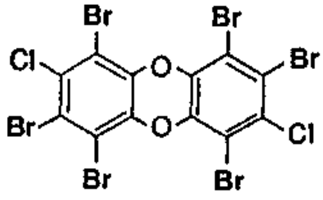
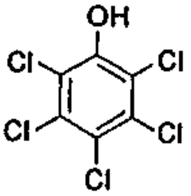
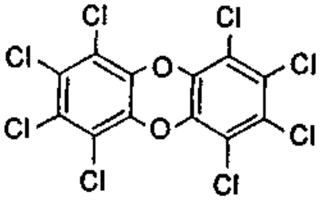
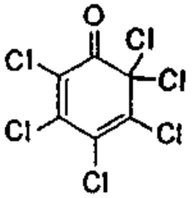
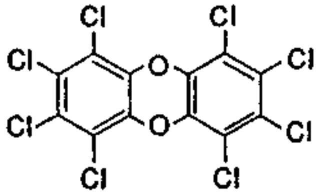
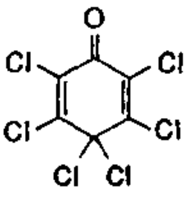
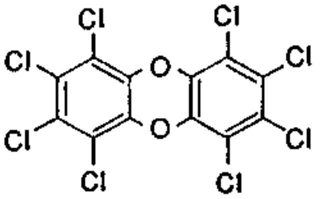
⑤	 35 g +  0.2 g (or Cl_2 or Br_2)	320°-360°C 35 min		(52%) (15g)	c
⑥	 30 g +  0.2 g (or Cl_2 or Br_2)	300°-350°C 30 min		(62%) (15g)	c
⑦		300°C		(4%) (POOR)	d e f
⑧		260°C			d
⑨		260°C			d

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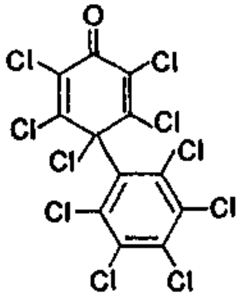
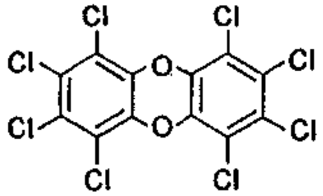
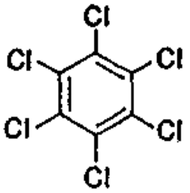
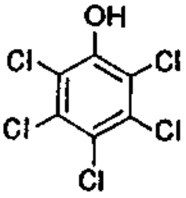
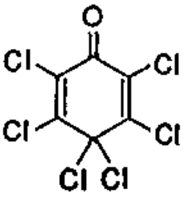
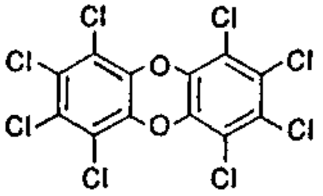
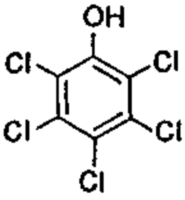
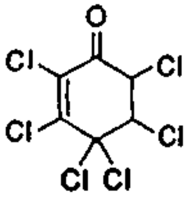
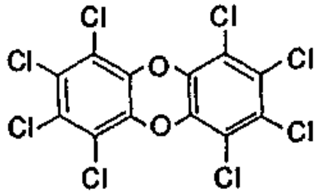
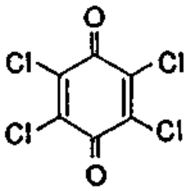
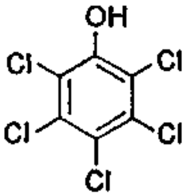
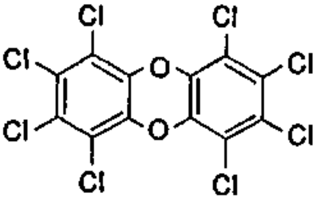
TABLE 1 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑩		260-280°C	 + 		d
⑪	 200 g +  75 g	120-200°C		(84%)	g
⑫	 222 g +  62 g	120-200°C		(80%)	g
⑬	 + 	270°C IN QUINOLINE			d

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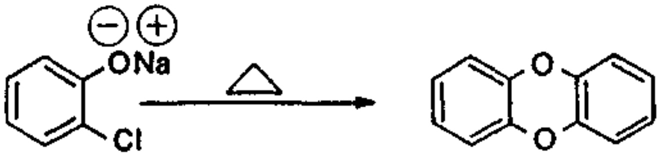
[a] If no yield is stated, no value is reported in reference.
[b] Kulka 1965.
[c] Kulka 1961.
[d] Denivelle, Fort, and Pham 1959.
[e] Gribble 1974.
[f] Sandermann, Stockmann, and Casten 1957.
[g] Kaupp and Klug 1962.

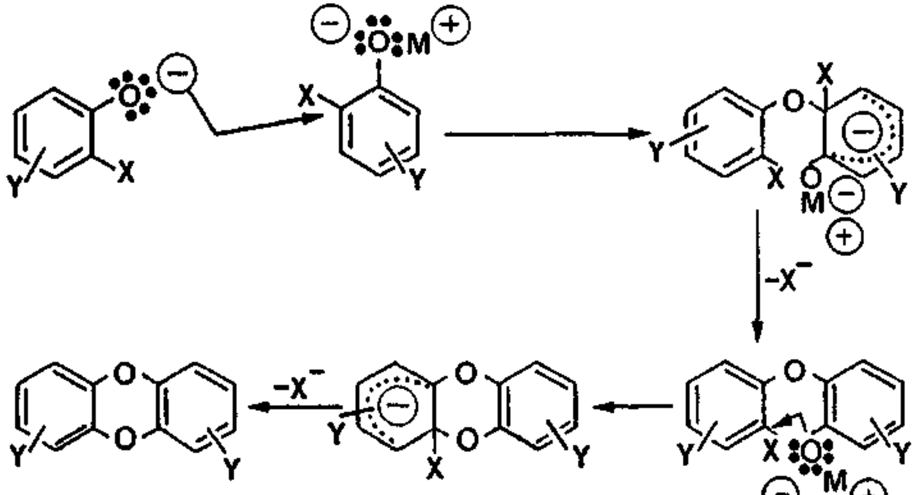


(9) (8)

Ullmann's preparation of diphenylamines (Ullman 1903) and generally referred to as a modified Ullman condensation (Aniline 1973). Although the yields of the modified Ullmann reaction rarely exceed 30 percent, this procedure was standard for the preparation of both substituted and unsubstituted dioxins until the early 1970's. Examples of the utilization of this process are given in Table 2, showing minor as well as major products of reaction, where applicable.

As the reactions in Table 2 show, dioxins have been formed from the alkali metal salts of ortho-halophenols through pyrolysis at temperatures of 200° to 300°C for several hours, usually in the presence of copper powder or copper salts. Entries 23 and 24 in Table 2 show that much milder conditions (pyridine as the base and a temperature of only 145°C for 2 to 3 hours) can give significant concentrations of dibenzo-p-dioxins (Ueda 1963).

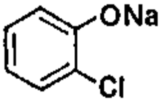
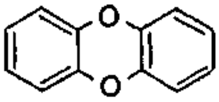
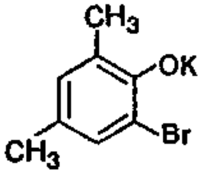
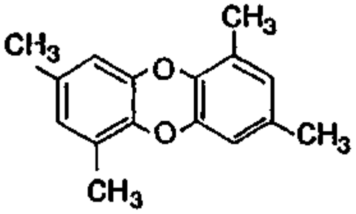
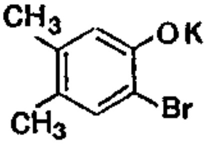
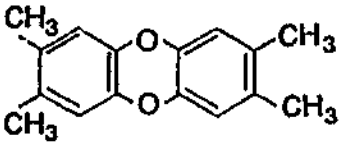
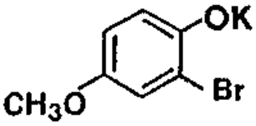
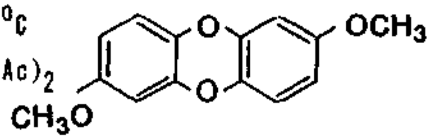
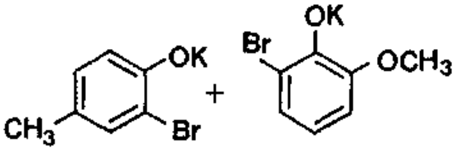
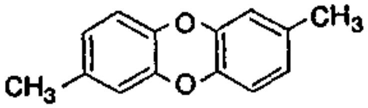
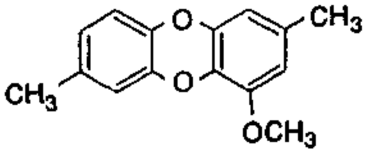
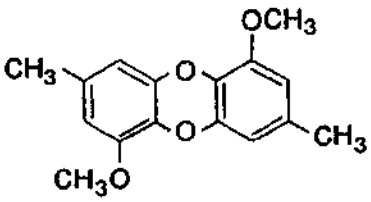
The mechanism for this type of reaction was generally believed to involve a nucleophilic attack of the phenoxy ion on a second phenolate ring (Buser 1975), followed by expulsion of the halide to give the o-halophenoxyphenate (10) (also known as predioxin). An intramolecular nucleophilic aromatic substitution followed by expulsion of a halide gives the dibenzo-p-dioxin (11).



(11) (10)

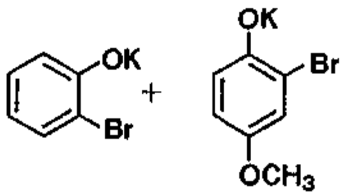
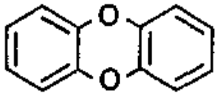
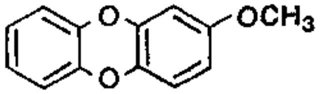
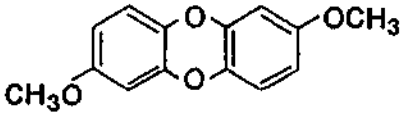
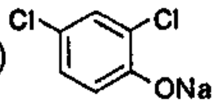
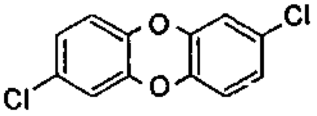
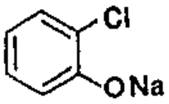
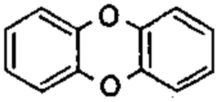
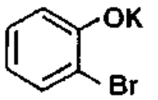
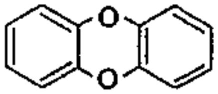
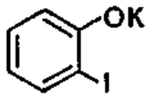
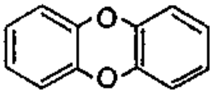
X=leaving group
(e.g. Cl, F, Br, I, NO_2, SO_3R)
M=alkali metal cation
Y=any substituent group

TABLE 2. ULLMAN CONDENSATION REACTIONS

Item	Reactant	Conditions	Product	(Yield)^{a}	Ref.
①		220°, 10 h		(25%)	b
②		190-200°C Cu, Cu(OAc)$_2$			c
③		190-200°C Cu, Cu(OAc)$_2$			c
④		190-200°C Cu, Cu(OAc)$_2$			c
⑤			  		d

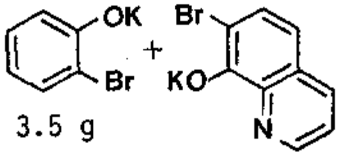
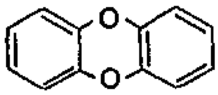
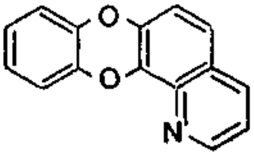
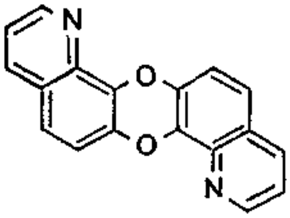
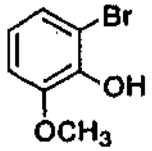
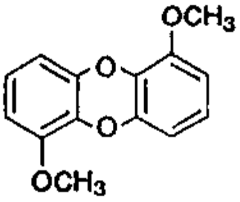
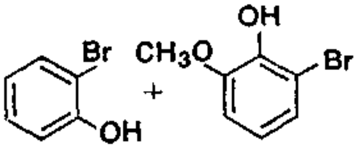
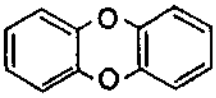
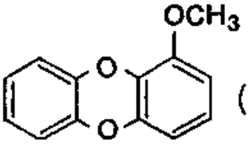
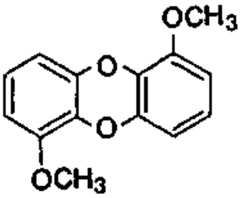
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑥			  		d
⑦		160°C Cu 1 h			e
⑧		160°C Cu 1 h			f
⑨		160°-220°C Cu, 110 min		(50%)	f
⑩	 6 g	200°C, Cu 3 h		(0.2g)	g

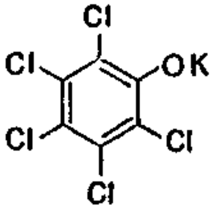
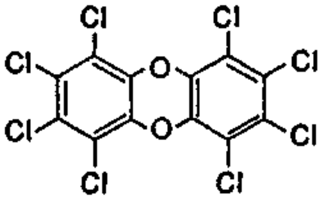
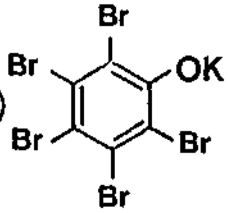
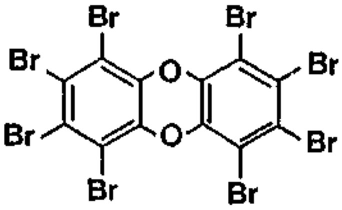
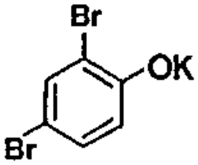
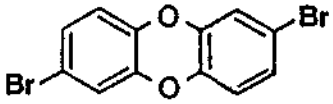
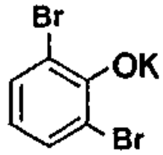
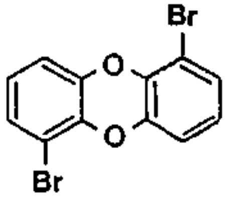
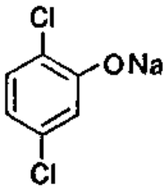
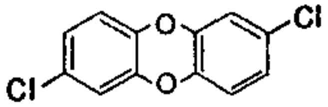
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑪	 3.5 g 4.5 g	190°C Cu 2 h		(0.09 g)	h,j
				(0.08 g)	
				(TRACE)	
⑫		180°C 30 min			g
⑬	 5.78 g 6.58 g	180°C KOH, Cu 30 min		(0.164 g)	k
				(0.287 g)	
				(0.132 g)	

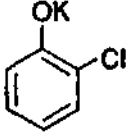
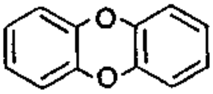
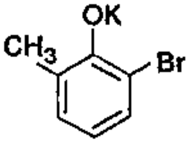
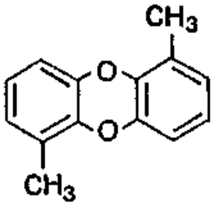
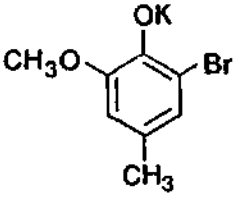
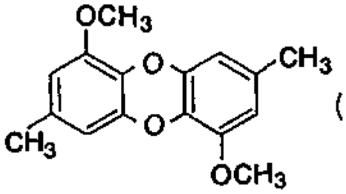
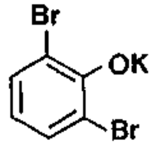
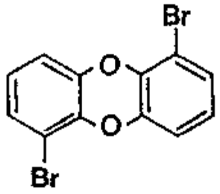
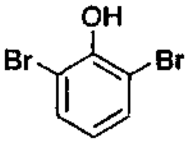
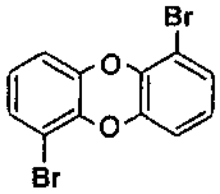
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	Yield^{a}	Ref.
⑭	 3.25 g	200°C Cu 2 h		(20 mg)	1
⑮	 3.15 g	200°C Cu 2 h		(40 mg)	1
⑯	 3.25 g	185°C Cu 1.5 h		(40 mg)	1
⑰	 1.75 g	180°C Cu 1.5 h		(40 mg)	1
⑱	 3.7 g	210°C 0.3g Cu 3 h		(0.9 g)	m

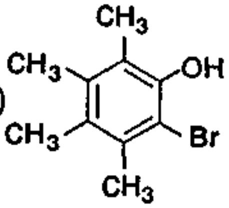
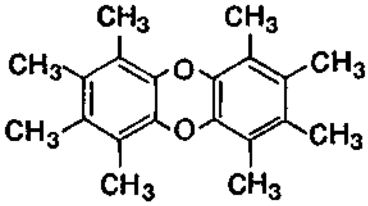
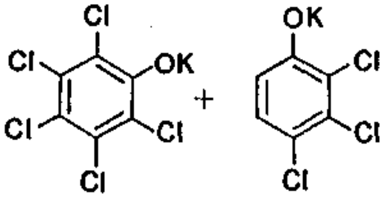
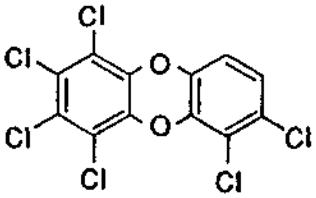
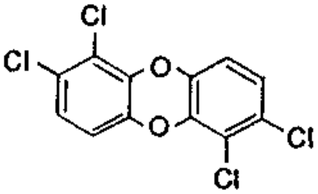
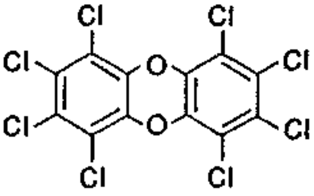
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑲		190^0C Cu 4 h		(25%)	m
⑳	 2 g	195^0C Cu POWDER 30 min		(60 mg)	n
㉑	 10 g	200^0C Cu POWDER, 1.5 h		(250 mg)	n
㉒	 6 g	190^0C Cu POWDER 1 h		(3.1 g)	o
㉓	 1 g	145^0C Cu POWDER, PYRIDINE 2.5 h		(10 mg)	o

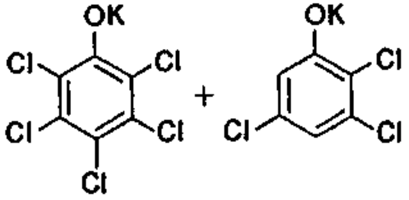
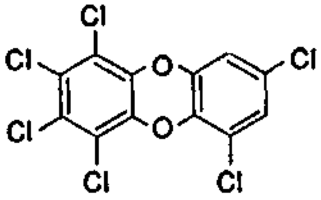
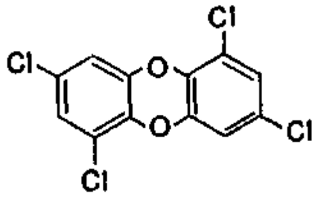
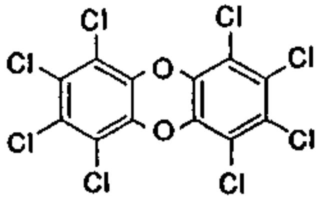
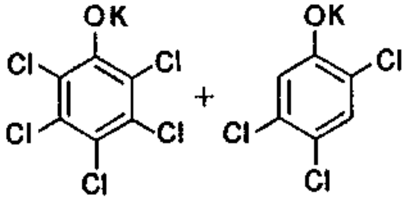
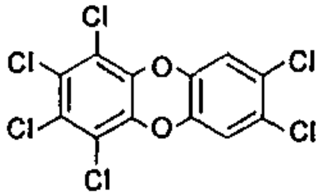
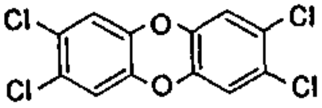
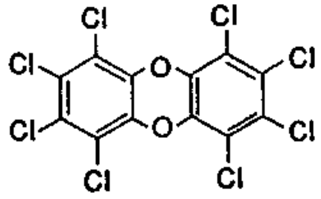
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
㉔	 1.17 g	145°C Cu POWDER, PYRIDINE 3 h		(8 mg)	p
㉕		290°C 1-4 h			q
					
					

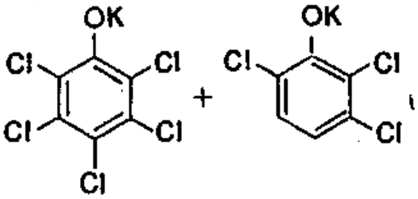
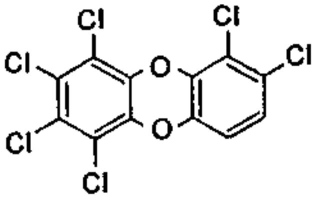
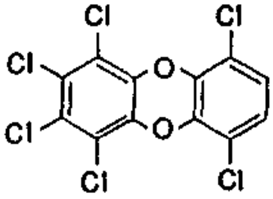
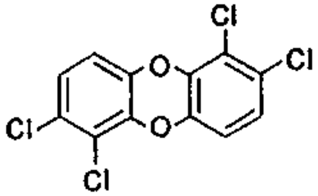
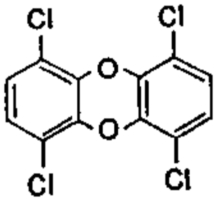
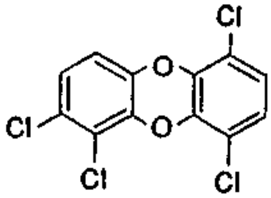
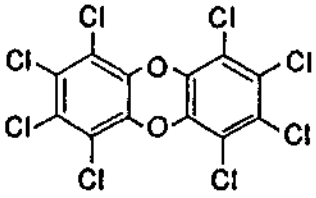
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a] Ref.
㉖		290°C 1-4 h		q
				
				
㉗		290°C 1-4 h		q
				
				

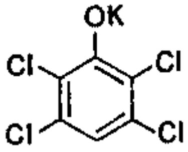
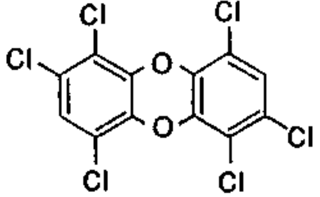
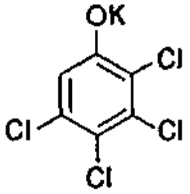
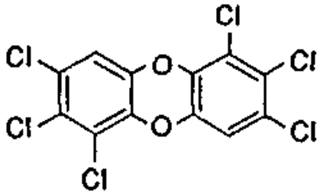
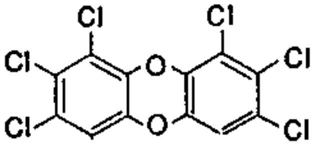
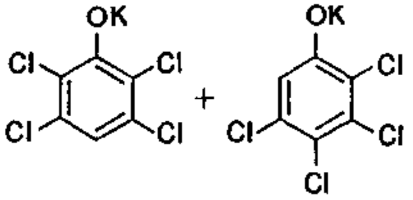
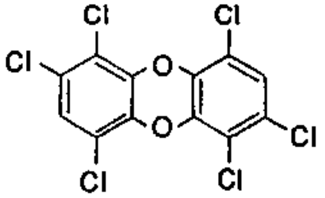
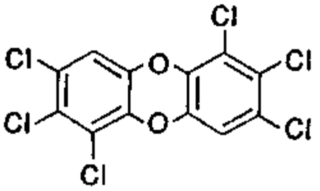
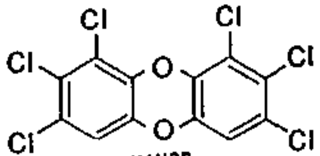
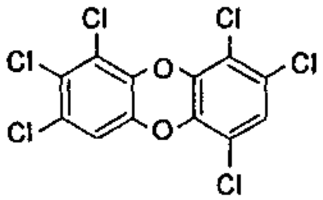
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)^{a} Ref.
㉘		290°C 1-4 h		q
				
				
				
				
				

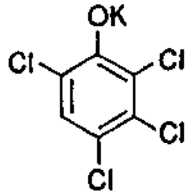
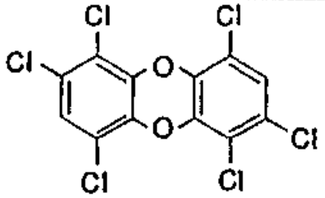
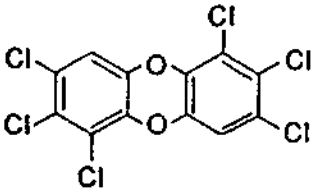
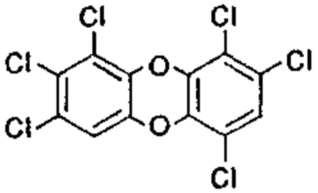
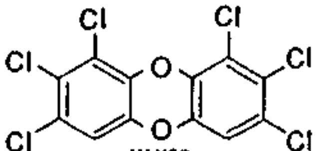
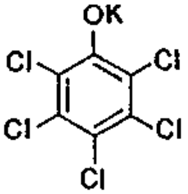
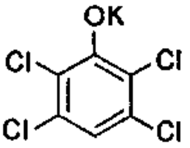
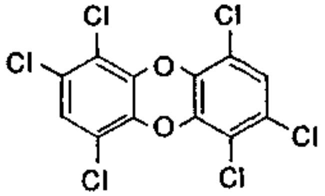
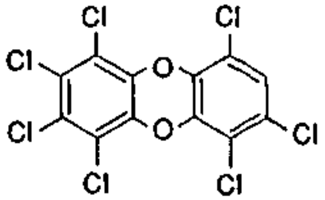
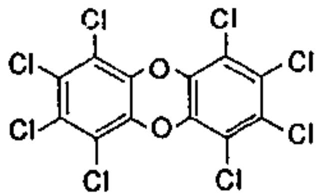
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a] Ref.
㉙		290°C 1-4 h		q
㉚		290°C 1-4 h	 MAJOR  MINOR	q
㉛		290°C 1-4 h	   MINOR 	q

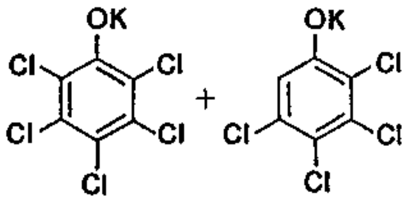
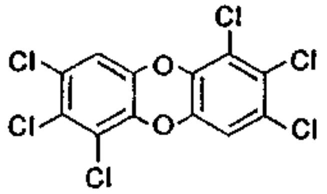
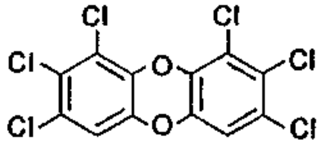
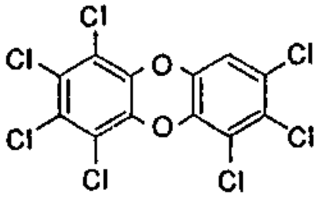
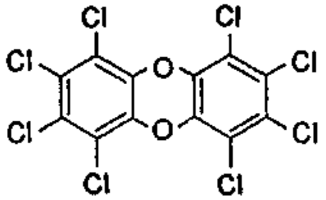
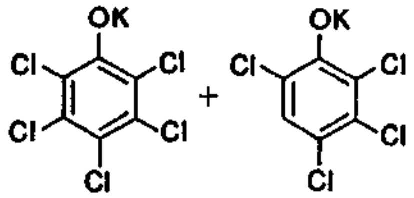
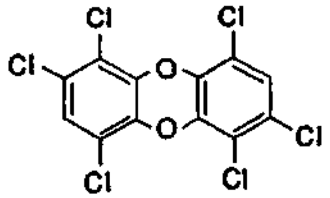
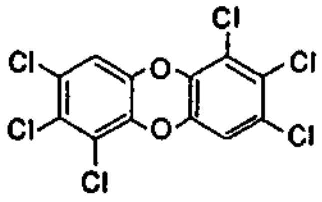
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a] Ref.
㉜		290°C 1-4 h	    MINOR	q
㉝	 + 	290°C 1-4 h	  	q

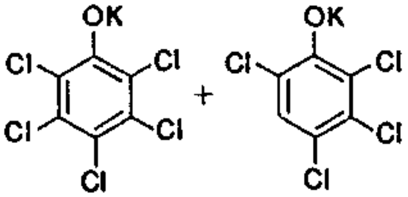
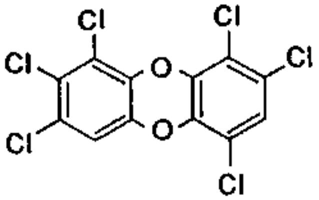
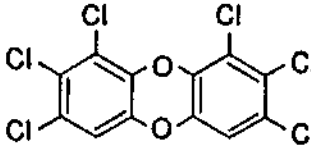
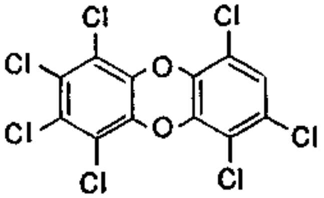
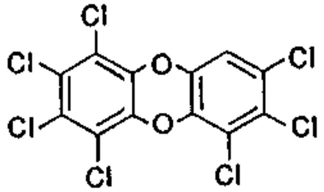
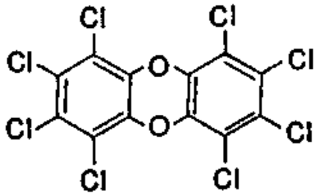
(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a] Ref.
㉞		290°C 1-4 h	  MINOR  	q
㉟		290°C 1-4 h	 	q

(continued)

TABLE 2 (continued)

Item	Reactant	Conditions	Product	(Yield)[a] Ref.
㉟		290°C 1-4 h	  (MINOR)   	q

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[a] If no yield is stated, no value is reported in reference.

[b] Cullinane and Davies 1936.

[c] Tomita 1933.

[d] Tomita and Tani 1942.

[e] Julia and Baillarge 1953.

[f] *Tomita, Nakano, and Hirai 1954.*

[g] Tomita and Yagi 1958.

[h] Fujita and Gota 1955.

[i] Fujita et al. 1956.

[k] Inubushi et al. 1959.

[l] Tomita, Ueda, and Narisada 1959.

[m] Denivelle, Fort, and Hai 1960.

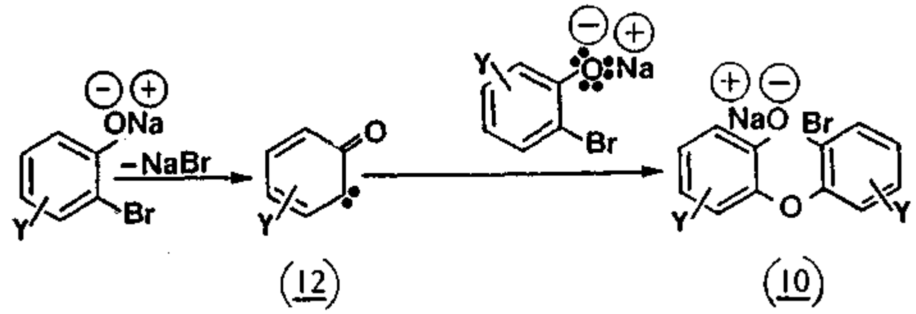
[n] Ueda 1962.

[o] *Ueda and Akio 1963.*

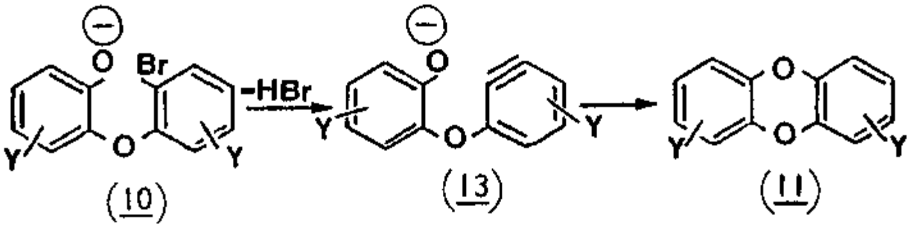
[p] Ueda 1963.

[q] Buser 1975.

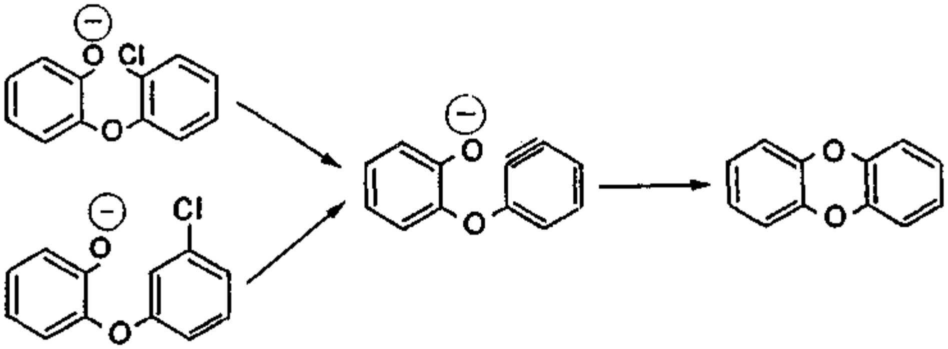
In 1974 Cadogan, Sharp, and Trattles proposed a more reasonable mechanism involving the α-ketocarbene (<u>12</u>), which is attacked by the phenoxide to give (<u>10</u>).



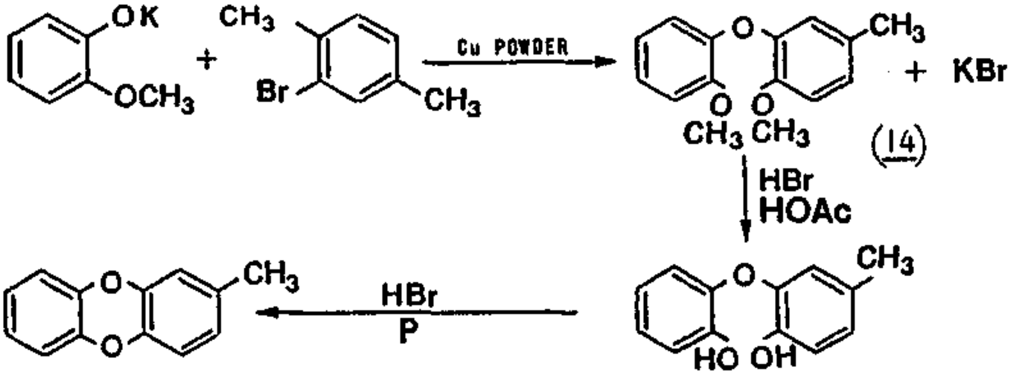
They also proposed that the conversion of the o-halophenoxyphenate to dibenzo-p-dioxin occurs via a benzyne intermediate (<u>13</u>).



The evidence in favor of this mechanism is quite convincing since both ortho- and meta-halophenoxyphenates are converted to the same dibenzodioxin, as shown below.



As shown in Table 2 (items 5, 6, 11, 13, 25-28, and 31-35), complex mixtures result from attempts to prepare unsymmetrical dibenzo-p-dioxins using the modified Ullmann reaction. An early attempt to circumvent this problem involved the synthesis of a protected form of the unsymmetrical predioxin intermediate (<u>14</u>) (Tomita 1938) followed by its conversion to the dioxin in a separate procedure as shown below (Tomita 1938; Kermatsu 1936).

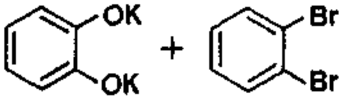
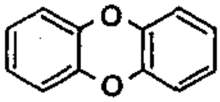
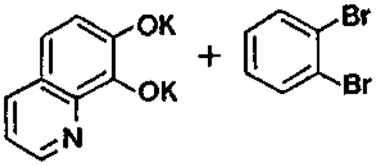
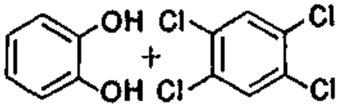
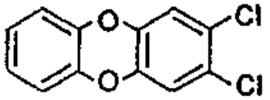
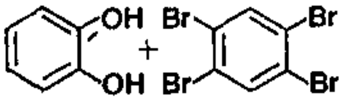
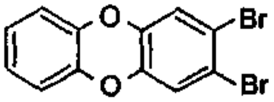
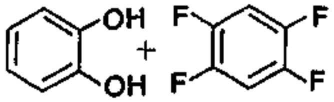
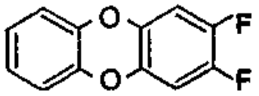
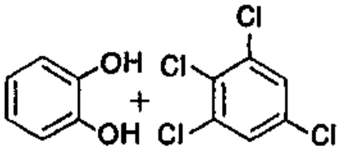
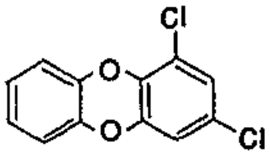
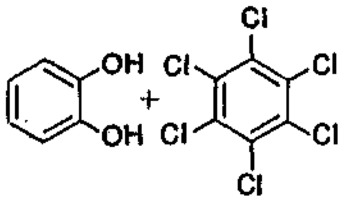
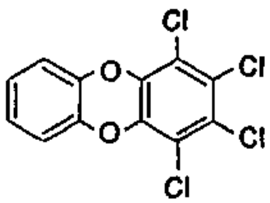


This procedure has the advantage of giving a single dibenzo-p-dioxin isomer; however, it is limited, in that yields of the dioxin rarely exceed 10 percent (Tomita 1938).

A newer and more general procedure for the preparation of unsymmetrical (as well as symmetrical) dibenzo-p-dioxins involves the reaction of catechol salts with ortho-dihalobenzenes in dimethylsulfoxide (DMSO) (Pohland 1972; Kende 1974).

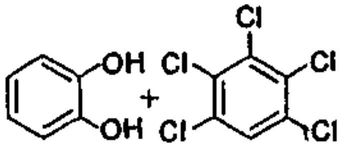
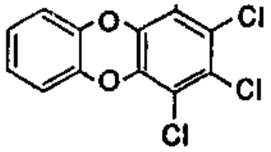
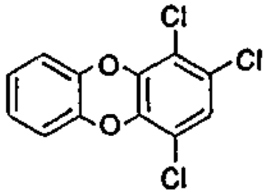
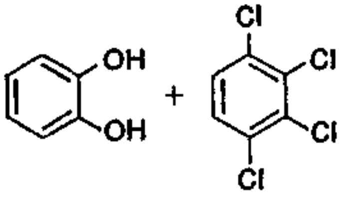
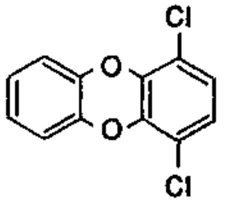
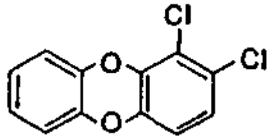
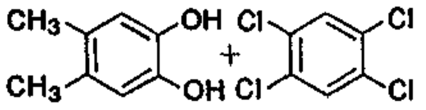
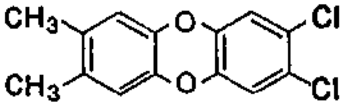
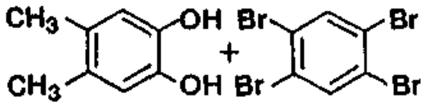
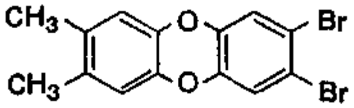
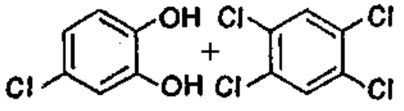
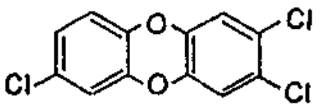
This procedure is a modification of a much earlier approach to the synthesis of dibenzo-p-dioxin, which suffered low yields (Tomita 1932) or no dioxin formation (Fujita 1955). The improved process gives very high yields of dibenzo-p-dioxins when dimethylsulfoxide is used as the solvent. Whether this result is simply a solvent effect or DMSO plays a chemical role in the reaction has not been determined. Examples of the utilization of this reaction for the preparation of dibenzo-p-dioxins are included in Table 3.

TABLE 3. CATECHOL-BASED REACTIONS

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
①	 2.75 g 5.9 g	200°C Cu POWDER $CuNO_3$ 3 h			b
②		190°C Cu POWDER 2 h	(NO REACTION)		c
③		KOH DMSO, Δ		(81%)	d
④		KOH DMSO, Δ		(25%)	e
⑤		KOH DMSO, Δ		(41%)	e
⑥		KOH DMSO, Δ		(31%)	e
⑦		KOH DMSO, Δ		(41%)	e

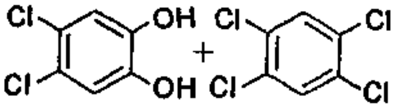
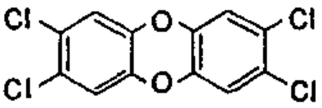
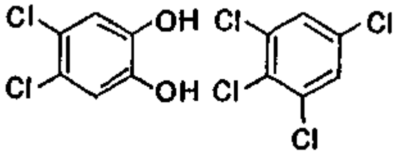
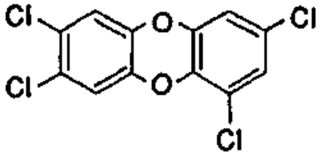
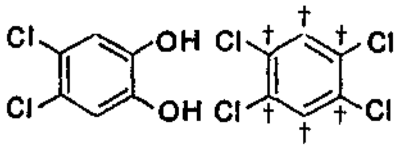
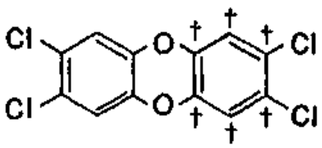
(continued)

TABLE 3 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑧		KOH DMSO, Δ	 + 	(35% TOTAL)	e
⑨		KOH DMSO, Δ	 + 	(40% TOTAL)	e
⑩		KOH DMSO, Δ		(49%)	e
⑪		KOH DMSO, Δ			e
⑫		KOH DMSO, Δ		(50%)	e

(continued)

TABLE 3 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑬		KOH DMSO, Δ		(19%)	e
⑭		KOH DMSO, Δ		(40%)	e
⑮		KOH DMSO, Δ		‡	f

† Evenly distributed carbons.

‡ Preparation of uniformly labelled ^{14}C TCDD isomers (148 millicurie/millimole).

[a] If no yield is stated, no value is reported in reference.

[b] Tomita 1932.

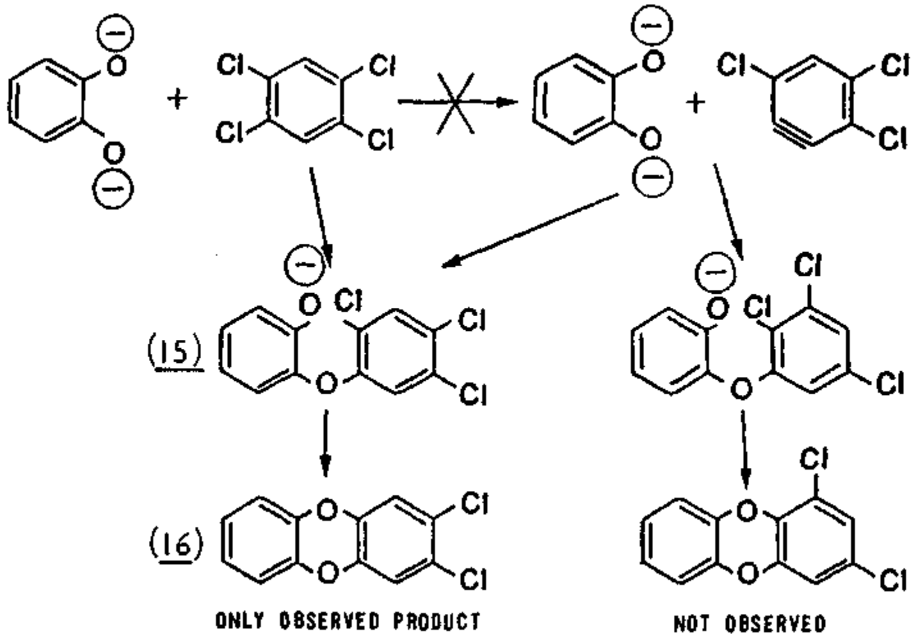
[c] Fujita and Gota 1955.

[d] Pohland and Yang 1972.

[e] Kende et al. 1974.

[f] Rose et al. 1976.

Although no mechanistic studies of this reaction have been reported, it is clear that the initial attack of the catechol dianion on the polyhalobenzene does not occur via a benzyne intermediate, since in item 3 of Table 3 one would expect two different dioxins, which is not the result. This does not preclude the possibility that a benzyne intermediate is involved in the conversion of the predioxin (15) to the 2,3-dichlorodibenzo-p-dioxin (16), as has been proposed for similar predioxin cyclizations (Cadogan 1974).



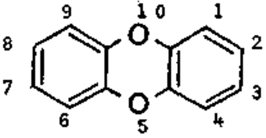
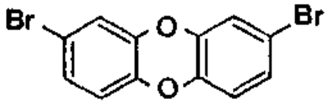
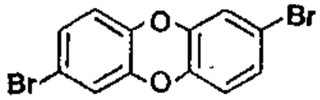
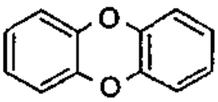
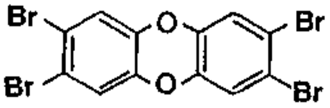
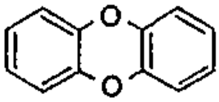
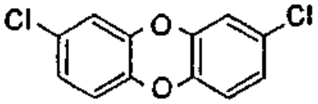
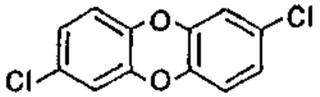
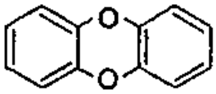
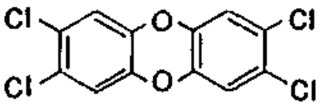
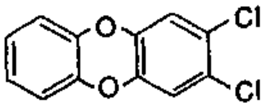
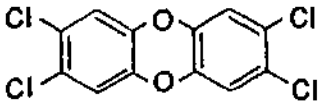
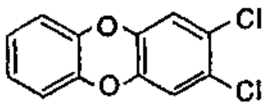
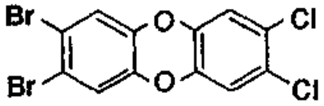
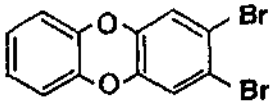
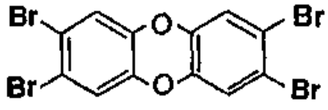
Numerous approaches to the preparation of substituted dioxins are based on elaboration of the dibenzo-p-dioxin skeleton via electrophilic aromatic substitution reactions. These applications are summarized in Table 4.

As indicated in Table 4, electrophilic aromatic substitution occurs first at position 2. (The dioxin numbering sequence is shown in item 1.) If the newly introduced substituent is deactivating (halogen or nitro), the next attack occurs at either position 7 or 8. Gilman (1957; 1958) found that position 1 can be metalated by treatment of dibenzo-p-dioxin with alkyl or phenyllithium reagents allowing this position to be substituted.

MISCELLANEOUS DIOXIN PREPARATIONS

Buser (1976) has developed a method for the preparation of qualitative standards of polychlorinated dioxins based on the photodechlorination of octachlorodioxin (Crosby 1971; 1973). Irradiation of octachlorodibenzo-p-dioxin yields a mixture of tri-, tetra-, penta-, hexa- and heptachlorodibenzo-p-dioxin that is useful for the analysis of materials suspected to contain polychlorodioxins.

TABLE 4. SUBSTITUTION REACTIONS

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
①	 + Br_2		 		b
②	 + Br_2	$Fe(Br)_3$, CAT.			b
③	 + Cl_2		 		b
④	 + Cl_2	$Fe(Cl)_3$	 + PENTA-CDD AND TRI-CDD	(LOW)	b
⑤	 + Cl_2			(41%)	c
⑥	 + Br_2			(76%)	c
⑦	 + Br_2			(87%)	c

(continued)

TABLE 4 (continued)

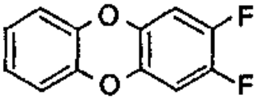
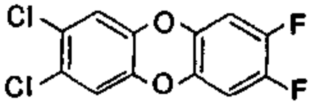
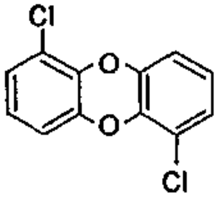
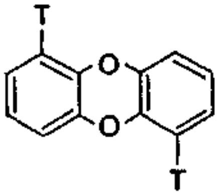
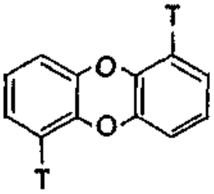
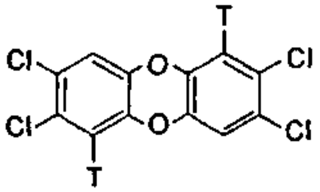
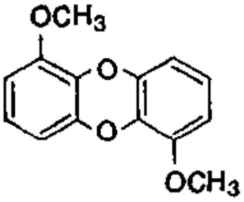
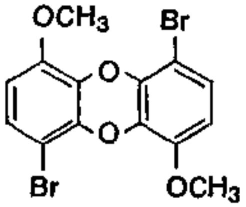
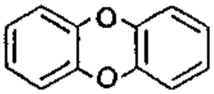
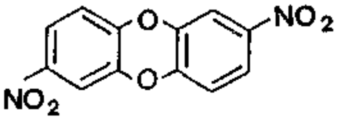
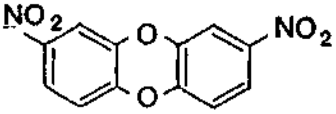
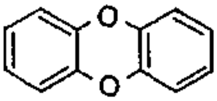
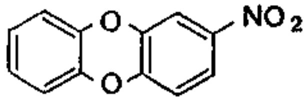
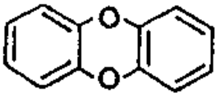
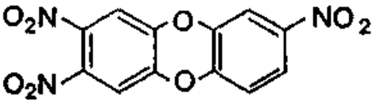
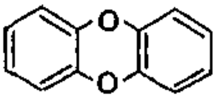
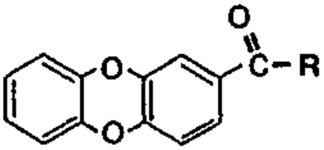
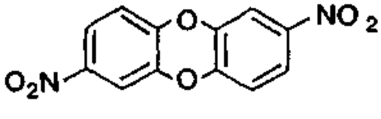
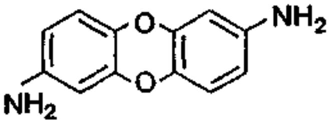
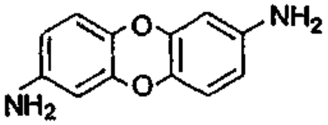
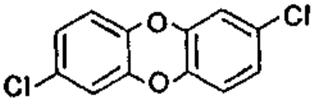
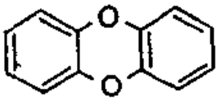
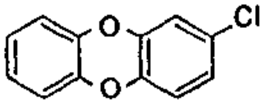
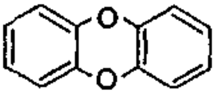
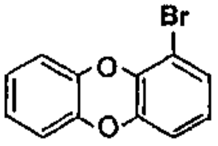
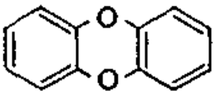
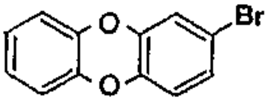
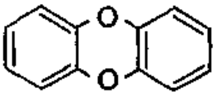
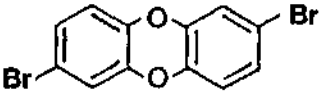
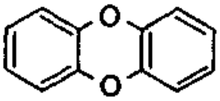
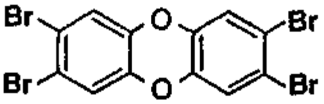
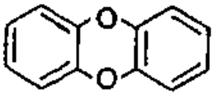
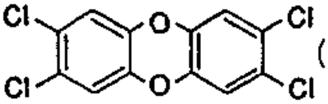
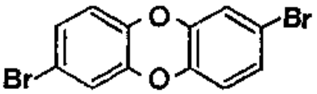
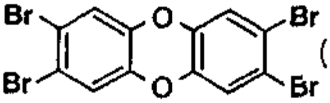
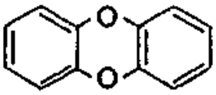
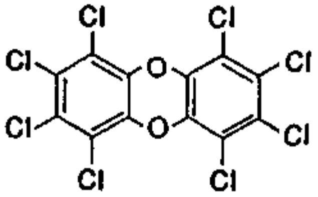
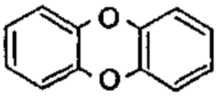
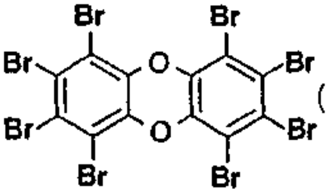
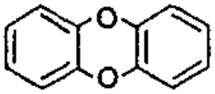
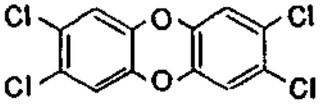
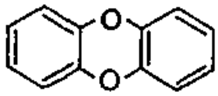
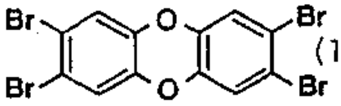
Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑧	 + Cl_2			(24%)	c
⑨	 + TRITIUM	CAT			d
⑩	 + Cl_2	$FeCl_3$, I_2(CAT)			d
⑪	 + Br_2			(90%)	e
⑫		HNO_3, Δ			f
					f
⑬		HNO_3 HOAc, 0°C			f
		HNO_3, Δ			

TABLE 4 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
⑭	 + RCOCl	$AlCl_3$			g
⑮		H_2/Pd			h
⑯		HONO, CuCl			h
⑰	 4.6 g	Cl_2, HOAc		(1 g)	j,k
⑱	 9.2 g	1. PHENYLLITHIUM 2. Br_2		(1 g)	j,k
⑲		KBr $KBrO_3$, HOAc, 120°C		(40%)	j,k
⑳	 4.6 g	Br_2, HOAc, 120°C		(0.6 g)	j,k

(continued)

TABLE 4 (continued)

Item	Reactant	Conditions	Product	(Yield)[a]	Ref.
㉑		Br_2,HOAc, 120°C			j,k
㉒	 26 g	Cl_2, $FeCl_3$, I_2		(20 g)	l
㉓	 50 mg	Br_2, HOAc		(60 g)	m
㉔		Cl_2, $FeCl_3$, I_2			m
㉕	 0.5 g	Br_2		(0.7 g)	n
㉖	 0.2 g	Cl_2		(0.1 g)	n
㉗	 0.5 g	Br_2		(1.54 g)	n

[a] If no value is stated, no value reported in reference.

[b] Gilman and Dietrich 1957.

[c] Kende et al. 1974.

[d] Vinopal, Yamamoto, and Casida 1973.

[e] Ueda 1963.

[f] Tomita 1935.

[g] Tomita 1937.

[h] Ueo 1941.

[j] Gilman and Dietrich 1957.

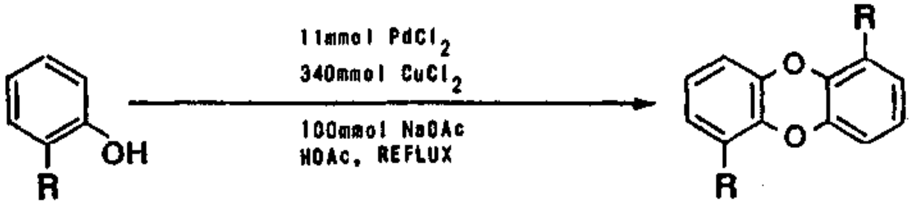
[k] Gilman and Dietrich 1958.

[l] Sanderman, Stockmann, and Casten 1957.

[m] Tomita, Ueda, and Narisada 1959.

[n] Deniville, Fort, and Hai 1960.

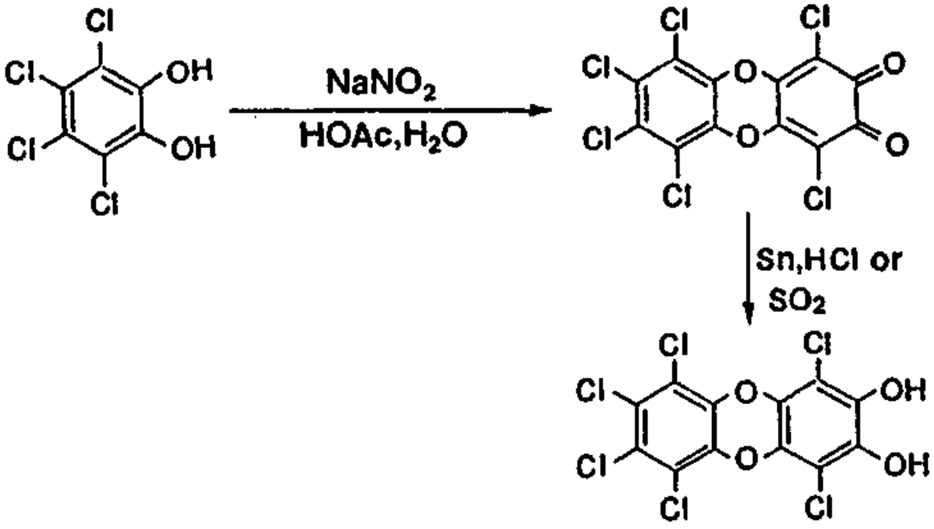
Lester and Brennan (1972) have patented a process for the direct conversion of substituted phenols to substituted dibenzo-p-dioxins with a palladium-copper catalyst.



$R = H, CH_3, CH_2CH_3, OCH_3, NO_2$

Although the mechanism of the reaction has not been studied, the reaction is important in light of the widespread industrial uses of phenol and phenol derivatives.

An interesting procedure for preparation of dihydroxydibenzo-p-dioxins is based on the oxidative coupling of polyhalocatechols found by reduction of the resulting quinone (Frejka 1937).



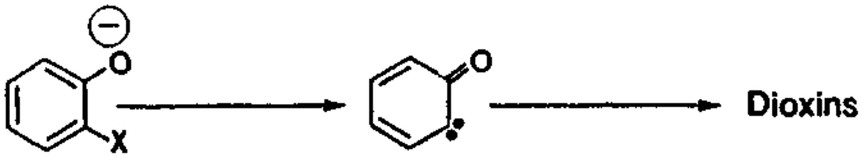
Although the yields from this process are modest (15 to 35 percent), the reaction proceeds under very mild conditions.

DISCUSSION OF REACTION CHEMISTRY

On the basis of the data presented thus far, certain generalizations can be made about the conditions under which formation of dioxins (both halogenated and nonhalogenated) is probable.

First, and most likely, is the formation of dioxins on treatment of o-halophenols with base at elevated temperatures. The strength of the base required to effect this reaction depends on the particular phenol involved; however, there is adequate precedent for the ability of relatively weak organic bases such as pyridine or quinoline to effect dioxin formation. The temperature range required for dioxin formation varies with the particular o-halophenol; however, 1 percent yields of halogenated dioxins have been formed at temperatures as low as 145°C. (See Table 2, item 23.)

The presence of an ortho-halogen on the phenolic starting material is not an absolute requirement for dioxin formation. According to the mechanism proposed by Cadogan, Sharp, and Trattles (1974), all that is required is a substituent ortho to the phenol that is capable of acting as a leaving group.



Other substituents should be capable of elimination to give the α-ketocarbene and thus dioxins. Among those in addition to the halogens are

Sulfonic acids

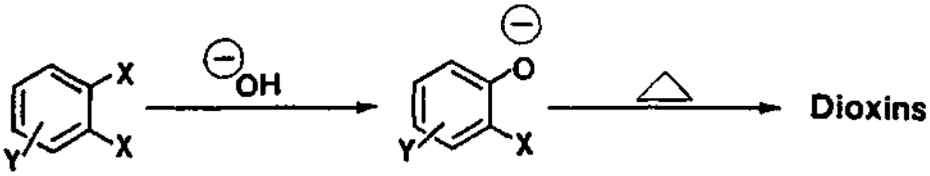
Sulfonate esters

Nitro groups

Carboxylate esters

A second possible source of dioxins is the treatement of halogenated phenols with reagents conducive to the formation of the corresponding polyhalogenated phenoxy radical (i.e., treatment with halogens or other mild oxidizing agents). Although this reaction has been used only for the preparation of perhalo dioxins (in yields of more than 80 percent and 200-gram quantities), there is no reason why the reaction could not produce the lower halogenated derivatives of dioxins. (See Table 1, item 2.)

A common practice in the preparation of polyhalobenzenes by electrophilic halogenation is neutralization of the acid byproduct with alkali hydroxides. This process (or simply a basic wash of product during the isolation procedure) can lead (via nucleophilic substitution) to a halogenated phenol, which upon distillation may produce dioxins.



The treatment of catechol salts with o-dihalobenzenes is a particularly efficient method for the formation of dioxins, both halogenated and nonhalogenated. Also, the treatment of polyhalocatechols with mild oxidants can produce significant quantities of halogenated dihydroxy-dioxins.

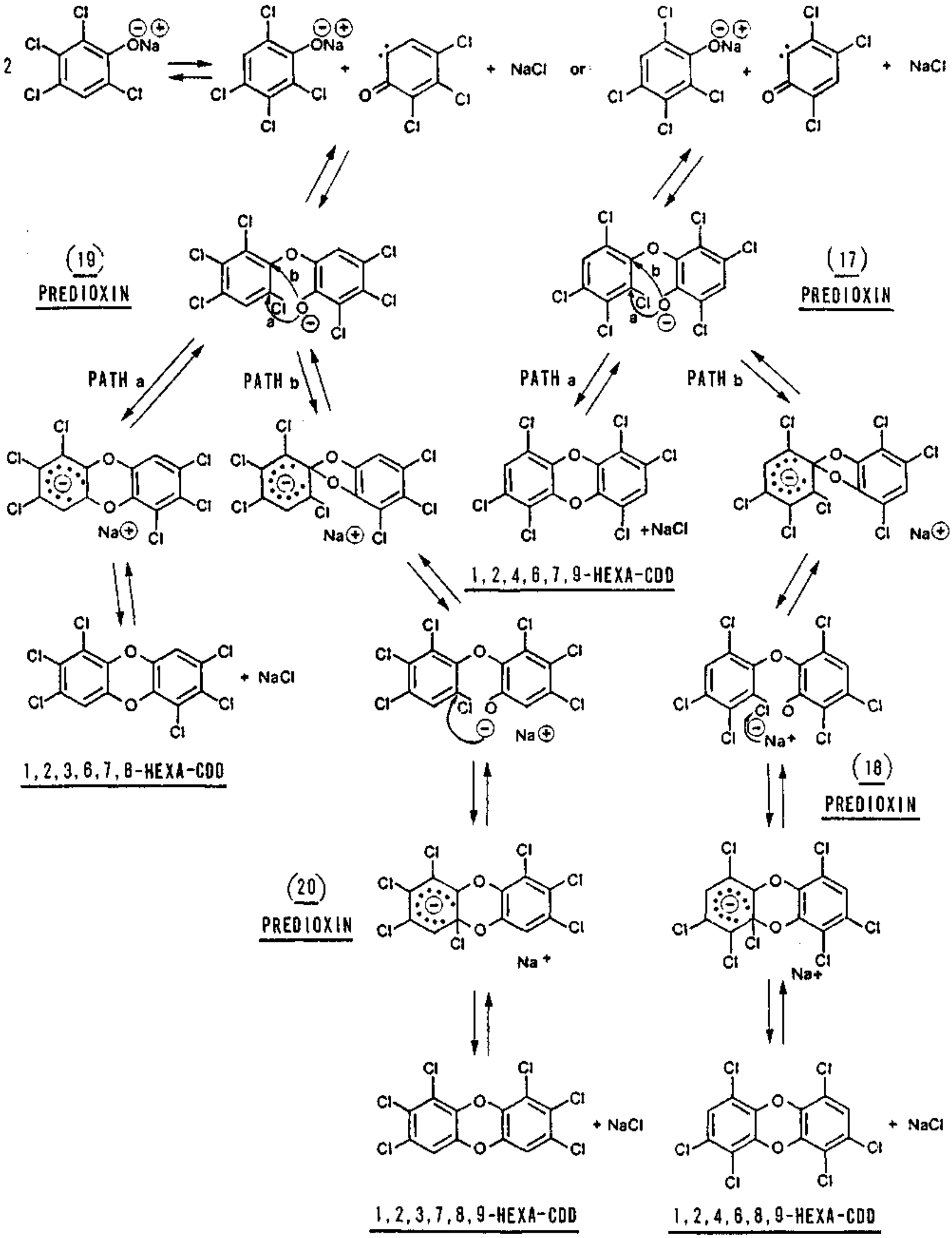
Of particular concern is the treatment of aromatic compounds under oxidizing conditions at elevated temperature. Several industrial processes involve the oxidation of benzene, toluene, and naphthalene under "semicombustion" conditions. In light of the studies such as that by Dow Chemical (Rawls 1979) on combustion sources of dioxins, the "tars" from these processes (which are often generated in considerable quantities) deserve further study.

The mechanistic aspects of dioxin formation discussed in this section represent the current understanding of these reactions; however, several experimental observations about dioxin formation cannot be explained by the current theories. The formation of four isomers of hexa-CDD on pyrolysis of 2,3,4,6-tetrachlorophenate (Higginbotham 1968; Langer 1973), including the 1,2,3,7,8,9 hexa-CDD (Buser 1975), can be explained in terms of the predioxin intermediates, (17) and (19), undergoing the Smiles rearrangement as shown on the following page.

As the diagram shows, the initially formed predioxin intermediate can proceed directly toward dioxin formation (path a) or can undergo the Smiles rearrangement (path b), which leads to new predioxin intermediates 18 and 20. The newly formed predioxins can then react further to give a different dioxin or can undergo the Smiles rearrangement to regenerate the original predioxin. This interconvertability of predioxins often leads to mixtures of dioxin products which are otherwise difficult to understand.

An equally disturbing mechanistic point is the observation that numerous pesticides are contaminated by polychlorodioxins, which would not be anticipated on the basis of the feedstock materials and reaction conditions. An example reported by Fishbein (1973) is the presence of significantly higher concentrations of hepta- and octachlorodioxins than hexachlorodioxin in commercial 2,3,4,6-tetrachlorophenol, also known as Dowicide-6 (see Table 7).

The Dow Chemical Company (Rawls 1979) has proposed that the polychlorodibenzo-p-dioxins undergo disproportionation and establish an equilibrium mixture of halogenated dioxins. No experimental evidence in support of this proposal has been published.


2
+ NaCl
or
(19)
PREDIOXIN
(17)
PREDIOXIN
PATH a
PATH b
PATH a
PATH b
+NaCl
1,2,4,6,7,9-HEXA-CDD
+ NaCl
1,2,3,6,7,8-HEXA-CDD
(18)
PREDIOXIN
(20)
PREDIOXIN
+ NaCl
+ NaCl
1,2,3,7,8,9-HEXA-CDD
1,2,4,6,8,9-HEXA-CDD

SECTION 4

SPECULATIVE SOURCES OF DIOXINS

Dioxins can enter the environment in a variety of ways:

1. As contaminants in commercial chemical products whose normal processing conditions generate the dioxins as byproducts. Sections 5 and 6 detail the mechanisms by which this can occur in some of these commercial chemicals.

2. As contaminants in chemical processing under improperly controlled reaction conditions (Rappe 1978). Thus, dioxins would be present in the wastes from "bad batches." Chemical manufacture that might lead to dioxin presence under such circumstances is also reviewed in Sections 5 and 6.

3. As products of intentional dioxin preparations in the laboratory. Although the quantities involved from such sources probably would not be large, the concentrations would be high. Therefore any failure to practice proper disposal could be serious because of the high toxicity and concentration potential. Reported laboratory dioxin preparations are noted in Section 3.

4. As deliberate or unintentional products of reactions carried out by uninformed or irresponsible persons. The hazards in such cases would be enhanced because the dioxins formed would likely be subject to improper use or disposal.

5. As products of combustion of general municipal, commercial, and industrial wastes. Such wastes are likely to contain materials required for dioxin formation. The chlorine content of municipal waste is relatively high because of the widespread use of polyvinyl chloride and other chlorinated polymers.

6. As combustion products and residues from burning vegetation that has been sprayed with chlorinated herbicides (and other pesticides). This potential source is of two-fold interest. First, chemicals such as 2,4,5-T, 2,4-D, and others noted in Section 6 might be degraded to dioxins under relatively mild combustion conditions (Buu-Hoi 1971). Second, formation of dioxins might occur under combustion conditions, even from chemicals not directly related to dioxins, such as many insecticides (DDT, aldrin, dieldrin, etc.).

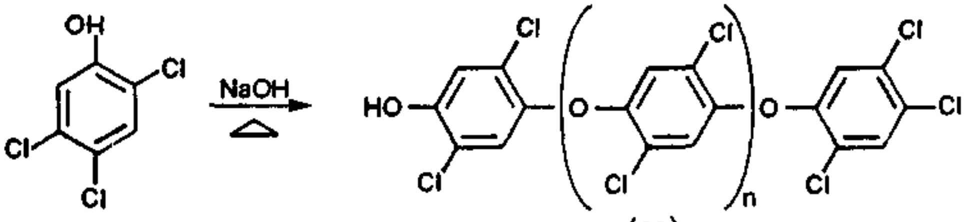
7. As incidental products of fires in facilities such as chemical and pesticide warehouses, farm buildings in which pesticides are stored, and facilities for storage of chemically treated wood products such as lumber or poles (Buu-Hoi 1971).

8. As waste disposal byproducts of materials such as polychlorinated biphenyls (PCB). These materials have been used extensively in electrical transformers, as heat transfer media, as lubricants, and in carbonless paper.

9. As derivative wastes from pentachlorophenol (PCP) and other wood-treating agents. Agents used in the treatment of wood products are likely to remain with the wood through its use cycle. Thus they are subjected to the same extremes of exposure as the wood, including ultimately combustion, which leads to dioxin formation (Buu-Hoi 1971).

10. As an unsuspected byproduct of the treatment of aromatic compounds under oxidizing conditions at elevated temperature. Several industrial processes involve the oxidation of benzene, toluene, and naphthalene under "semicombustion" conditions. In light of such studies as that by Dow Chemical (Rawls 1979) on combustion sources of dioxins, the "tars" from these processes (often occurring in considerable quantities) warrant further study.

11. As byproducts of miscellaneous chemical syntheses that may not be commercially significant at this time. An example might be the detected presence of 2,3,7,8-TCDD in chlorinated polyphenylene ethers (such as 21), which can be produced from 2,4,5-trichlorophenol (Cox 1965).

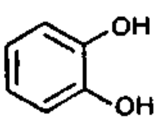


(21)

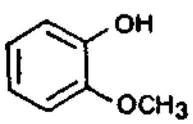
These polymers are not known to be of commercial significance, but serve as a cautionary example.

12. As a result of the combustion of naturally occurring compounds. Recent reports by chemists at the Dow Chemical Company maintain that dioxin formation is a natural consequence of combustion (Dow 1978). There are numerous naturally occurring compounds that could, during the complex process of combustion, serve as precursors of dioxins. Combustion of these compounds in the presence of chlorine-containing compounds (e.g., DDT or polyvinyl chloride)

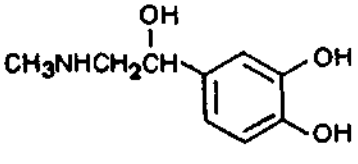
could lead to the formation of chlorinated dioxins. Examples of such naturally occurring "potential" dioxin precursors are given below.


(22)

CATECHOL

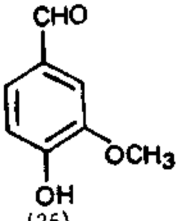

(23)

GUAIACOL

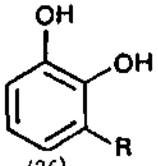

(24)

ADRENALINE (EPINEPHRINE)

Catechol (22) occurs in nature as the product of phenol biodegradation and as a major product of tannin pyrolysis (Wertheim 1939). Guaiacol (23) occurs as the major phenolic component in several hardwood trees and is also prepared synthetically for use as an ingredient in cough syrups (Merck 1978; U.S. EPA Draft 1979). Adrenaline (24) is a naturally occurring mammalian hormone and is also prepared synthetically for use in many drug formulations (U.S. EPA Draft 1979). Other naturally occurring compounds that contain the orthohydroxy or alkoxy groups include vanillin (25), which is the flavoring ingredient in vanilla extract; urushiol (26), a mixture of compounds that are the toxic constituents of poison ivy; eugenol (27), the pungent principle of cloves; capsaicin (28) the pungent principle of various peppers; and safrole (29), the major volatile constituent of sassafras.


(25)

VANILLIN


(26)

$R = C_{15}H_{31}$

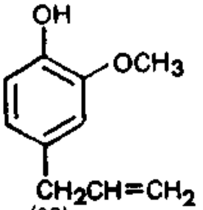
$= C_{15}H_{29}$

$= C_{15}H_{27}$

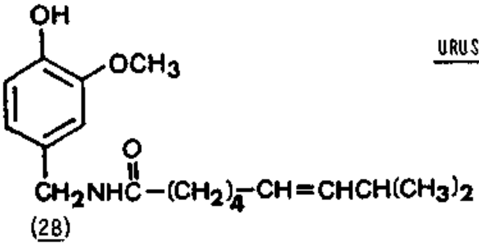
$= C_{15}H_{25}$

$= C_{15}H_{23}$

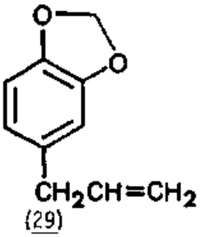
URUSHIOL


(27)

EUGENOL


(28)

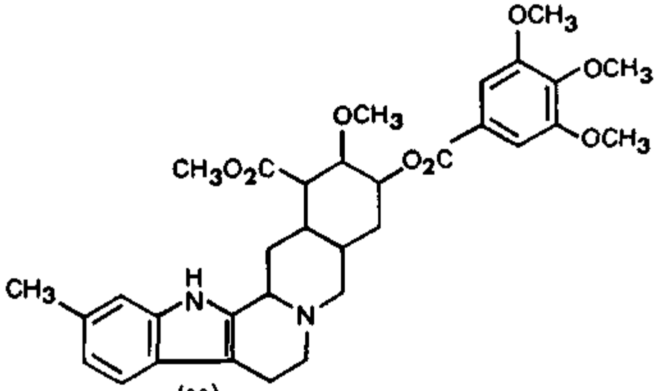
CAPSAICIN


(29)

SAFROLE

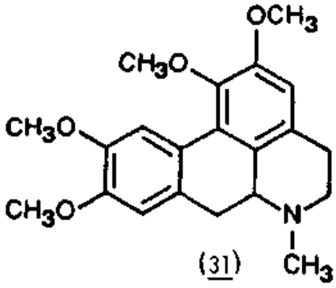
Among many plant alkaloids that include the structure are reserpine (30), glaucine (31), and colchicine (32). Other potential dioxin precursors are found in the fomecin (33) series of antibiotics, produced by a fungus, and also in one of the active ingredients of creosote.

A constituent of animal urine is 4-hydroxy-3-methoxymandelic acid (Merck Index 1978). Since the structure is so common in living organisms, it is also often used in synthetic medicinal compounds, including phenisonone, isoproterenol, estil (an anaesthetic), methocarbanol, and the high-volume drugs guaifenesin and methyldopa (U.S. EPA 1979).



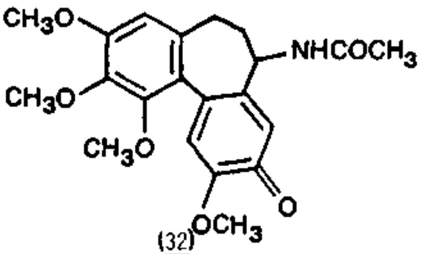
(30)

RESERPINE



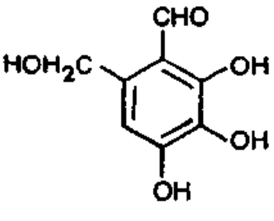
(31)

GLAUCINE



(32)

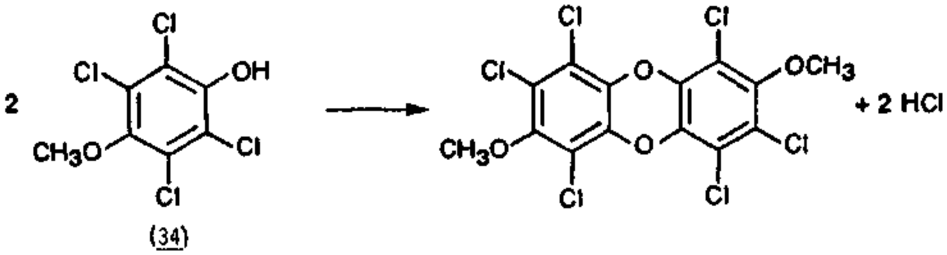
COLCHICINE



(33)

FOMECIN

At least one natural compound may be by itself a precursor for a chlorinated dioxin. A microorganism species creates a defensive chemical known as drosophyllin A (34), (p-methoxytetrachlorophenol) (Merck Index 1978). In theory it could, when heated, form a substituted hydroxy or methoxy chlorinated dioxin, one possibility of which is:



(34)

DROSOPHYLLIN A

SECTION 5

ORGANIC CHEMICALS

Organic chemical products with the greatest potential for byproduct formation of dioxins are considered in this section. Pesticides and pesticide manufacture are covered separately in Section 6.

Toxicity of the many substituted dibenzo-p-dioxins varies widely. None are excluded from consideration here since disproportionation and other composition shifts may bring about changes from lower toxicity forms to higher (Buser 1976).

Because of the very large number of organic compounds and their varying proclivities to form dioxins, the compounds were screened initially on the basis of:

Molecular structure

Process sequence

Commercial significance

As a means of focusing attention on those organic chemicals most likely to be associated with the formation of dioxins, they were placed in the following classifications:

> Class I - Polyhalogenated phenols, primarily with a halogen ortho to the hydroxyl group, with a high probability of dioxin formation. Products with such compounds appearing as intermediates are also considered. Manufacture of these materials normally involves reaction conditions of elevated temperature plus either alkalinity or free halogen presence, either of which is conducive to formation of halogenated dioxins.
>
> Class II - Ortho-halophenols and ortho-halophenyl ethers where the substituted groups are a mixture of halogens and nonhalogens. Processing conditions are similar to those defined for Class I and produce mixed substituted dioxins. The distinction between Classes I and II is arbitrary and does not indicate necessarily a difference in likelihood of dioxin formation.
>
> Class III - Other chemicals having the possibility, but less likelihood, of dioxin formation. These include 1) ortho substituted aromatic

compounds requiring an unusual combination of reaction steps to produce dioxins, 2) aromatic compounds that might form dioxins because of their production under semicombustion conditions, and 3) products that might contain dioxins by way of contamination of their starting materials.

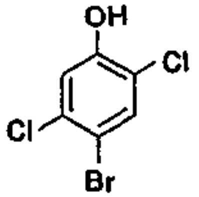
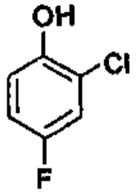
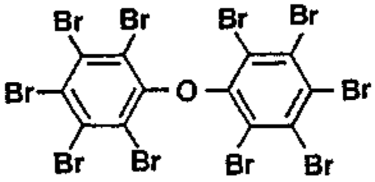
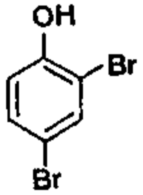
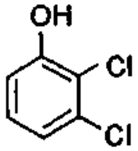
Since only commercially significant products are of interest in this study, the listing is limited to those produced in quantities in excess of 1000 pounds per year and/or whose sales reach $1000 per year, as required for listing in the SRI Directory of Chemical Producers. The product lists are based on commercial production during the past 10 years.

Table 5 lists and classifies commercial organic chemicals selected as having a relationship to dioxin formation or presence. Structures are shown for Classes I and II, the chemicals of primary importance. Class III compounds are listed by name only.

Most of the organic chemicals considered are used as manufacturing intermediates or at least are subjected to subsequent formulation or fabrication. Thus further processing may introduce additional possibilities for dioxin formation, contamination, and exposure not contemplated within the scope of this study.

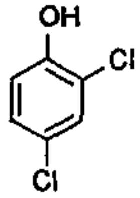
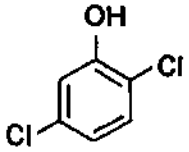
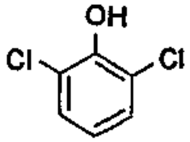
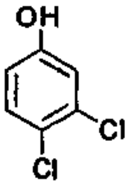
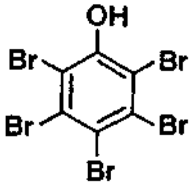
The intended reaction mechanisms for each Class I organic chemical are shown in Figures 1 through 11. The sequence is shown from left to right across the top of each figure, and the possible dioxin side reaction mechanism diverges to typical dioxin byproducts at the bottom of the figure. The specific dioxin products shown are those for which reasonably straightforward mechanisms can be postulated. In many cases more complex and secondary mechanisms may produce dioxins in addition to those shown.

TABLE 5. LIST OF ORGANIC CHEMICALS

Class I	
4-BROMO-2,5-DICHLOROPHENOL	
2-CHLORO-4-FLUOROPHENOL	
DECABROMOPHENOXYBENZENE	
2,4-DIBROMOPHENOL	
2,3-DICHLOROPHENOL	

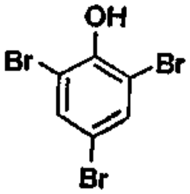
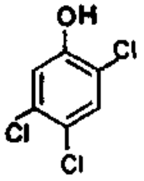
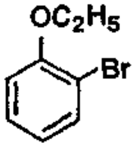
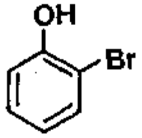
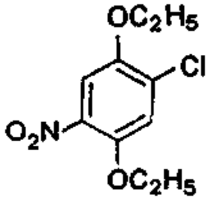
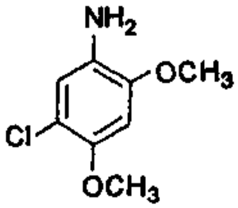
(continued)

TABLE 5 (continued)

Class I (continued)	
2,4-DICHLOROPHENOL	
2,5-DICHLOROPHENOL	
2,6-DICHLOROPHENOL	
3,4-DICHLOROPHENOL	
PENTABROMOPHENOL	

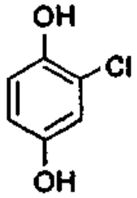
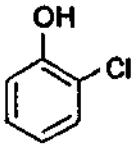
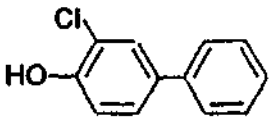
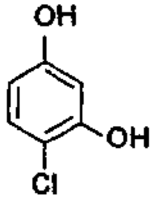
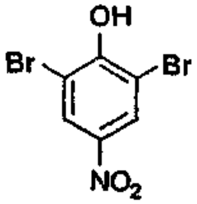
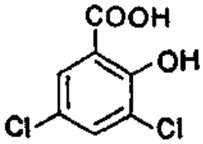
(continued)

TABLE 5 (continued)

Class I (continued)	
2,4,6-TRIBROMOPHENOL	
2,4,5-TRICHLOROPHENOL	
Class II	
BROMOPHENETOLE	
O-BROMOPHENOL	
2-CHLORO-1,4-DIETHOXY-5-NITROBENZENE	
5-CHLORO-2,4-DIMETHOXY-ANILINE	

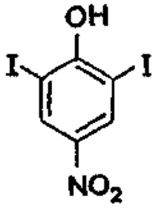
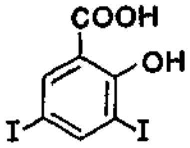
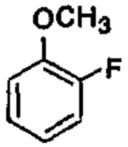
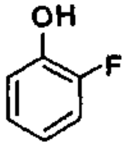
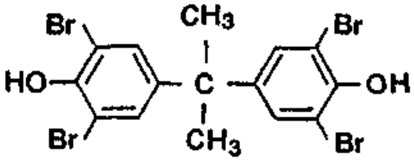
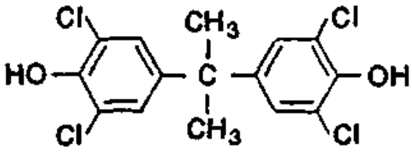
(continued)

TABLE 5 (continued)

Class II (continued)	
CHLOROHYDROQUINONE	
O-CHLOROPHENOL	
2-CHLORO-4-PHENYLPHENOL	
4-CHLORORESORCINOL	
2,6-DIBROMO-4-NITROPHENOL	
3,5-DICHLOROSALICYLIC ACID	

(continued)

TABLE 5 (continued)

Class II (Continued)	
2,6-DIIODO-4-NITROPHENOL	
3 ,5-DIIODOSALICYLIC ACID	
O-FLUOROANISOLE	
O-FLUOROPHENOL	
TETRABROMOBISPHENOL -A	
TETRACHLOROBISPHENOL-A	

(continued)

TABLE 5 (continued)

Class III
3-Amino-5-chloro-2-hydroxybenzenesulfonic acid
2-Amino-4-chloro-6-nitrophenol
o-Anisidine
Benzaldehyde
Bromobenzene
o-Bromofluorobenzene
o-Chlorofluorobenzene
3-Chloro-4-fluoro-nitrobenzene
3-Chloro-4-fluorophenol
4-Chloro-2-nitrophenol
Chloropentafluorobenzene
2,4-Dibromofluorobenzene
3,4-Dichloroaniline
o-Dichlorobenzene
3,4-Dichlorobenzaldehyde
3,4-Dichlorobenzotrichloride
3,4-Dichlorobenzotrifluoride
1,2-Dichloro-4-nitrobenzene

(continued)

TABLE 5 (continued)

Class III (continued)
3,4-Dichlorophenylisocyanate
3,4-Difluoroaniline
o-Difluorobenzene
1,2-Dihydroxybenzene-3,5-disulfonic acid, disodium salt
2,5-Dihydroxybenzenesulfonic acid
2,5-Dihydroxybenzenesulfonic acid, potassium salt
2,4-Dinitrophenol
2,4-Dinitrophenoxyethanol
3,5-Dinitrosalicylic acid
Fumaric acid
Hexabromobenzene
Hexachlorobenzene
Hexafluorobenzene
Maleic acid
Maleic anhydride
o-Nitroanisole
2-Nitro-p-cresol
o-Nitrophenol

(continued)

TABLE 5 (continued)

Class III (continued)
Pentabromochlorocyclohexane
Pentabromoethylebenzene
Pentabromotoluene
Pentachloroaniline
Pentafluoroaniline
o-Phenetidine
Phenol (From chlorobenzene)
1-Phenol-2-sulfonic acid, formaldehyde condensate
Phenyl ether
Phthalic anhydride
Picric acid
Sodium picrate
Tetrabromophthalic anhydride
1,2,4,5-Tetrachlorobenzene
Tetrachlorophthalic anhydride
Tetrafluoro-m-phenylenediamine
Tribromobenzene
1,2,4-Trichlorobenzene
2,4,6-Trinitroresorcinol

4-BROMO-2,5-DICHLOROPHENOL

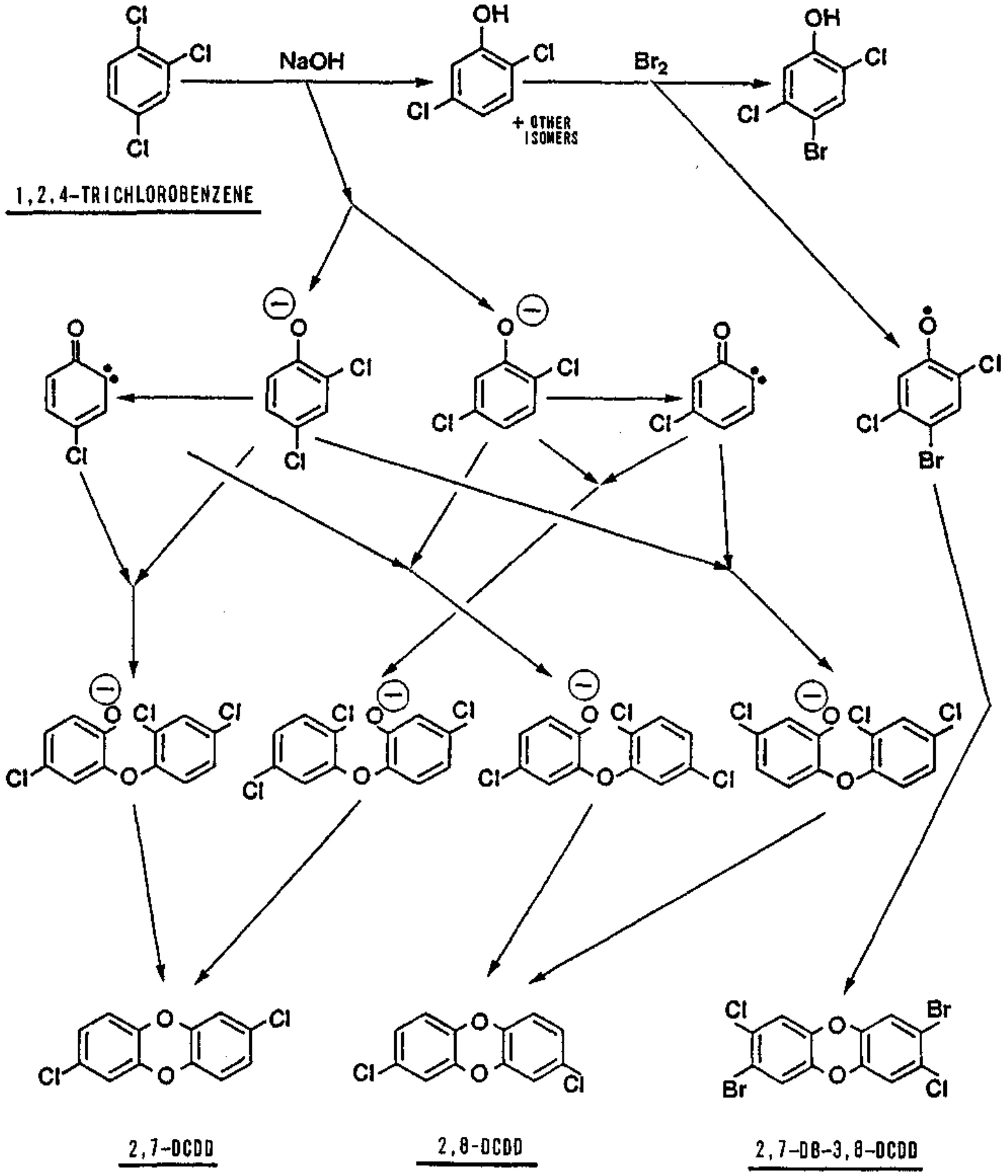


Figure 1. 4-Bromo-2,5-dichlorophenol.

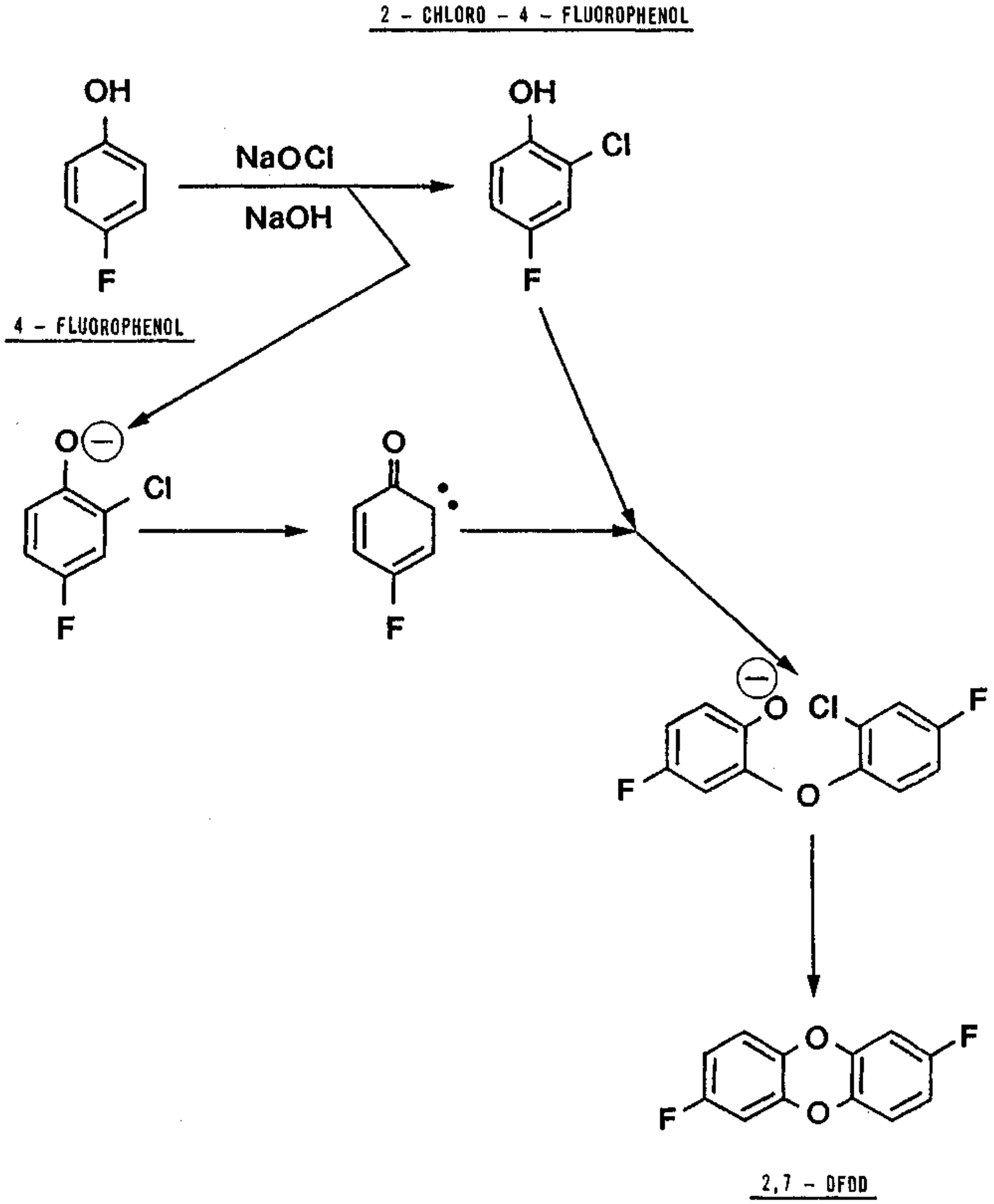


Figure 2. 2-Chloro-4-fluorophenol.

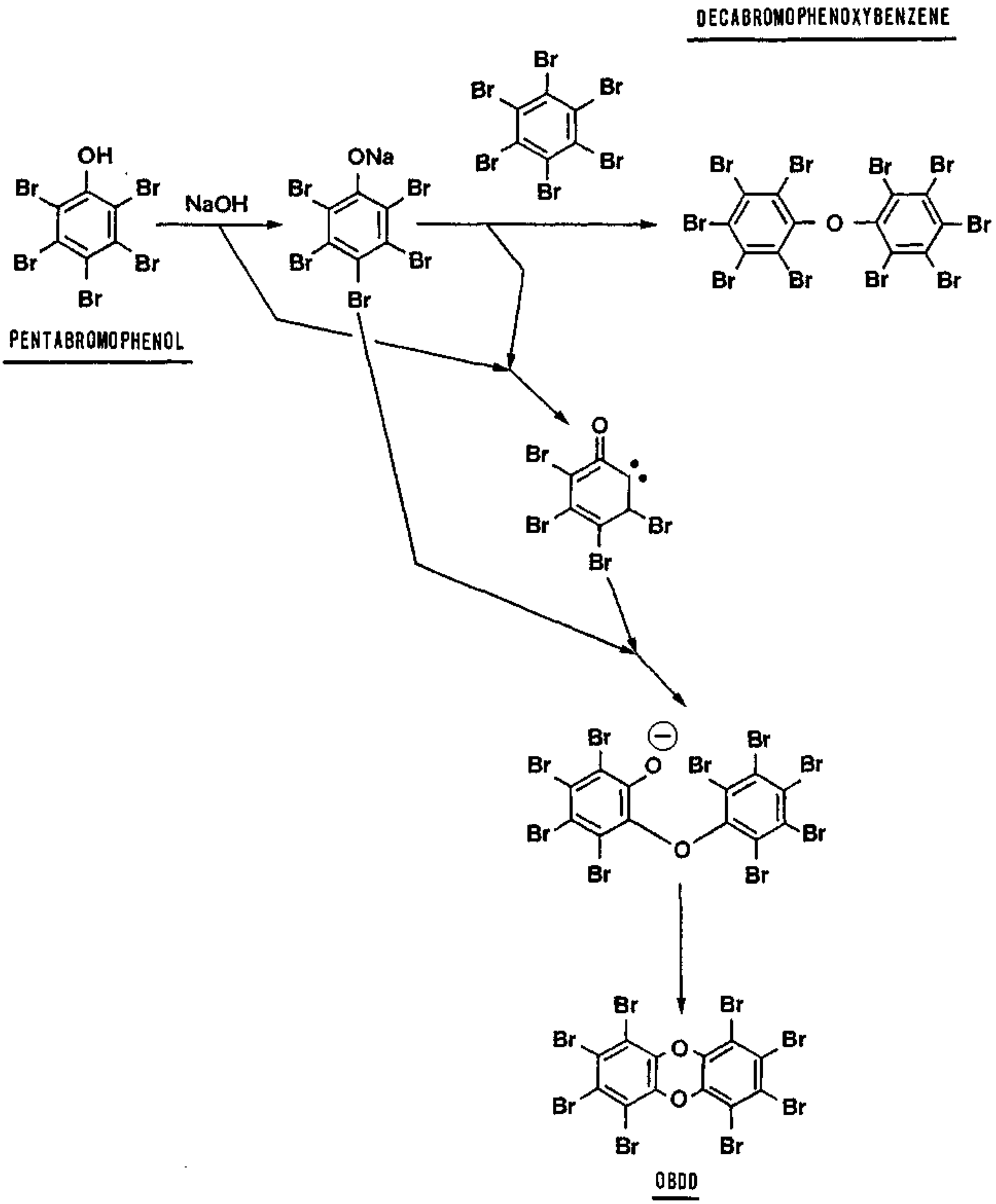


Figure 3. Decabromophenoxybenzene.

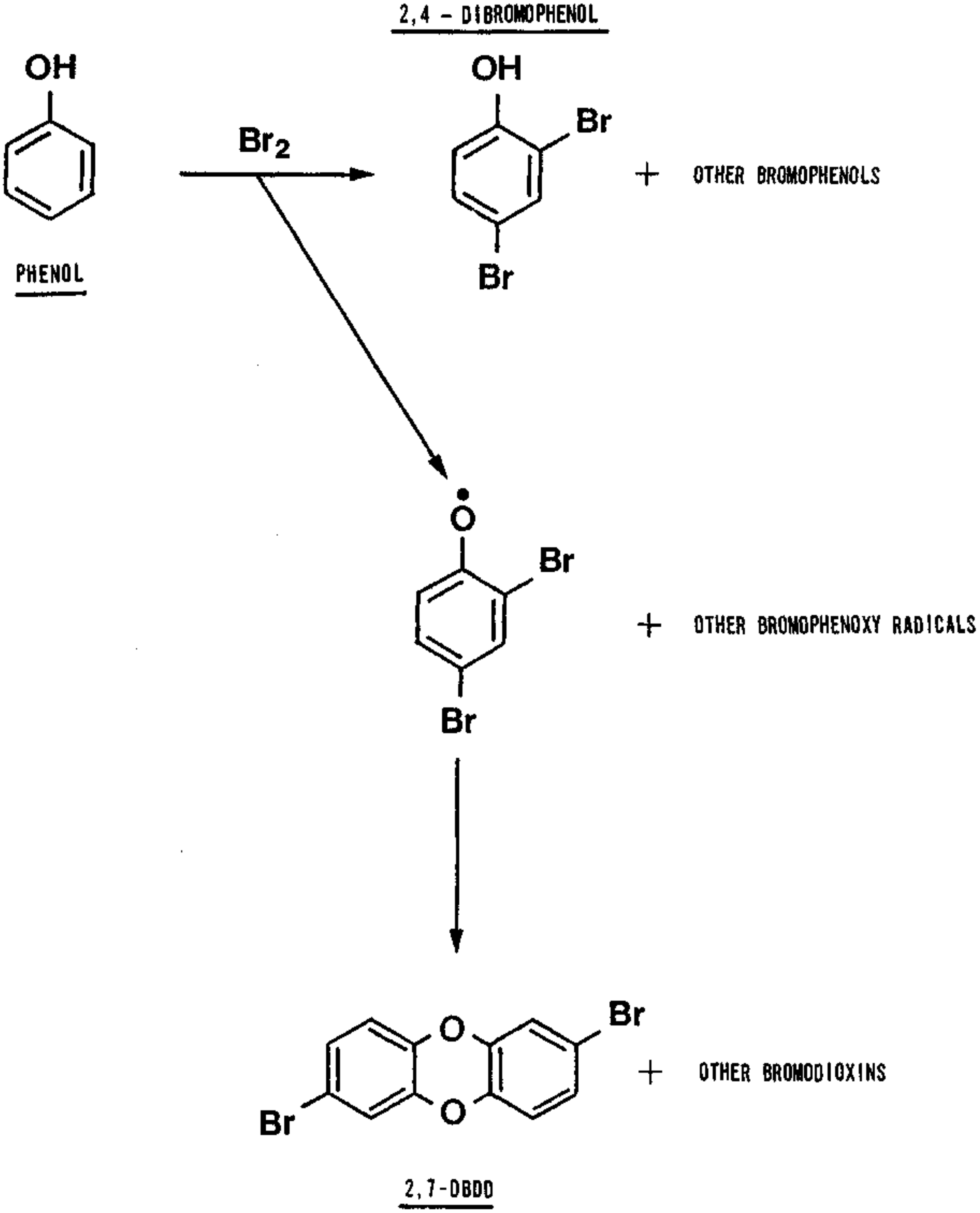


Figure 4. 2,4-Dibromophenol.

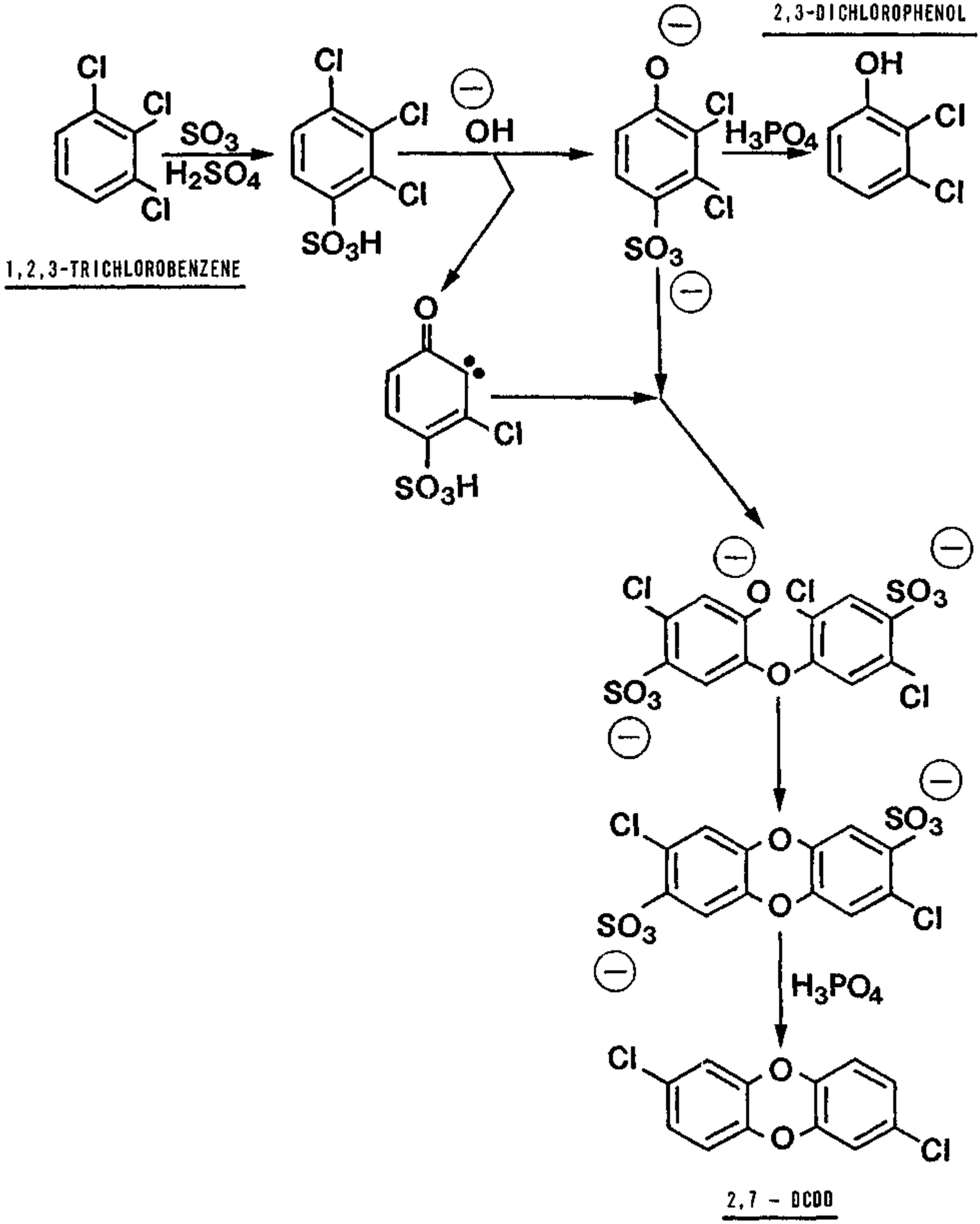


Figure 5. 2,3-Dichlorophenol.

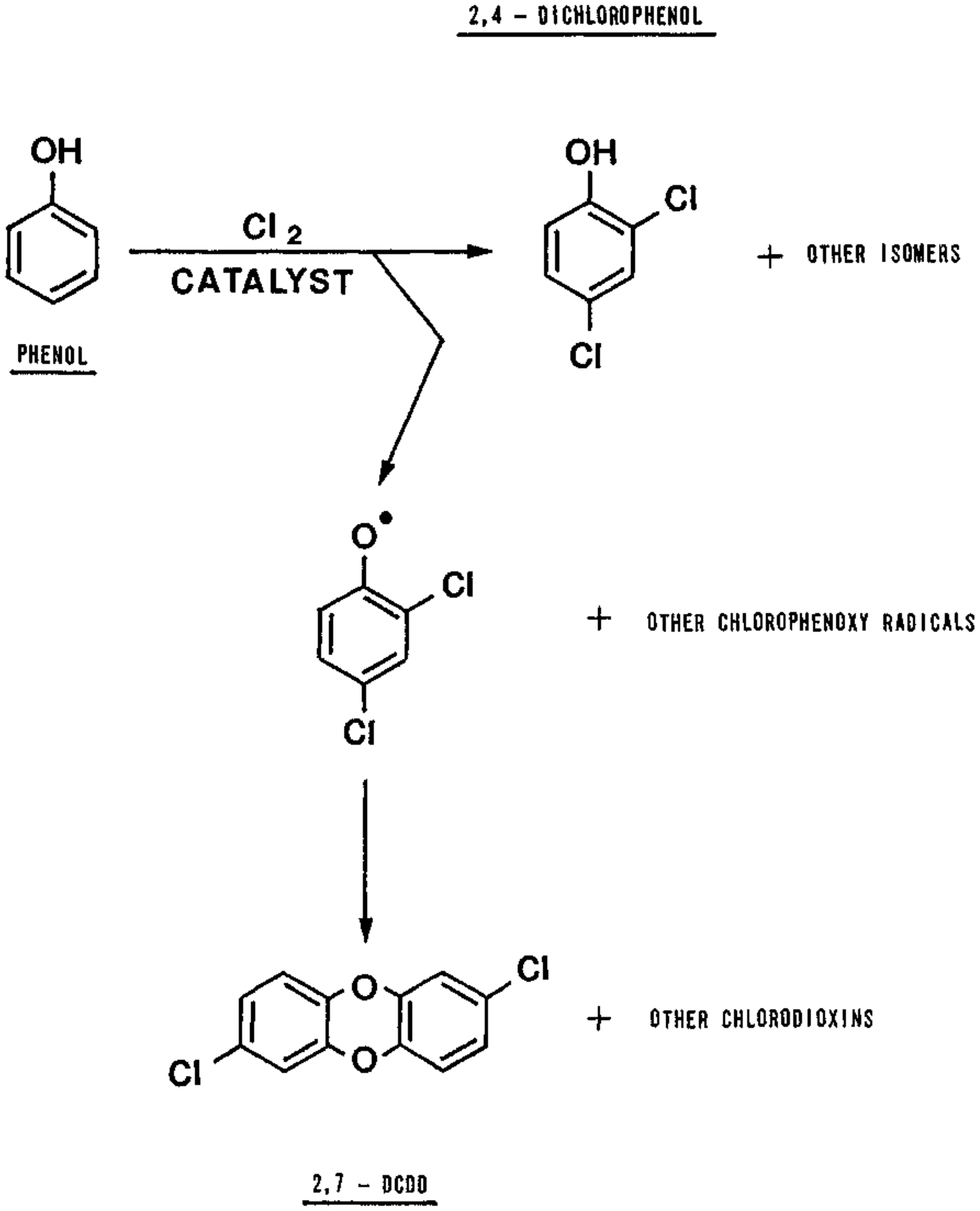


Figure 6. 2,4-Dichlorophenol.

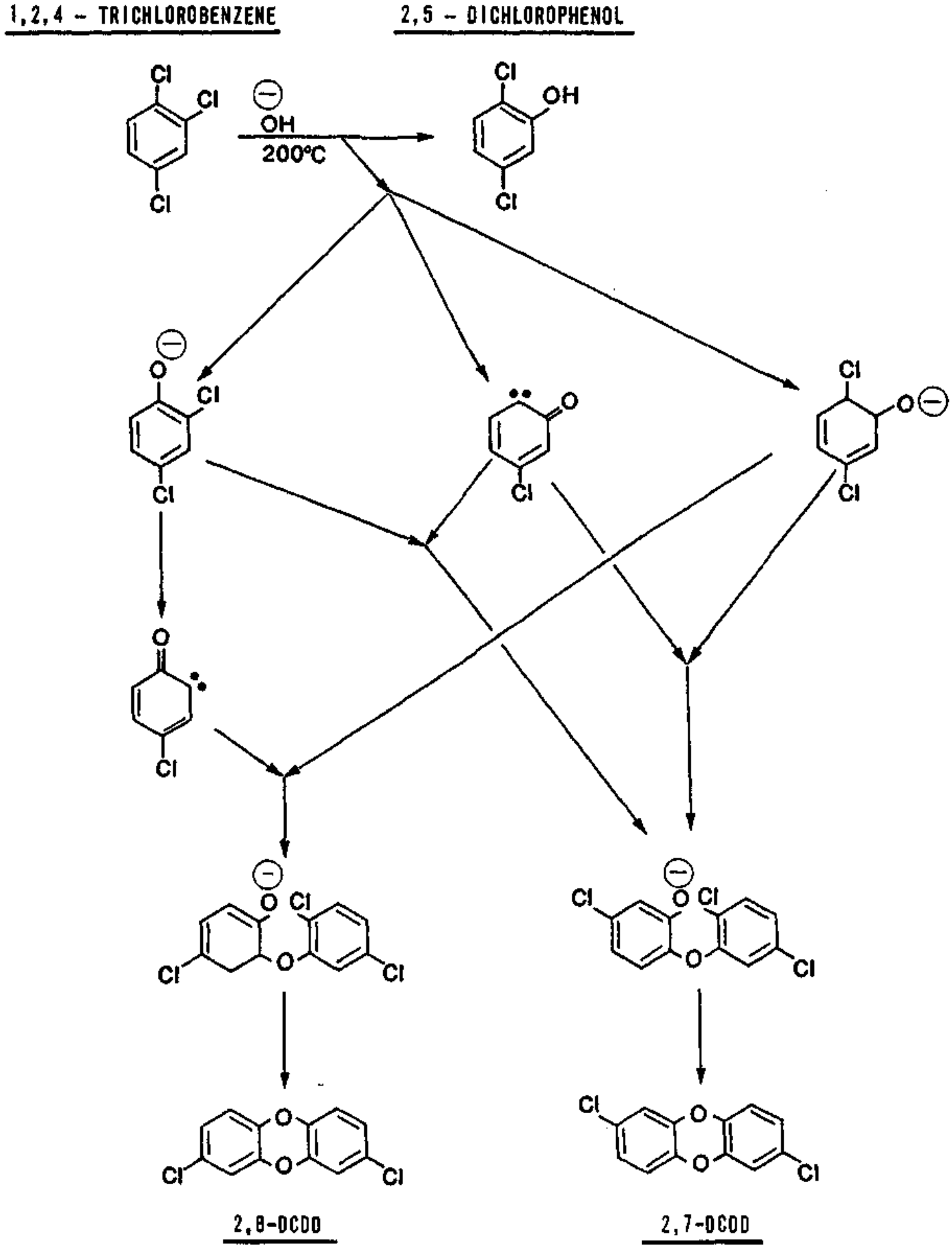


Figure 7. 2,5-Dichlorophenol.

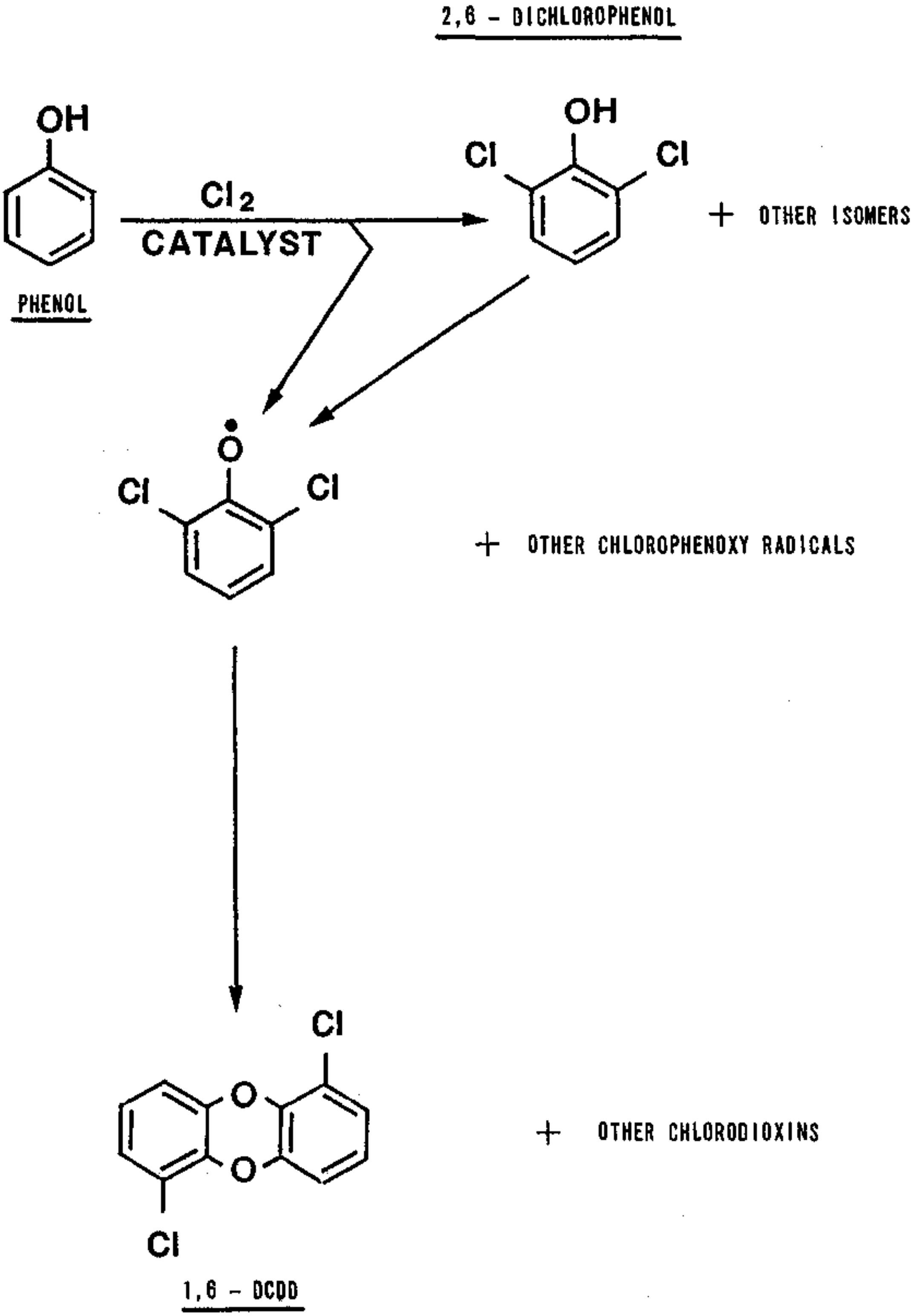


Figure 8. 2,6-Dichlorophenol.

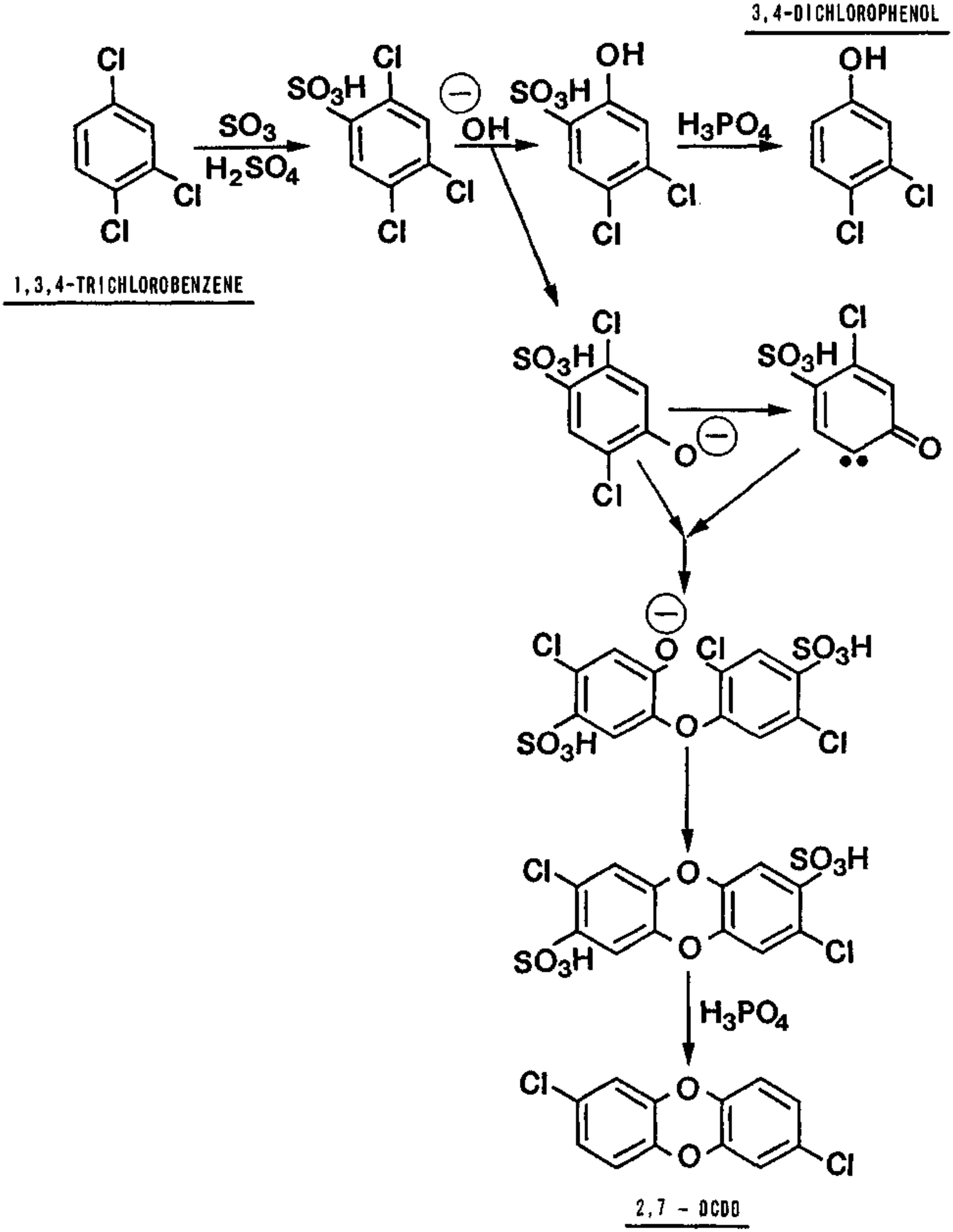


Figure 9. 3,4-Dichlorophenol.

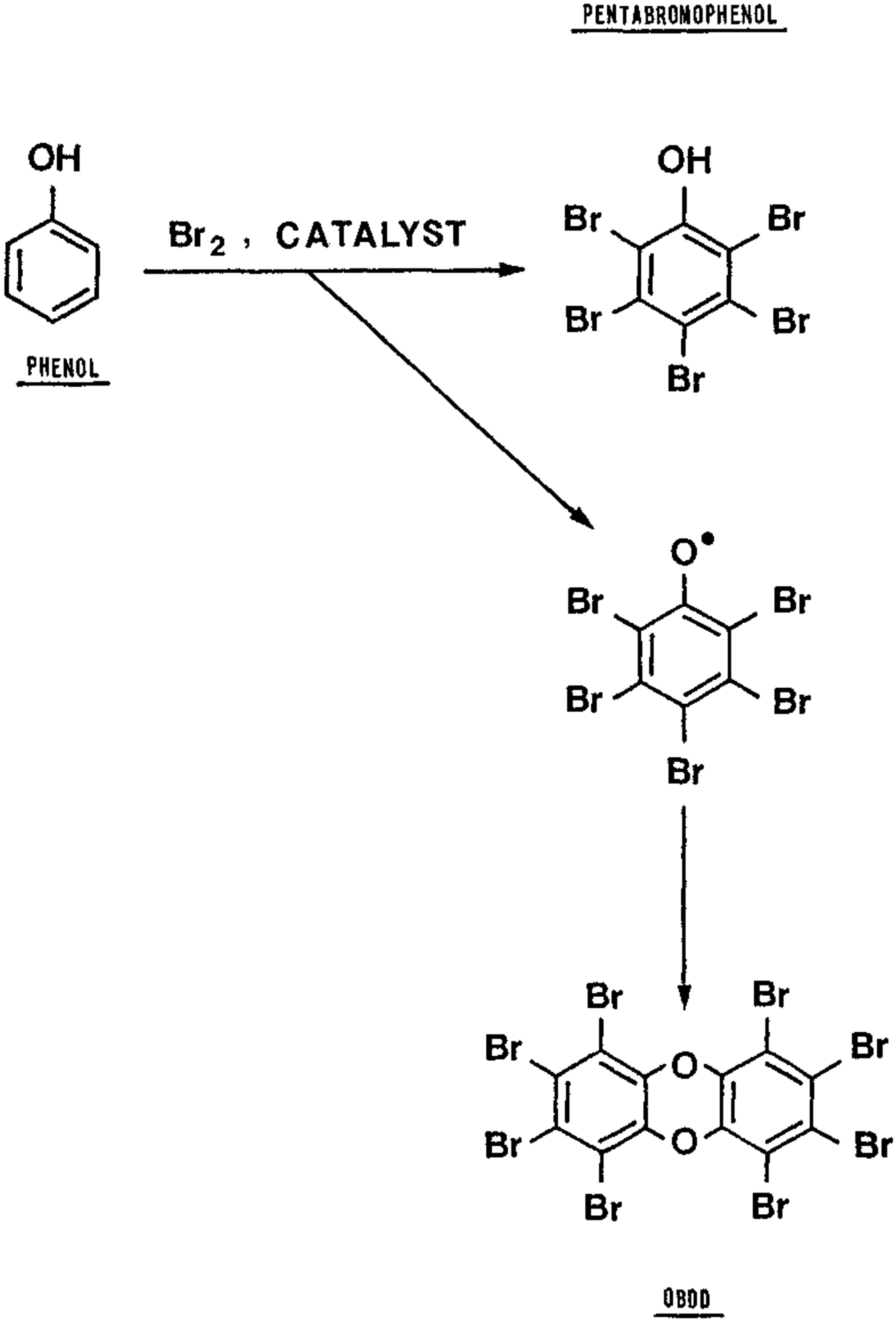


Figure 10. Pentabromophenol.

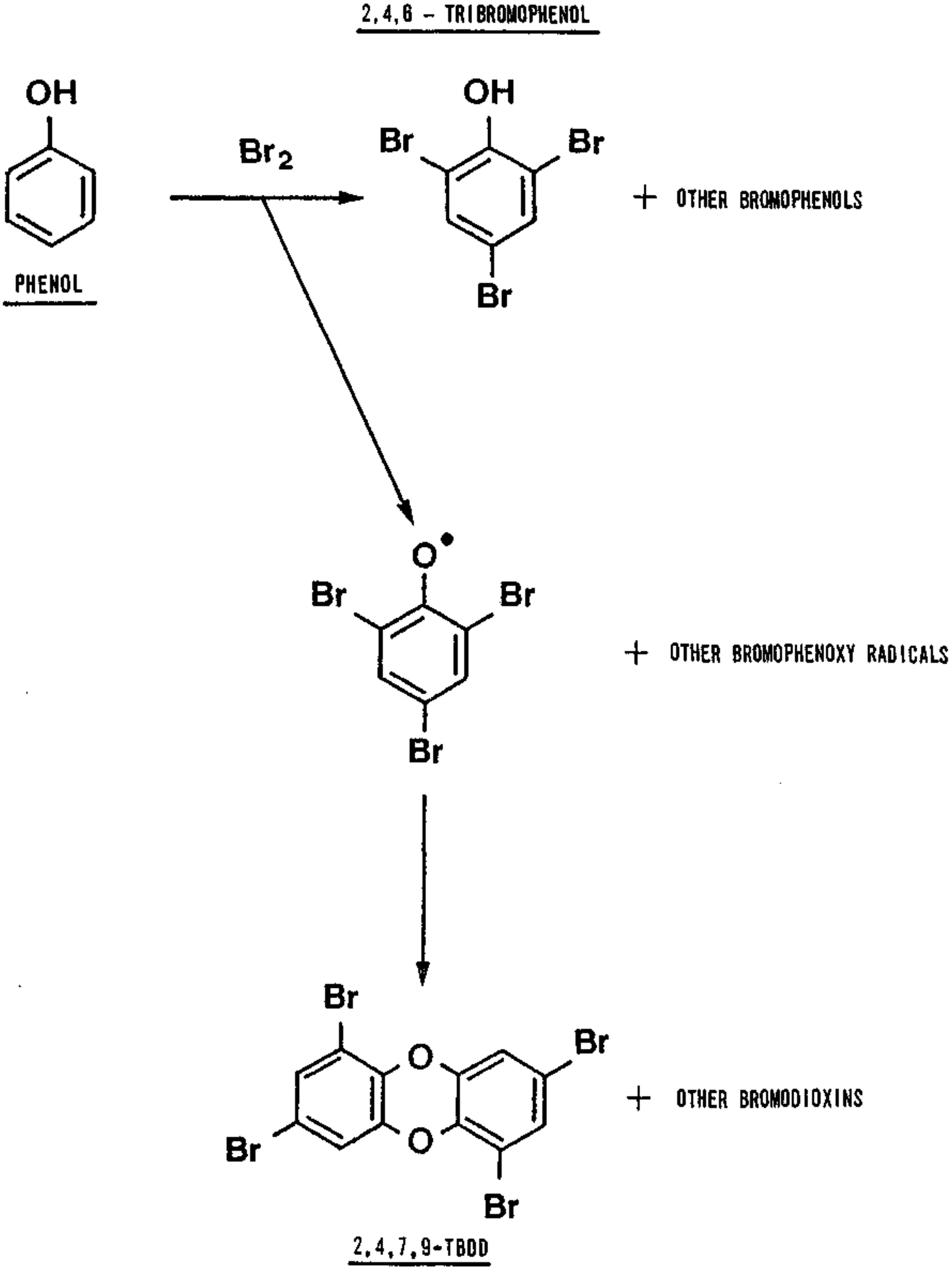


Figure 11. 2,4,6-Tribromophenol.

SECTION 6

PESTICIDE CHEMICALS

Pesticides are the most significant group of organic chemicals in relation to dioxin occurrence. This statement is based on the structure and reaction mechanism analogy, reaction conditions, detected presence of dioxins in a number of commercial pesticide products, and a history of environmental contamination problems, particularly with trichlorophenol and 2,4,5-T.

Chlorinated dibenzo-p-dioxins are known to be present in at least trace amounts in a number of pesticide chemicals. These include 2,4,5-T, silvex, 2,4-D, erbon, Sesone, DMPA, ronnel, tetradifon, and the various chlorophenols (Fishbein 1973). In addition, the chemical structures, reactions, and process conditions for a number of others indicate dioxin content potential.

This study deals with production of the basic pesticide chemicals. Thus it does not address problems of dioxin formation possibly resulting from formulation, storage, distribution, and utilization of the pesticides. If exposure to alkaline formulation media or elevated temperatures is encountered in any of the diverse procedures for handling and use of these pesticides, dioxin formation could be a significant problem.

SELECTION AND CLASSIFICATION

The pesticide chemicals were selected for evaluation in this study on the basis of molecular structure, from those listed as commercial pesticides in the Farm Chemicals Handbook. The primary criterion was an ortho halophenolic structure, or the derivative esters and salts thereof. Also considered were ortho dihalo aromatic structures, which conceivably could convert to phenols upon exposure to alkaline conditions.

A second criterion was a minimum commercial production level of 1000 pounds or $1000 value per year. These correspond to the minimum levels required for inclusion in the Stanford Research Institute Directory of Chemical Producers, which was a primary reference. The lists are based on production during the past 10 years.

The pesticide chemicals considered in this study are listed in Table 6. They are grouped into classes representing likelihood of dioxin formation, as follows:

TABLE 6. LIST OF PESTICIDE CHEMICALS

General name	Chemical name
Class I	
Bifenox	Methyl-5-[2,4-dichloroephenoxy]-2-nitrobenzoate
Chloranil	2,3,5,6-Tetrachloro-2,5-cyclorhexadiene-1,4-dione
2,4-D and esters and salts	(2,4-Dichlorophenoxy)acetic acid and esters and salts
2,4-DB and salts	2,4-Dichlorophenoxybutyric acid and salts
Dicamba	3,6-Dichloro-2-methoxybenzoic acid
Dicamba, dimethylamine salt	3,6-Dichloro-2-methoxybenzoic acid, dimethylamine salt
Dicapthon	Phosphorothioic acid o-(2-chloro-4-nitrophenyl) o,o-dimethyl ester
Dichlofenthion	Phosphorothioic acid o-2,4-dichlorophenyl o,o-diakyl ester
Disul sodium (Sesone)	2,4-Dichlorophenoxyethyl sulfate, sodium salt
2,4-DP	2-[2,4-Dichlorophenoxy] propionic acid
Erbon	2,2-Dichloropropanoic acid 2-(2,4,5-trichlorophenoxy) ethyl ester
Hexachlorophene	2,2'-Methylene bis (3,4,6-trichlorophenol)
Isobac 20	2,2'-Methylene bis (3,4,6-trichlorophenol), monosodium salt
Nitrofen	2,4-Dichlorophenyl-p-nitorphenyl ether
Pentachlorophenol (PCP) and salts	Pentachlorophenol and salts

(continued)

TABLE 6 (continued)

General name	Chemical name
Ronnel	Phosphorothioic acid, o,o-dimethyl 0-(2,4,5-trichlorophenyl) ester
Silvex and esters and salts	2-(2,4,5-Trichlorophenoxy) propionic acid and esters and salts
2,4,5-T and esters and salts	(2,4,5-Trichlorophenoxy) acetic acid
-	2,3,4,6-Tetrachlorophenol
-	2,4,5-Trichlorophenol
<u>Class II</u>	
	o-Benzyl-p-chlorophenol
Bromoxynil and esters	3,5-Dibromo-4-hydroxybenzonitrile
Carbonphenothion	Phosphorodithioic acid s-[[(4-chlorophenyl) thio]methyl] o,o-diethyl ester
DCPA	2,3,5,6-Tetrachloro-1,4-benzenedicarboxylic acid dimethyl ester
Dichlone	2,3-Dichloro-1,4-haphthalenedione
Dinitrobutylphenol, ammonium salt	2,4-Dinitro-6-sec-butyl phenol, ammonium salt
Loxynil	3,5-Diiodo-4-hydroxybenzonitrile
Lindane	1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer
MCPA	(4-Chloro-o-toloxy) acetic acid
MCPB	4-(2-Methyl-4-chlorophenoxy) butyric acid
Mecoprop	2-(4-Chloro-2-methylphenoxy) propionic acid
Parathion	Phosphorothioic acid o,o-diethyl o-(4-nitrophenyl) ester
PCNP	Pentachloronitrobenzene

(continued)

TABLE 6 (continued)

General name	Chemical name
-	Pipecolinopropyl-3,4-dichlorobenzoate
Piperalin	3-(2-methylpiperidino)propyl-3,4-dichlorobenzoate
Propanil	3,4-Dichloropropionanilide
Tetradifon	1,2,4-Trichloro-5-[(4-chlorophenyl)-sulfonyl] benzene
-	2,3,6-Trichlorobenzoic acid
-	2,3,6-Trichlorophenylacetic acid and sodium salt
-	Triiodobenzoic acid

Class I - Highly likely to be associated with the presence of halogenated dibenzo-p-dioxins because of the presence of an ortho-halogenated phenol in the reaction sequence, with subjection to elevated temperature (≥145°C+) plus either alkalinity or the presence of free halogen.

Class II - Reasonable but lesser probability of such dioxin association because of the presence of phenolic or aromatic structures related to dioxins; although not directly involving dioxin precursive conditions, such chemicals might form dioxins under irregular operating conditions.

CHEMICAL REACTIONS

Higher chlorinated dioxins have been detected in samples of a number of pesticides produced from 1950 to 1970. Data from these analyses were summarized by Fishbein (1973), as shown in Table 7.

Many of the dioxins present differ from those expected on the basis of the straightforward mechanisms hypothesized. Possible reasons for this may be that other mechanisms are at work or that substantial disproportionation is occurring among the dioxins initially formed, as has been suggested by Dow Chemical (Rawls 1979) and others (Buser 1976).

Reaction mechanisms for the Class I pesticide products are shown in the following figures. The intended product reaction sequence is from left to right across the top of each figure, and the possible dioxin side reaction mechanism diverges to typical dioxin byproducts at the bottom of the figure. The specific dioxin products shown are those for which reasonably straightforward mechanisms can be postulated. In many cases, more complex and secondary mechanisms may produce dioxins in addition to those shown, as evidenced by their analytical detection in a number of products (Fishbein 1973).

The initial reaction steps in producing many of the Class I pesticides are very similar and thus the pesticides are grouped by common mechanism. Similarity is noted in 2,4,5-T, silvex, ronnel, 2,4-D, erbon, Sesone, dichlofenthion, dicapthon, bifenox, and dicamba. The final substitution pattern differs in each case, as does the precise halophenol or chlorobenzene starting structure.

The first step in production of 2,4,5-T, silvex, ronnel, and erbon is identical (Figures 12 through 15). Treatment of 1,2,4,5-tetrachlorobenzene with caustic yields 2,4,5-trichlorophenol. The reaction conditions are sufficiently drastic, including alkalinity and elevated temperature, to cause formation of the α-ketocarbene, which reacts with the chlorophenylate to give the predioxin, which then reacts to yield 2,3,7,8-TCDD. Continued alkaline processing, which occurs with each of these product items, also contributes to the same transient intermediates and consequently to formation of 2,3,7,8-TCDD.

TABLE 7. HIGHER CHLORINATED DIOXINS FOUND IN COMMERCIAL PESTICIDES[a]

Pesticide	Chlorodibenzo-p-dioxin detected[b]				Sample	
	Tetra-	Hexa-	Hepta-	Octa-	Number contaminated	Number tested
Phenoxyalkanoates						
2,4,5-T	++	++	-	-	23	42
Silvex	+	-	-	-	1	7
2,4-D	-	+	-	-	1	24
Erbon	-	-	-	++	1	1
Sesone	-	+	-	-	1	1
Chlorophenols						
Tri-	-	+	+	+	4	6
Tetra-	-	++	++	++	3	3
Penta-(PCP)	-	++	++	++	10	11
Others[c]	-	++	++	+	5	22

[a] Fishbein, 1973.

[b] concentration range:
++ = >10 ppm
+ = 0.5 to 10 ppm
- = <0.5 ppm

[c] DMPA, ronnel, and tetradifon were found to contain chlorodioxin contamination.

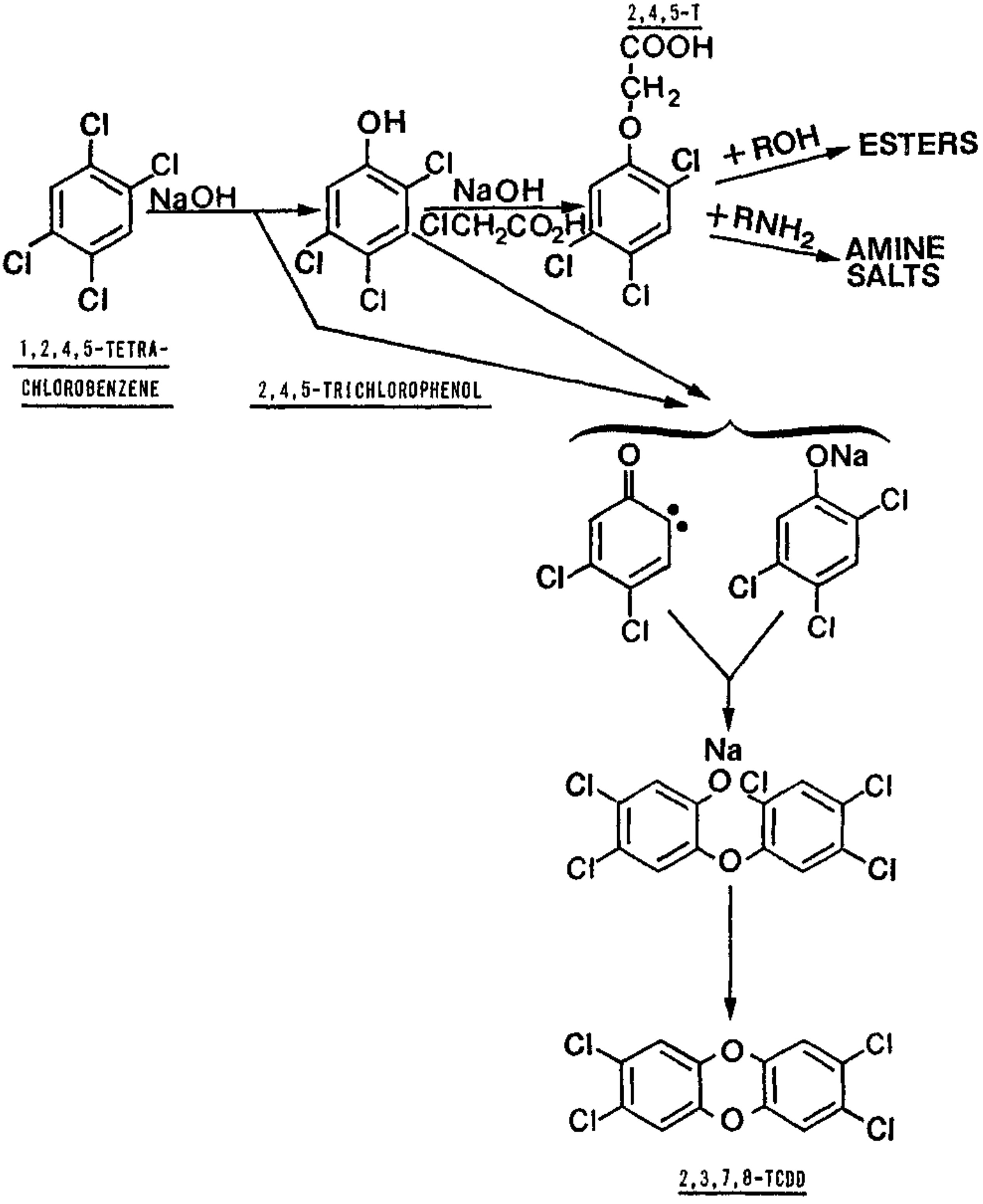


Figure 12. 2,4,5-Trichlorophenol, 2,4,5-T and esters and salts.

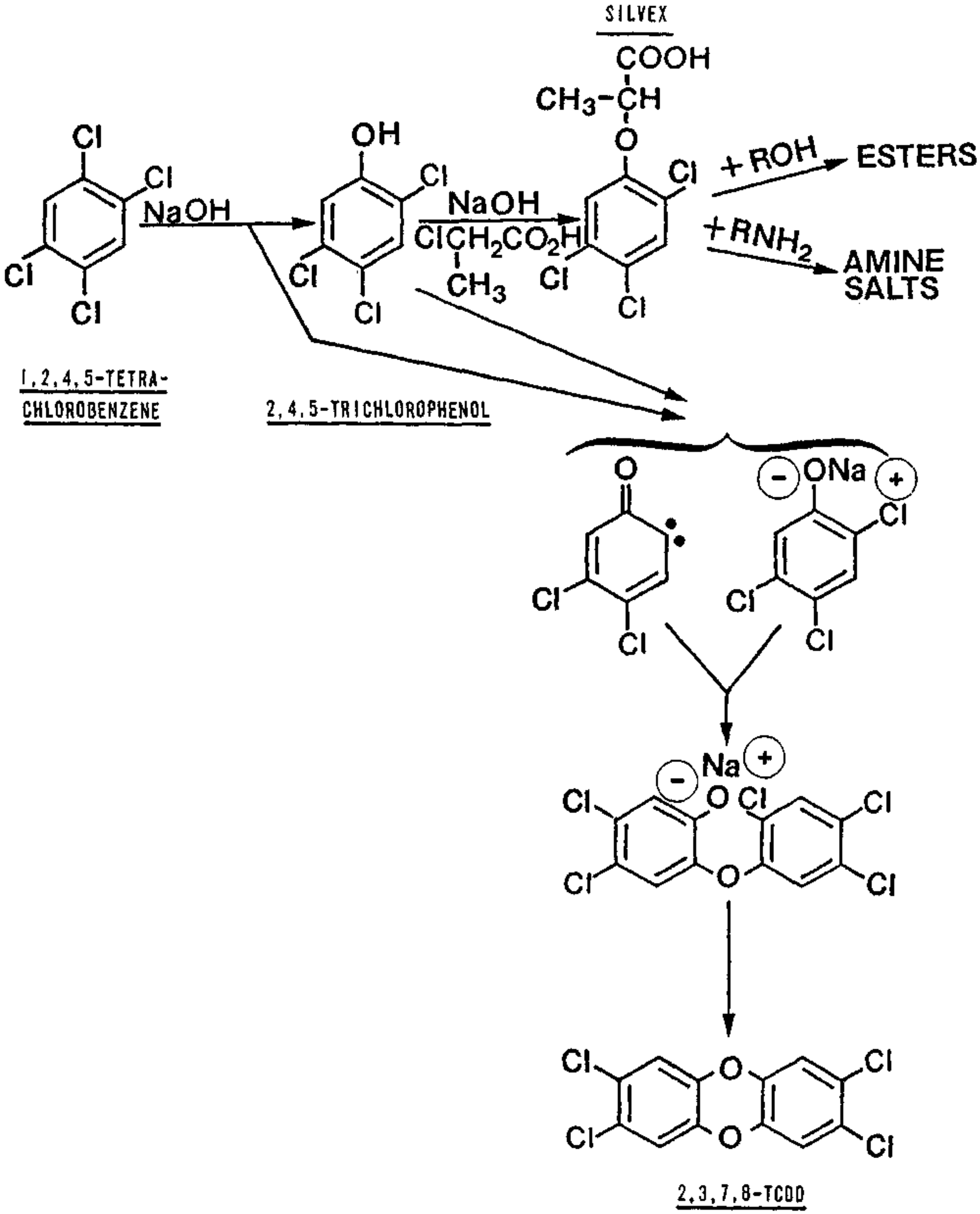


Figure 13. Silvex and esters and salts.

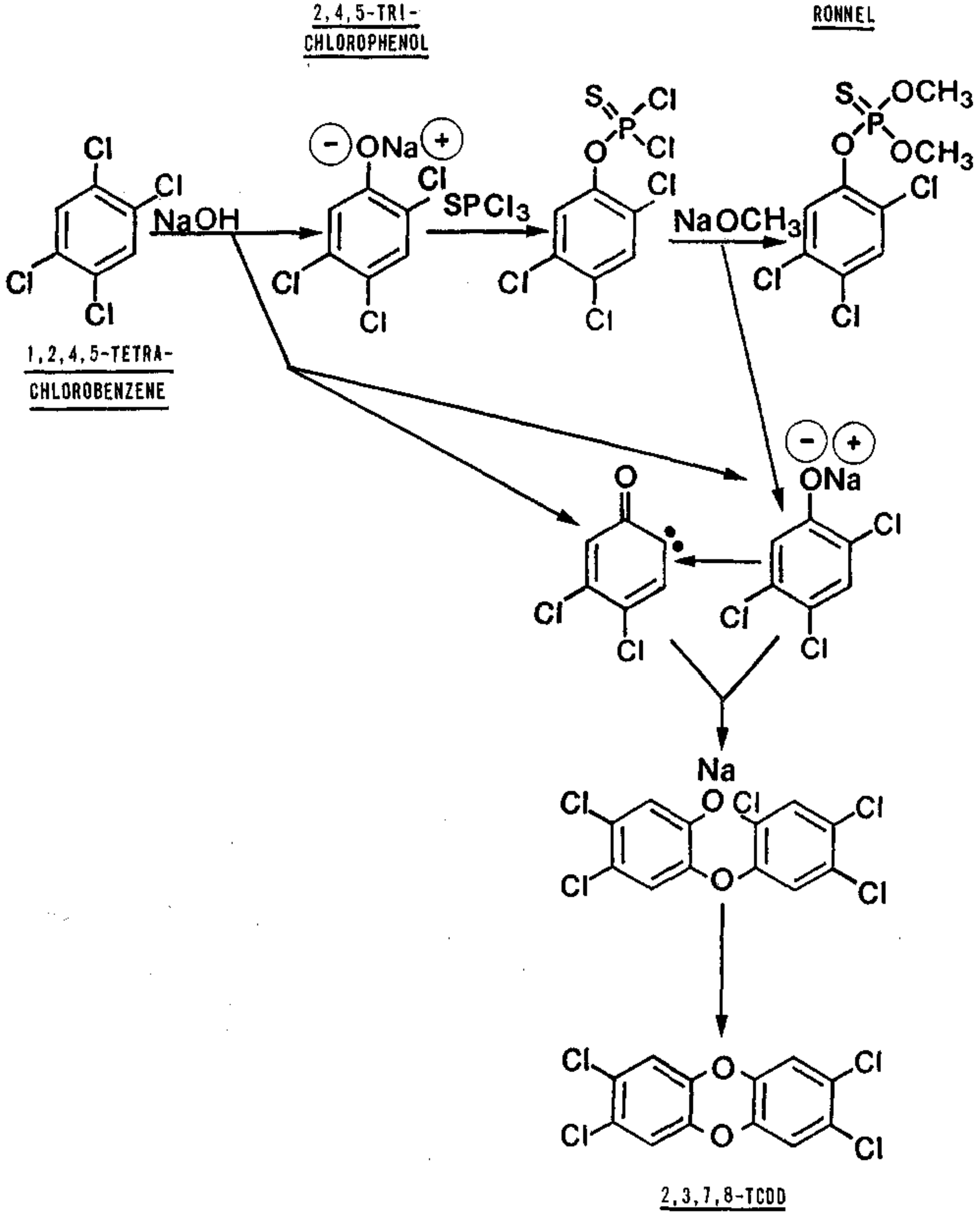


Figure 14. Ronnel.

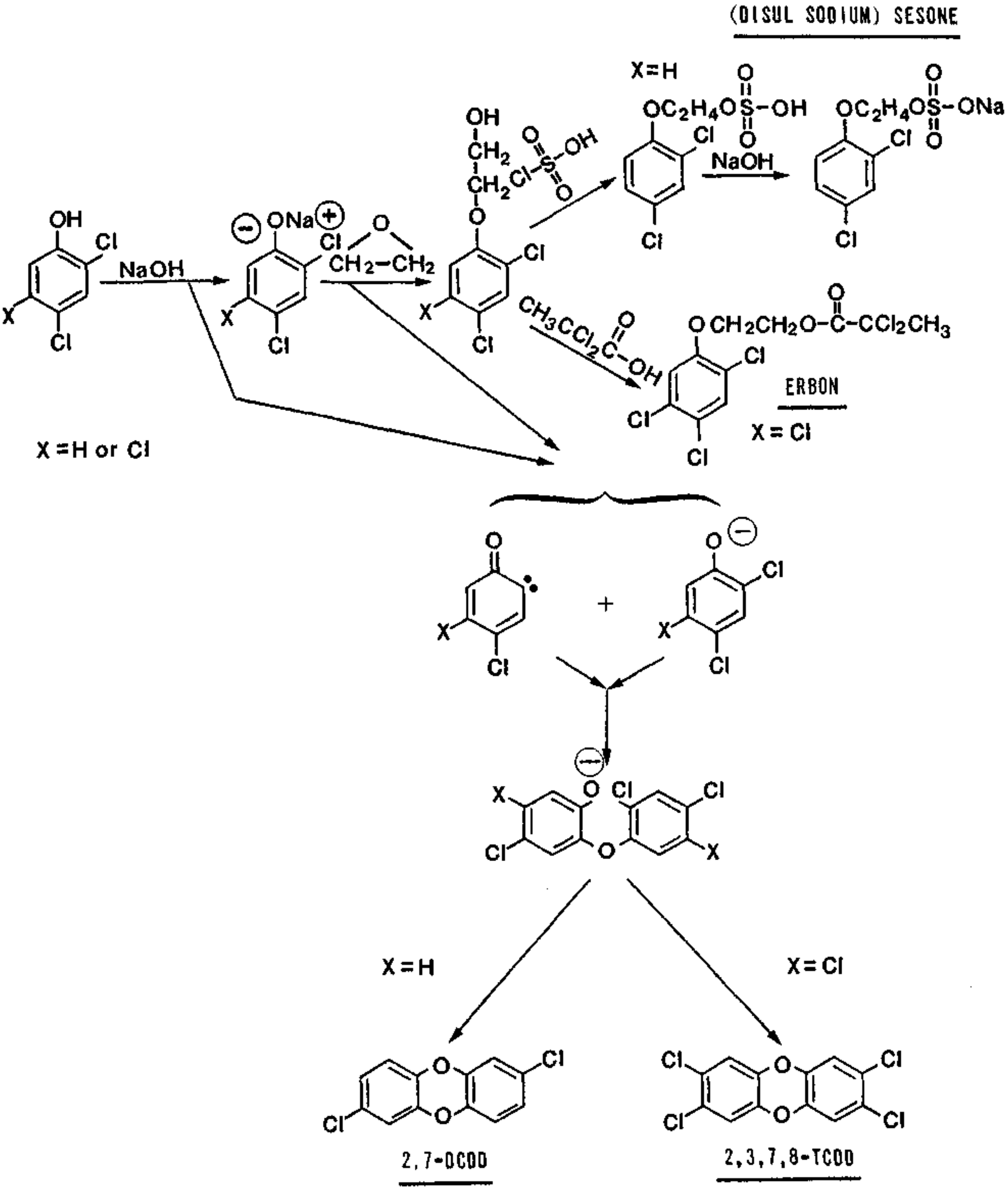


Figure 15. Erbon and Sesone.

The normal reaction sequences for 2,4-D, 2,4-DB, 2,4-DP, disul sodium (Sesone), dichlofenthion, bifenox, and nitrofen (sequences shown in Figures 15 through 21) are analogous in their early steps to those of 2,4,5-T and others in the group just described, but occur via 2,4-dichlorophenol rather than 2,4,5-trichlorophenol. The dioxin formation sequence is likewise analogous but typically would produce 2,7-DCDD.

Note that the reaction mechanism for disul sodium is presented in the same figure (Figure 15) with that for erbon. This placement is not meant to imply that they are co-products, but rather is intended to demonstrate the analogous reaction patterns of typical pesticides differing as to halogenation and substitutions. Similar analogies can be drawn among nearly all of the pesticide chemicals studied.

Another point, important to dioxin formation, is demonstrated in Figure 16, showing the reaction for 2,4-D. The reaction sequence conventionally cited is chlorination of phenol to 2,4-dichlorophenol, followed by reaction with chloroacetic acid in the presence of caustic to produce 2,4-D. This last step with the dichlorophenol under alkaline conditions can result in dioxin formation. An alternative process sequence cited in the patent literature (Manske 1949) reverses the order of chlorination, as shown in the upper tier reaction of Figure 16. This sequence would be expected to reduce the likelihood of dioxin formation. A commercially feasible yield in excess of 80 percent is noted, but the extent of commercial utilization is not known. This reaction sequence could possibly be adapted to other dihalogenated phenoxyalkanoates, with an expected reduction in dioxin formation.

Dicamba (Figure 22) with its dimethylamine salt presents one of the more complex dioxin derivation patterns because of the continued alkaline conditions under which various substitutions are made. First, preparation of 2,5-dichlorophenol and its subsequent further exposure to caustic results in transient intermediates and predioxins that form 2,7-DCDD and 2,8-DCDD. In addition, similar alkaline processing of the carboxyl and methyl substituted forms can result in variously substituted dioxins, only two of which, for simplicity, are shown in Figure 22.

Pentachlorophenol (PCP), a commercially high-volume chemical, can be manufactured by two basic methods. One involves direct chlorination of phenol (Figure 23) in the presence of an $AlCl_3$ catalyst. The presence of normal excess chlorine is conducive to formation of a free-radical intermediate, then of the predioxin, and ultimately of OCDD. The alternative process based on caustic treatment of hexachlorobenzene (Figure 24) produces chlorinated transient intermediates analogous to the 2,4,5-T series but fully chlorine substituted. These in turn form the predioxin and finally OCDD.

The complex free-radical mechanism by which chloranil is made (Figure 25) results in transient intermediates similar to those occurring as by-product derivatives of PCP. Therefore, OCDD should be expected as a dioxin contaminant.

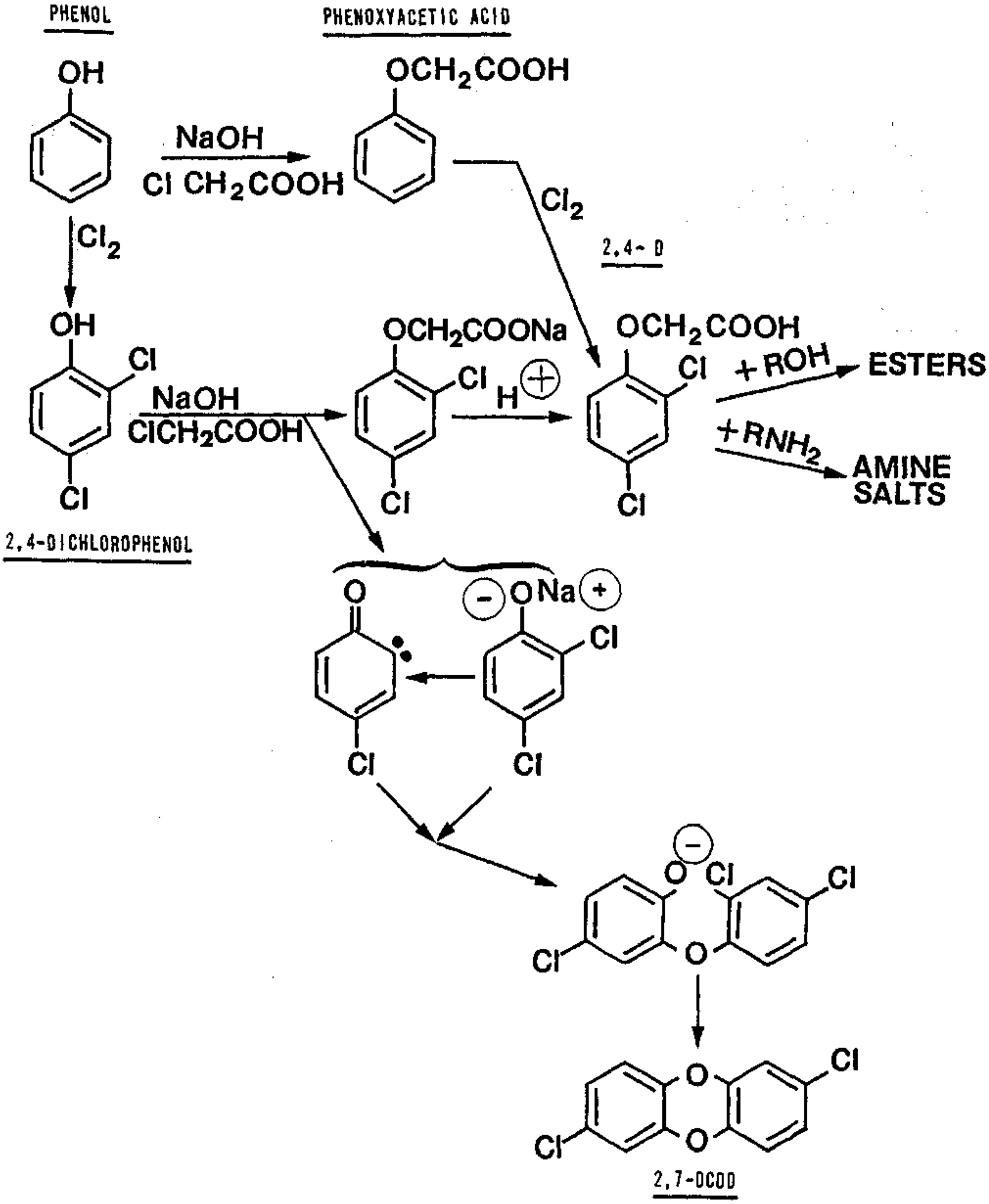


Figure 16. 2,4-D and esters and salts.

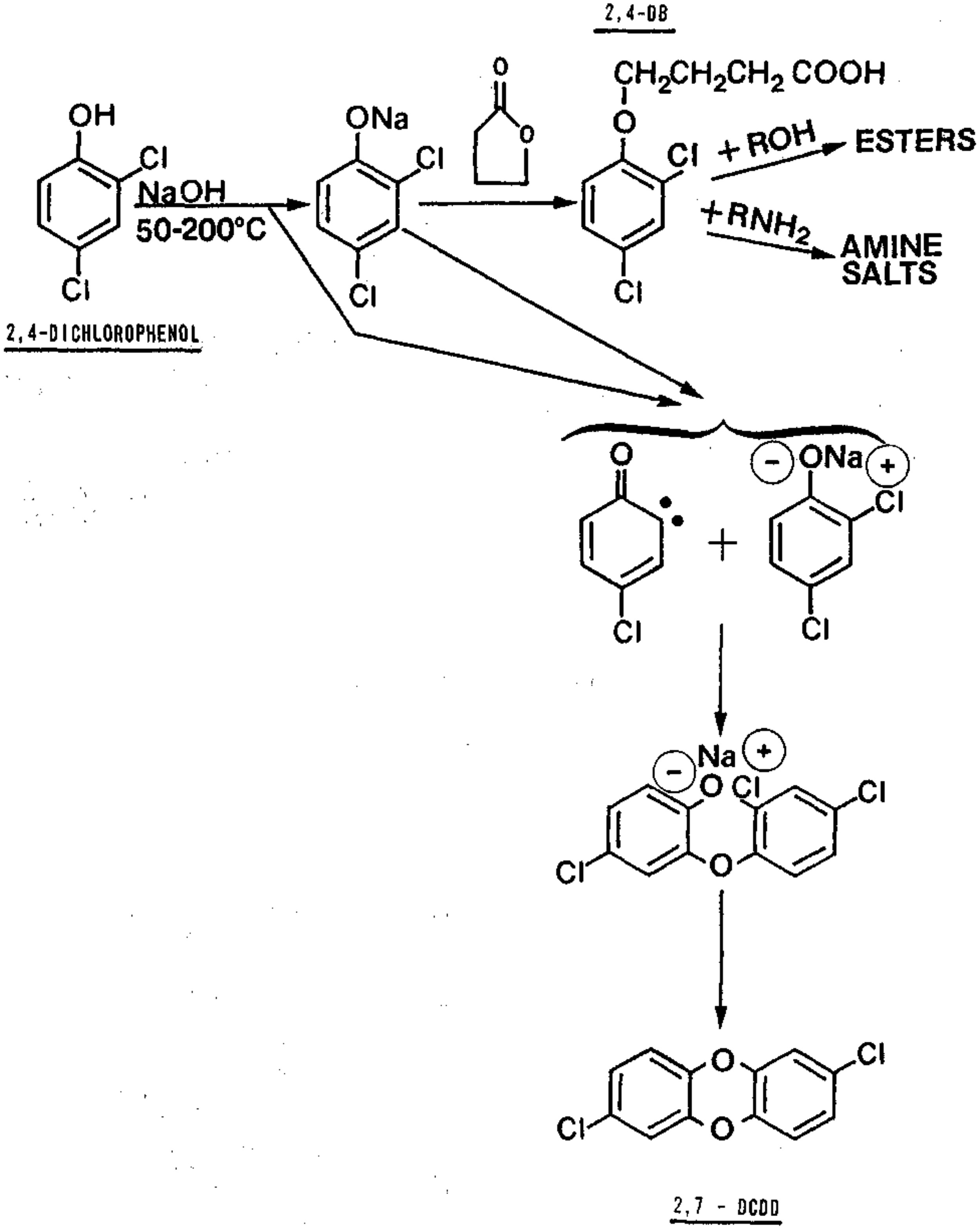


Figure 17. 2,4-DB.

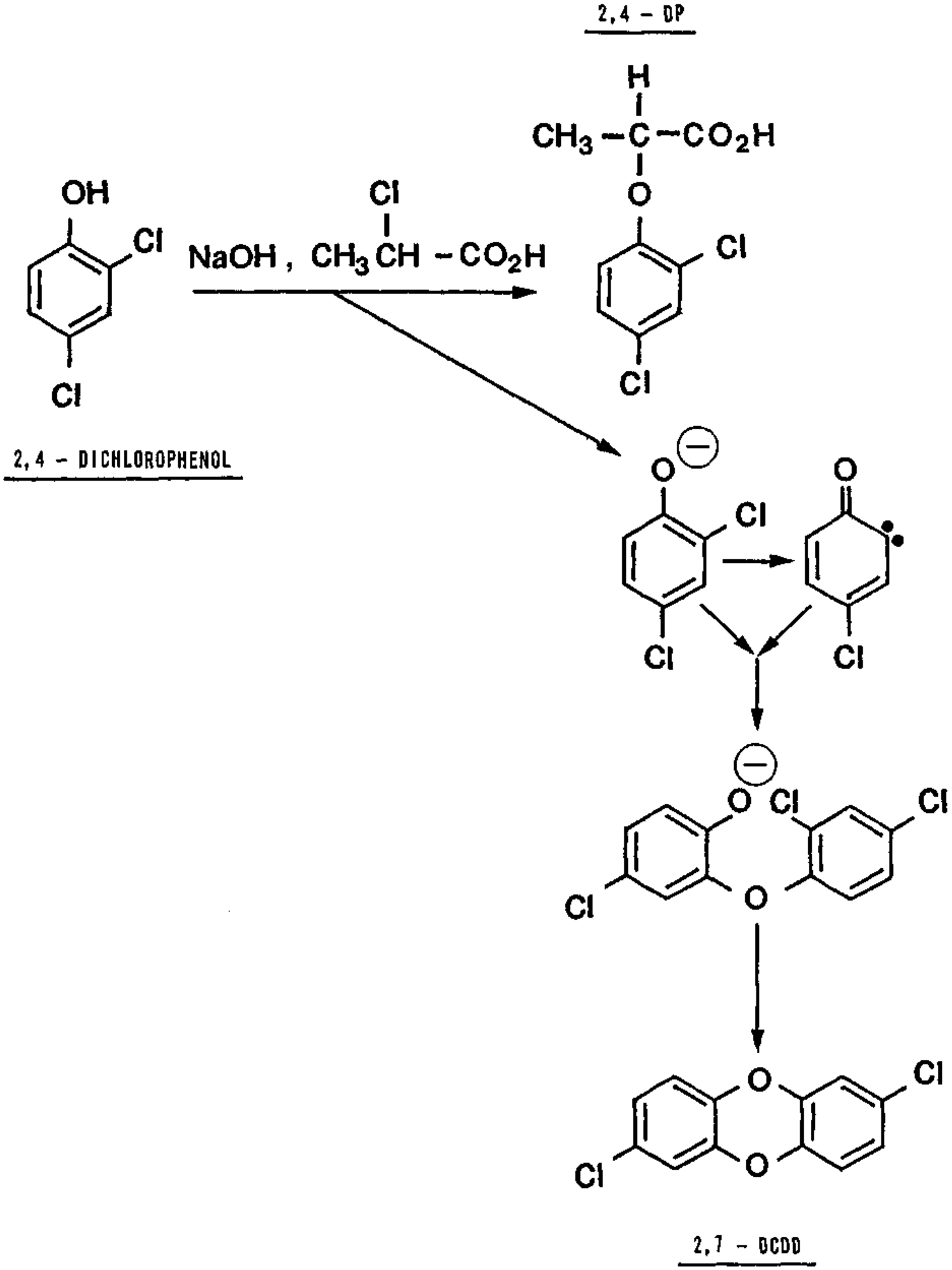


Figure 18. 2,4-DP.

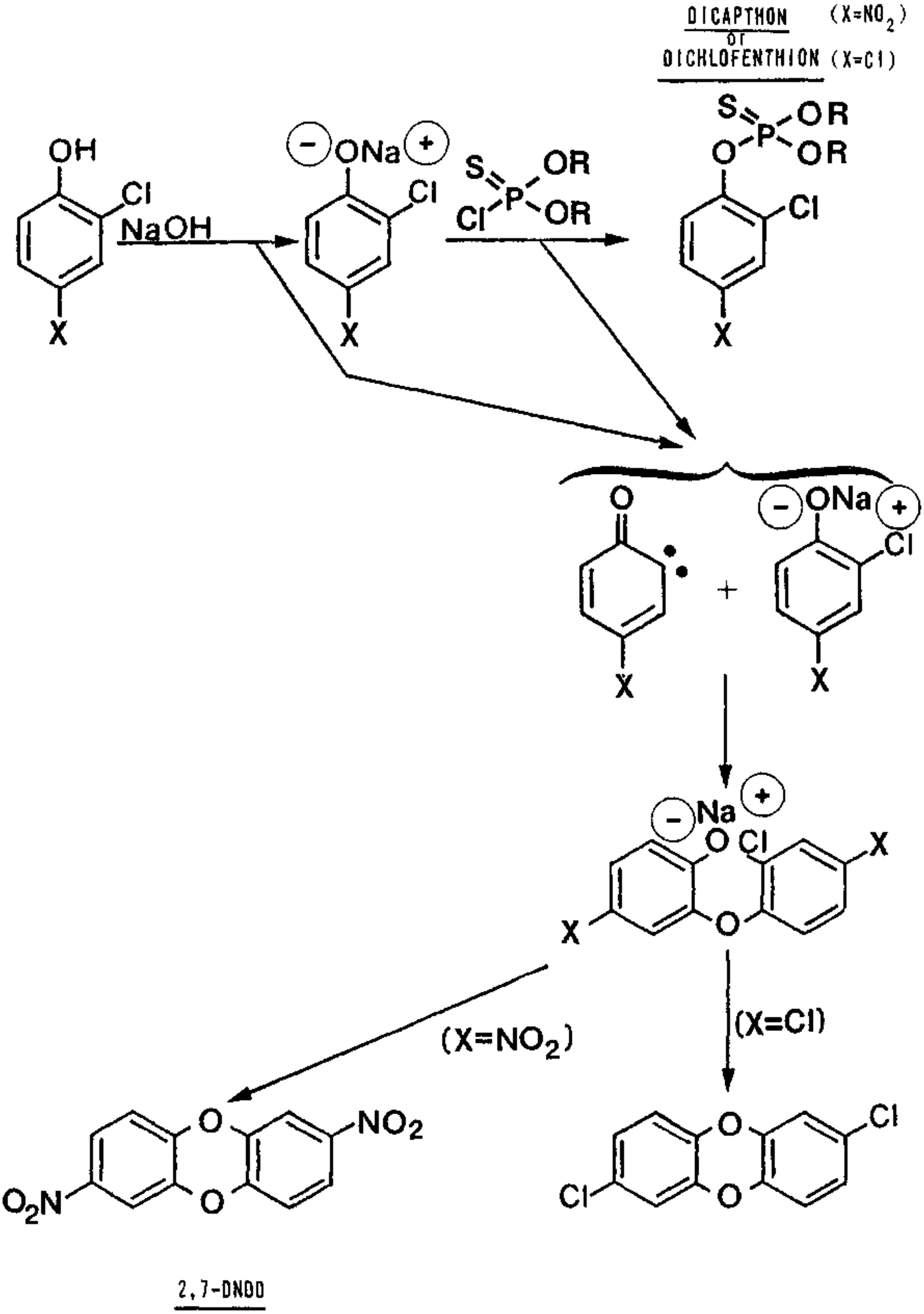
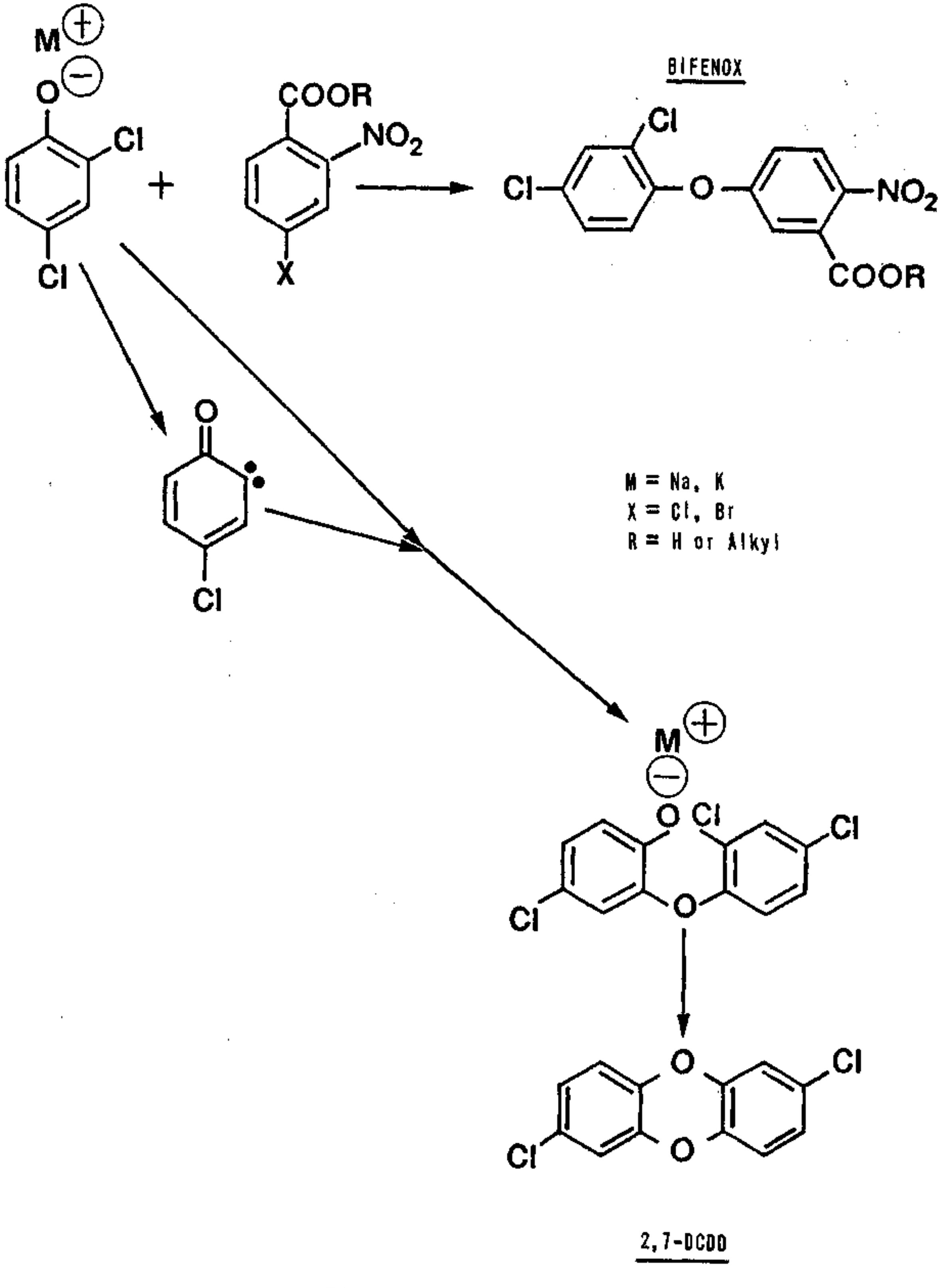


Figure 19. Dicapthon and Dichlofenthion.



M = Na, K
X = Cl, Br
R = H or Alkyl

Figure 20. Bifenox.

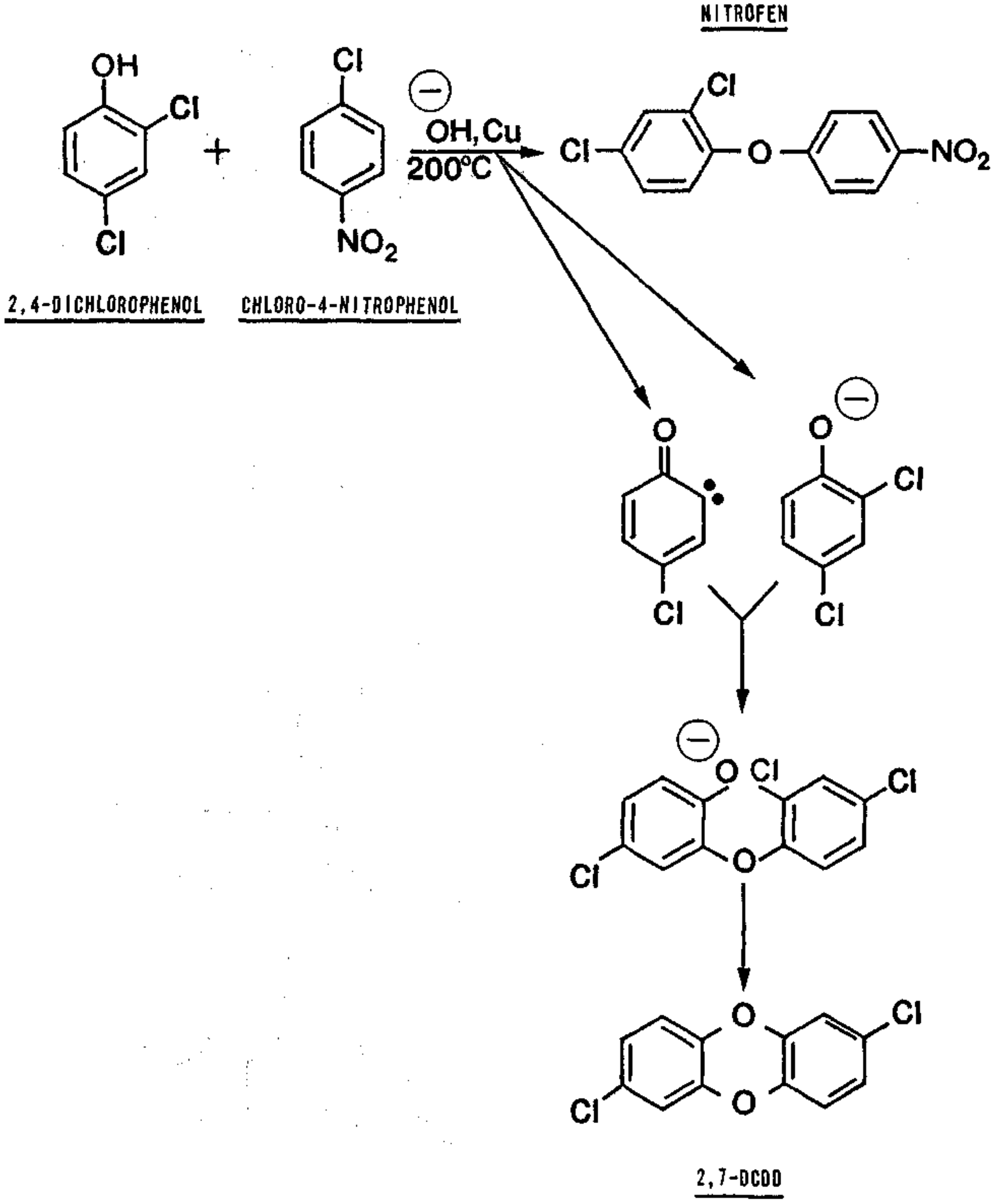


Figure 21. Nitrofen.

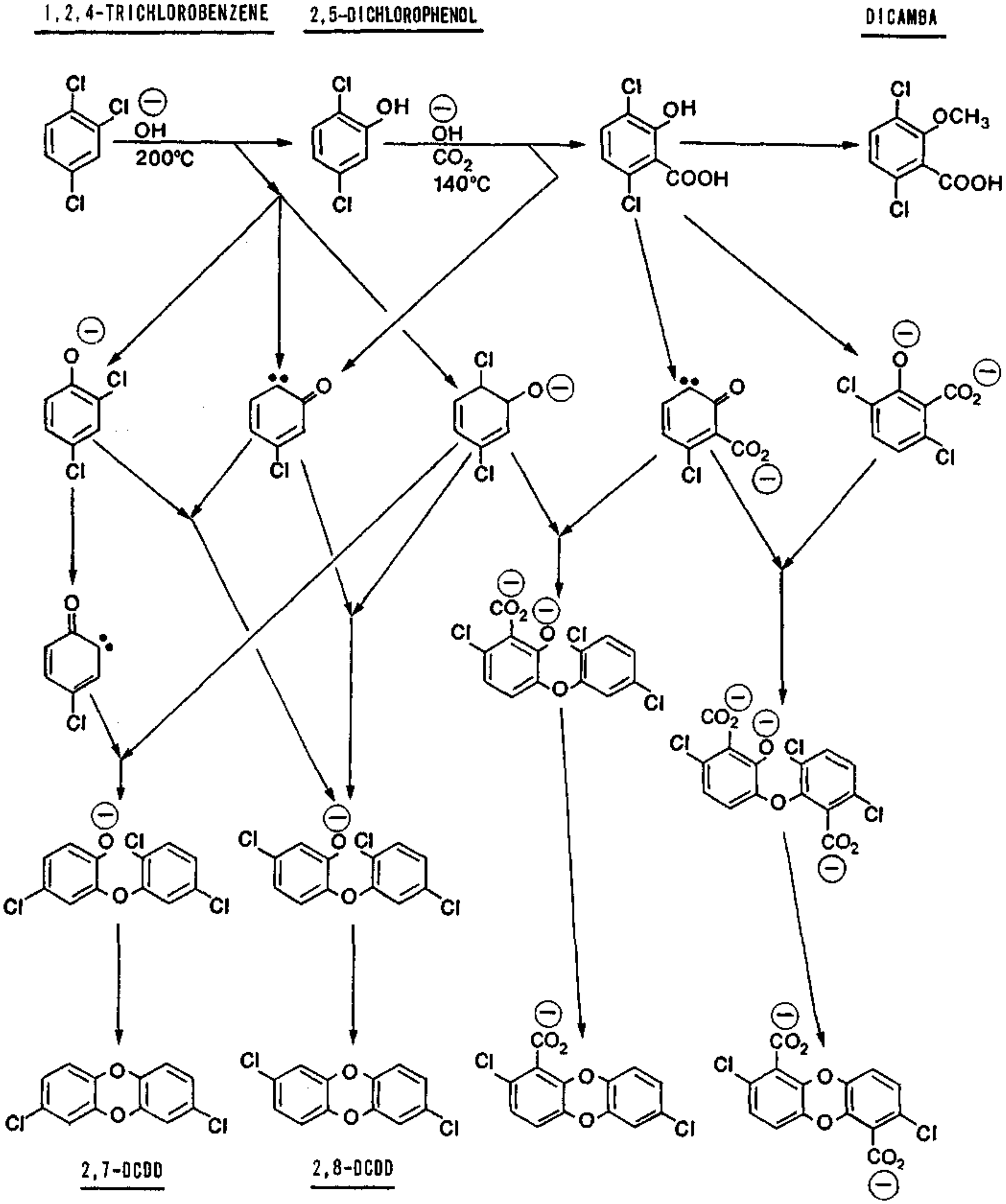


Figure 22. Dicamba.

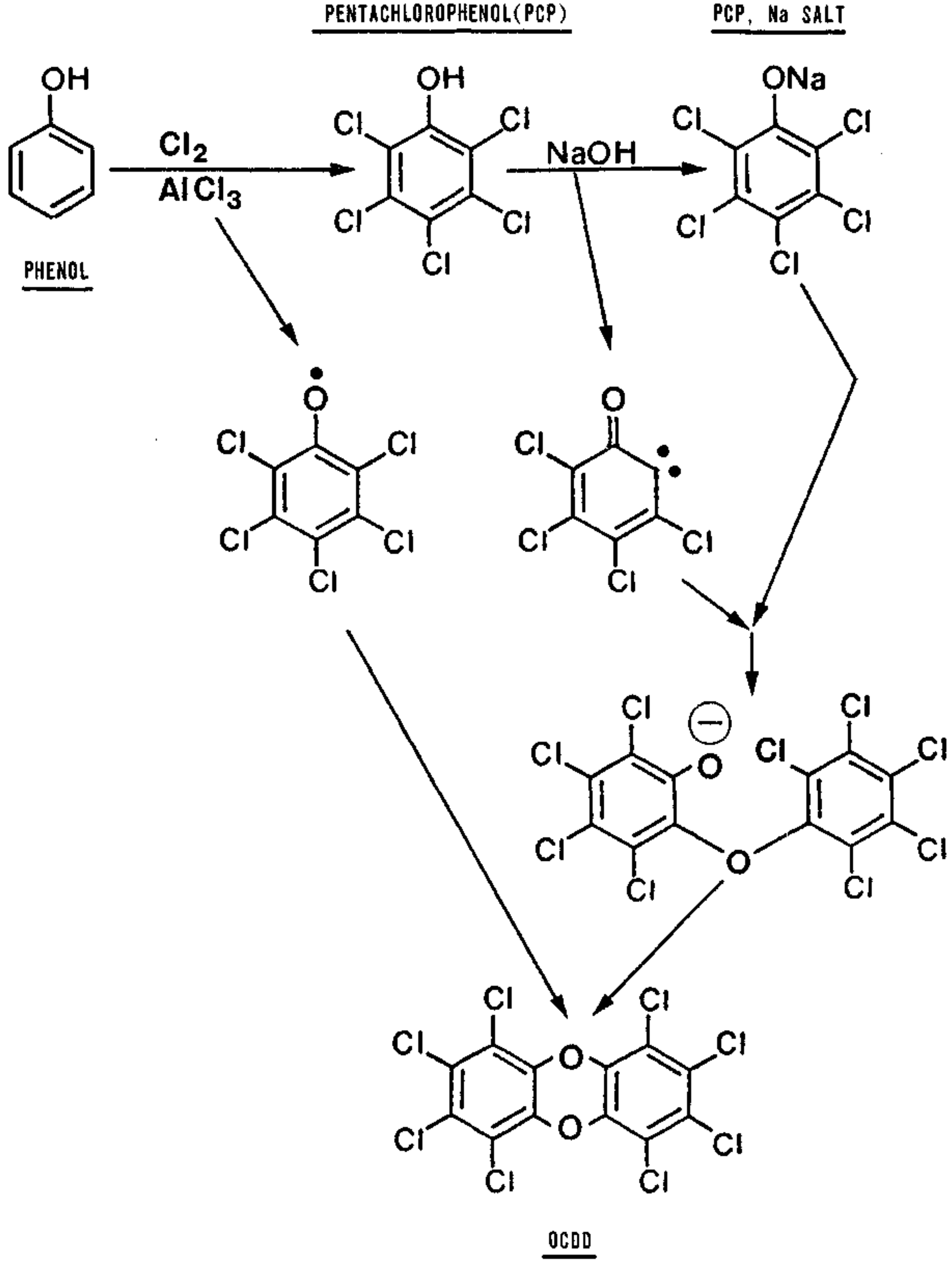


Figure 23. Pentachlorophenol (PCP) via phenol.

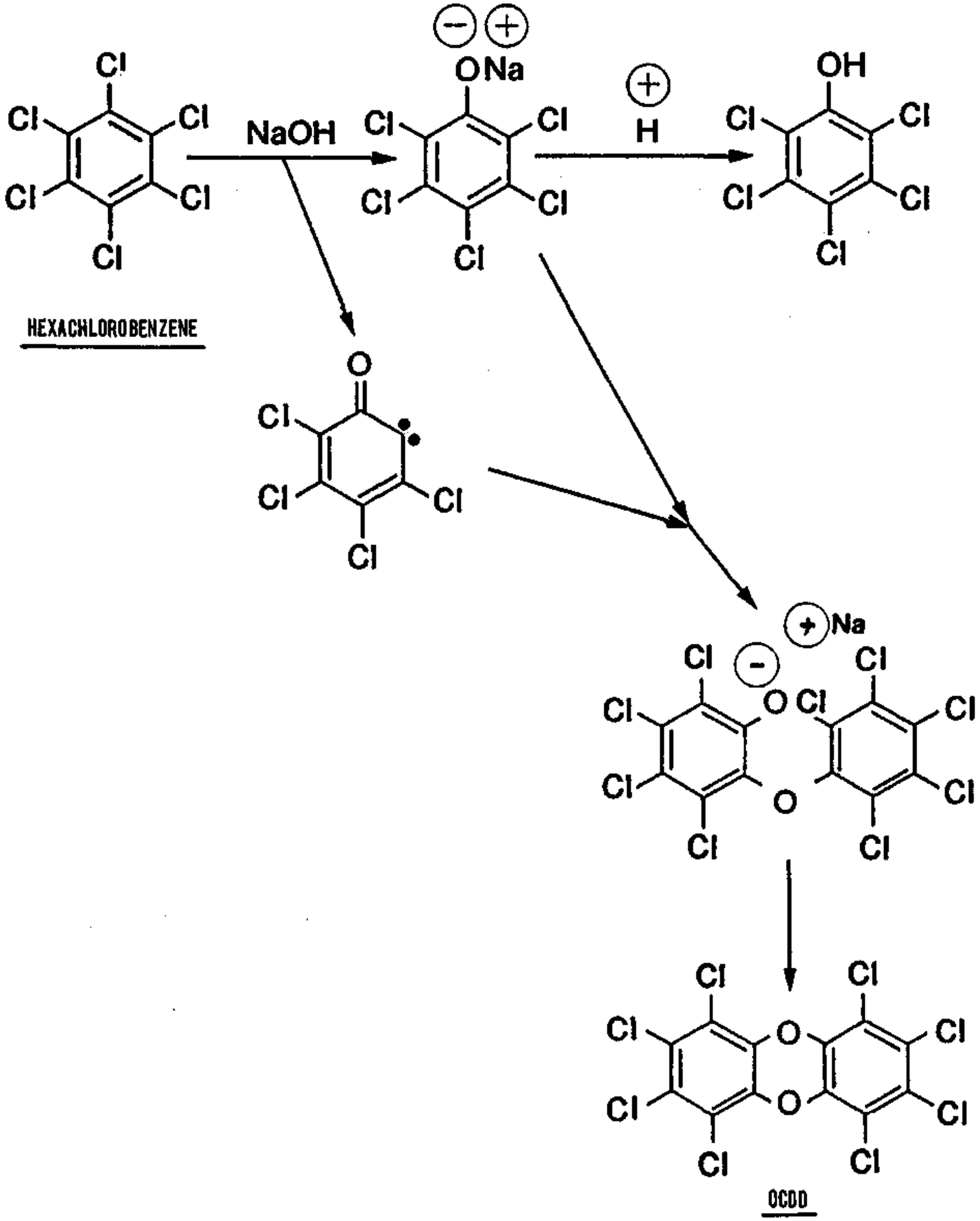


Figure 24. Pentachlorophenol (PCP) via hexachlorobenzene.

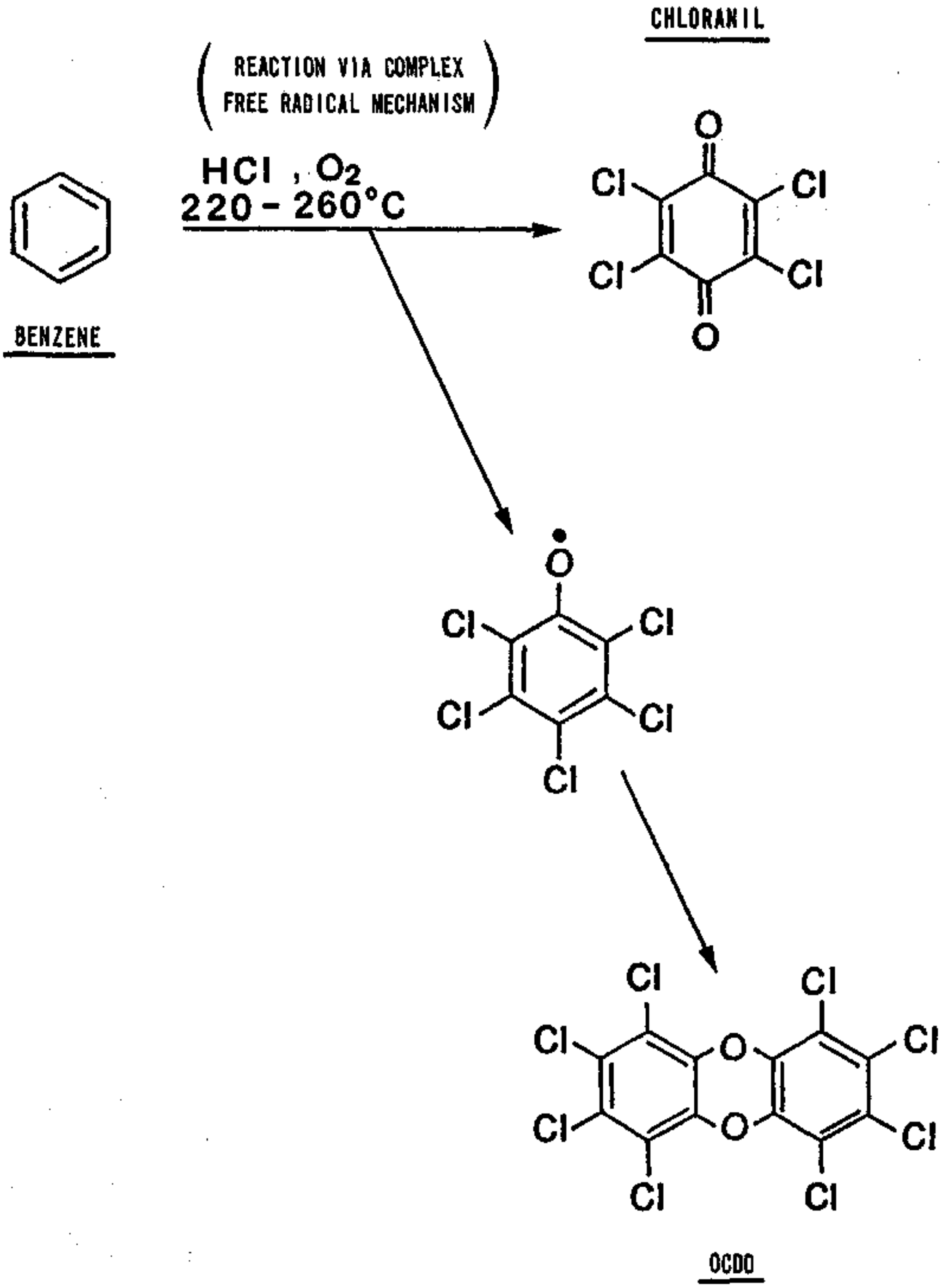


Figure 25. Chloranil.

Hexachlorophene and its sodium salt, Isobac 20, (Figure 26), are produced from 2,4,5-trichlorophenol whose preliminary production from 1,2,4,5-tetrachlorobenzene is carried out by reaction with caustic. This first step potentially forms dioxin precursors similar to the equivalent step in the manufacture of 2,4,5-T. Consequently, 2,3,7,8-TCDD is the anticipated byproduct dioxin.

The production of 2,3,4,6-tetrachlorophenol (Figure 27) by chlorination of phenol would be expected to yield trace byproducts of various isomeric hexachlorodibenzo-p-dioxins via a free-radical mechanism.

Again, because of the analytical evidence of many dioxins other than those hypothesized in these mechanisms, no specific dioxin presence should be presumed or excluded.

As an indication of the critical processing that might precede the reactions shown in this section, Table 8 summarizes the primary raw materials. Those materials potentially carrying trace dioxins are reviewed in Section 5.

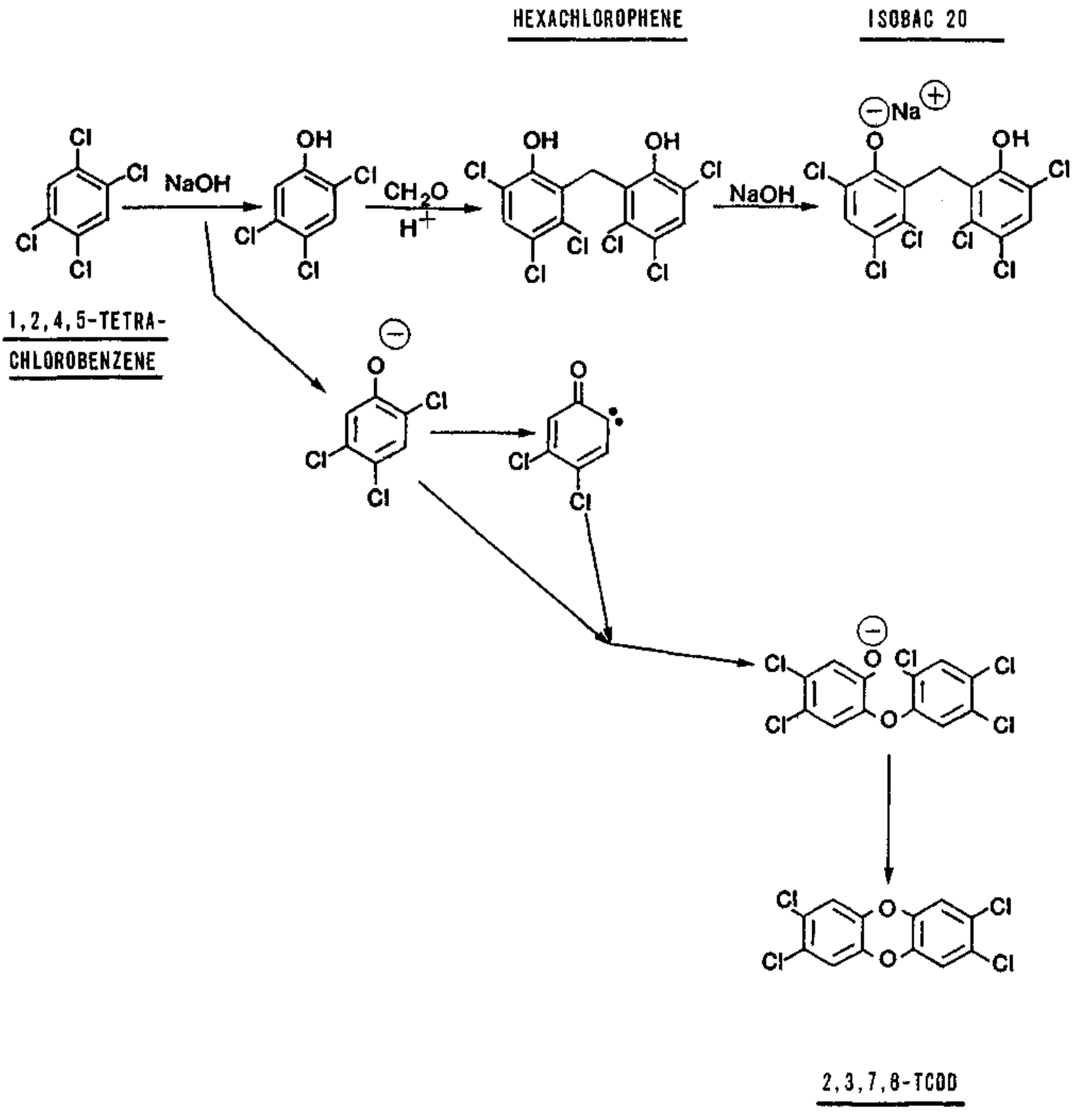


Figure 26. Hexachlorophene and Isobac 20.

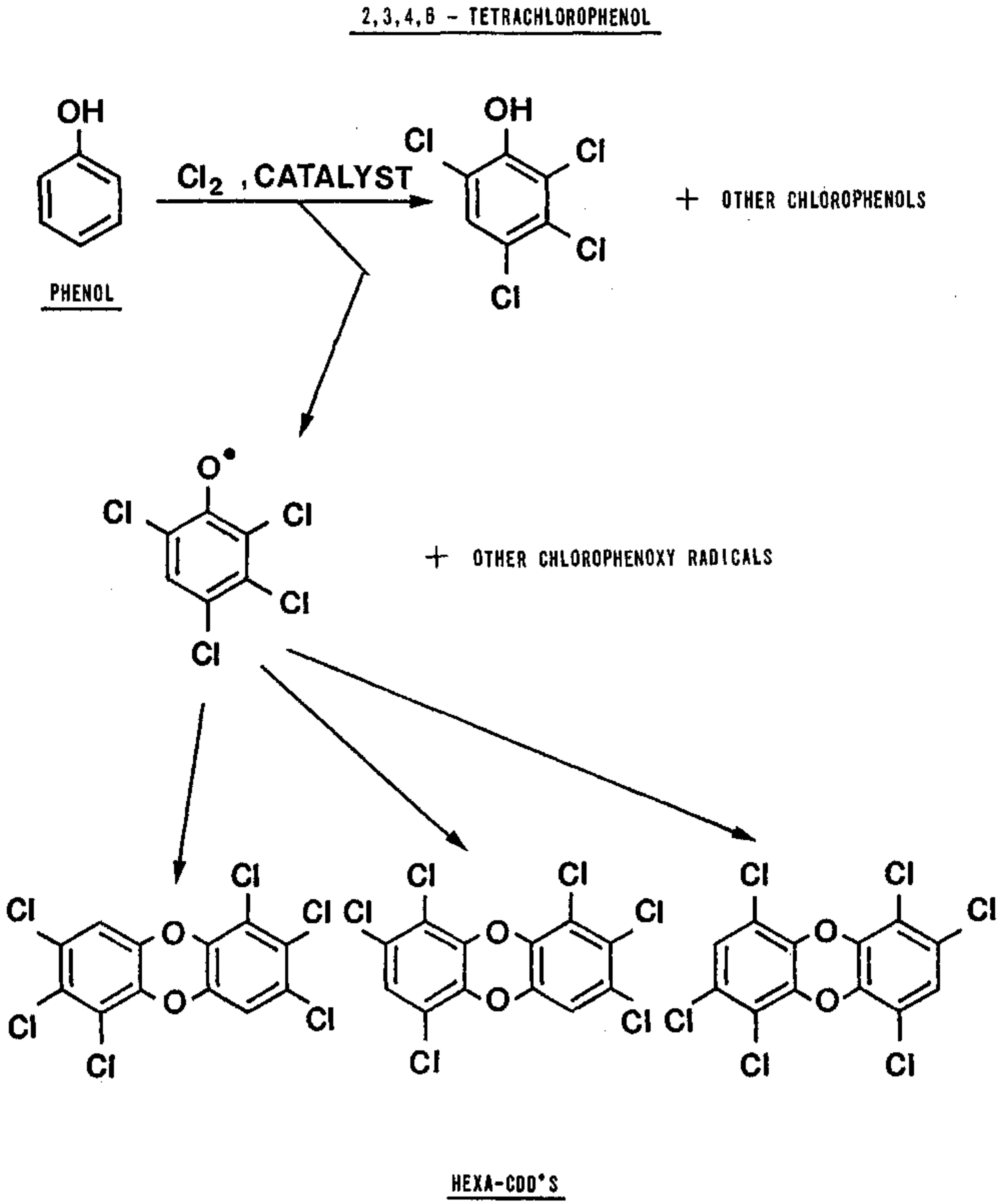


Figure 27. 2,3,4,6-Tetrachlorophenol.

TABLE 8. PESTICIDE RAW MATERIALS

Pesticide product	Raw materials
Bifenox	2,4-Dichlorophenol 3-Halo-o-nitrobenzoic acid ester NaOH
Chloranil	Benzene Hydrogen chloride Oxygen
2,4-D and esters and salts	Phenol Chloroacetic acid NaOH Cl_2 Alcohols (for esters) Amines (for amine salts)
2,4-DB and salts	Phenol Cl_2 NaOH Butyrolactone Alcohols (for esters) Amines (for amine salts)
Dicamba	1,2,4-Trichlorobenzene NaOH CO_2 Dimethyl sulfate
Dicapthon	2-Chloro-4-nitorphenol NaOH Chlorodimethylthiophosphonate
Dichlofention	2,4-Dichlorophenol NaOH Chlorodimethylthiophosphonate
Disul Dodium (Sesone)	2,4-Dichlorophenol NaOH Ethylene oxide Chlorosulfonic acid
2,4-DP	2,4-Dichlorophenol 2-Chloropropionic acid NaOH

(continued)

TABLE 8 (continued)

Pesticide product	Raw materials
Erbon	1,2,4,5-Tetrachlorobenzene NaOH Ethylene oxide 2,2-Dichloropropionic acid
Hexachlorophene and Isobac 20	1,2,4,5-Tetrachlorobenzene NaOH Ethylene oxide
Nitrofen	2,4-Dichlorophenol Chloro-4-nitrobenzene KOH
Pentachlorophenol PCP	Phenol Cl_2 (Phenol route) or Benzene Cl_2 (Hexachlorobenzene route) NaOH
Ronnel	1,2,4,5-Tetrachlorobenzene NaOH Phosphorus sulfochloride $NaOCH_3$
Silvex and esters and salts	1,2,4,5-Tetrachlorobenzene NaOH Chloropropionic acid Alcohols (for esters) Amines (for amine and salts)
2,4,5-T and esters and salts	1,2,4,5-Tetrachlorobenzene NaOH Chloracetic acid Alcohols (for esters) Amines (for amine salts)
2,3,4,6-Tetrachlorophenol	Phenol Cl_2
2,4,5-Trichlorophenol	1,2,4,5-Tetrachlorobenzene NaOH

SECTION 7

CHEMICALS, PRODUCERS, AND PLANT LOCATIONS

The tables that follow list organic chemicals and pesticides selected for study on the basis of potential dioxin contamination, with known producers and production locations, present and past. The primary source of producer information is the SRI Directory of Chemical Producers. The tabulations are by chemical, with producers and locations; and by producer and location, with chemicals. The tabulations by chemical (Tables 9, 10, 11, and 14) are segregated according to the classifications based on dioxin concern as defined in Section 5 (Organic Chemicals) and Section 6 (Pesticide Chemicals), respectively. The classification information is also noted in the producer location tables by means of Roman numerals following the chemical names.

The tabulations by producer and location (Tables 12 and 15) group all of the critical chemicals involved at each manufacturer location. These lists do not necessarily define the site subject to exposure, because many dumps are remote from the plants; they do provide a starting point for such definition. Abandoned production of a chemical or abandoned facilities may present special problems. Therefore, the production facilities noted since 1968 but no longer active in 1978 are footnoted and are also extracted in separate tables (Tables 13 and 16). Some of these sites remain active in other production, and some may retain production capability and/or minor production of the subject chemical. Other plant sites may be totally deactivated or abandoned. The producer listed is the last known operator.

Some of the company names of producers designate subsidiary or divisional names, with notation of the parent company. The underlined portion of the name indicates the short-form name used in other tables. Company addresses, from the SRI Directory and from the Thomas Register, are for the last known producer at a given location and are subject to the uncertainties introduced by acquisitions and name changes.

TABLE 9. PRODUCERS OF CLASS I ORGANIC CHEMICALS

Chemical	Producer	Location
4-Bromo-2,5-dichlorphenol	Velsicol	Beaumont, Tex.
2-Chloro-4-fluorophenol	Olin	Rochester, N. Y.
Decabromophenoxybenzene	Great Lakes Chem.	El Dorado, Ark.
2,4-Dibromophenol	Dow	Midland, Mich.
	White Chem.	Bayonne, N. J.
2,3-Dichlorophenol	Specialty Organics	Irwindale, Cal.
	Aldrich	Milwaukee, Wis.[a]
	Diamond Shamrock	Neward, N. J.[a]
2,4-Dichlorophenol	Dow	Midland, Mich.
	Monsanto	Sauget, Ill.
	Rhodia	Freeport, Tex.
	Transvaal	Jacksonville, Ark.
2,5-Dichlorophenol	Velsicol	Beaumont, Tex.
2,6-Dichlorophenol	Aldrich	Milwaukee, Wis.
	Specialty Organics	Irwindale, Cal.
3,4-Dichlorophenol	Aldrich	Milwaukee, Wis.
Pentabromophenol	Michigan Chem.	St. Louis, Mich.[a]
	R.S.A.	Ardsley, N. Y.[a]
	White Chem.	Bayonne, N. J.
2,4,6-Tribromophenol	Dow	Midland, Mich.[a]
	Eastern Chem.	Pequannock, N. J.[a]
	Guardian	Hauppauge, N. Y. Pequannock, N. J.[a]
	Velsicol	St. Louis, Mich.[a]
	R.S.A.	Ardsley, N. Y.[a]
	White Chem.	Bayonne, N. J.

[a] No longer produced at this location.

TABLE 10. PRODUCERS OF CLASS II ORGANIC CHEMICALS

Chemical	Producer	Location
Bromophenetole	R.S.A.	Ardsley, N. Y.
o-Bromophenol	Eastman Kodak	Rochester, N. Y.
	R.S.A.	Ardsley, N. Y.
2-Chloro-1,4-diethoxy-5-nitrobenzene	Fairmount Chem.	Newark, N. J.
	GAF	Rensselaer, N. Y.
	Pfister	Newark, N. J.[a]
5-Chloro-2,4-dimethoxy-aniline	GAF	Rensselaer, N. Y.
	Pfister	Ridgefield, N. J. Newark, N. J.[a]
Chlorohydroquinone	Eastman Kodak	Rochester, N. Y.
	Eastern Chem.	Pequannock, N. J.[a]
	Guardian	Hauppauge, N. Y.[a] Pequannock, N. J.[a]
o-Chlorophenol	Dow	Midland, Mich.
	Monsanto	Sauget, Ill.
2-Chloro-4-phenylphenol	Dow	Midland, Mich.
4-Chlororesorcinol	Am. Color & Chem.	Lock Haven, Pa.
	GAF	Rensselaer, N. Y.
2,6-Dibromo-4-nitro-phenol	Martin Marietta	Sodyeco, N. C.[a]
	Maumee	St. Bernard, Ohio[a]
	Sherwin Williams	St. Bernard, Ohio[a]
3,5-Dichlorosalicylic acid	Aceto	Carlstadt, N. J.
	Inmont Corp.	Carlstadt, N. J.[a]
2,6-Diiodo-4-nitrophenol	R.S.A.	Ardsley, N. Y.
3,5-Diiodosalicylic acid	Morton Chem.	Ringwood, Ill.[a]
	R.S.A.	Ardsley, N. Y.[a]
o-Fluoroanisole	Olin	Rochester, N. Y.
o-Fluorophenol	Olin	Rochester, N. Y.
Tetrabromobisphenol-A	Dow	Midland, Mich.
	Great Lakes	El Dorado, Ark.
	Velsicol	St. Louis, Mich.
Tetrachlorobisphenol-A	Dover	Dover, Ohio[a]

[a] No longer produced at this location.

TABLE 11. PRODUCERS OF CLASS III ORGANIC CHEMICALS

Chemical	Producer	Location
3-Amino-5-chloro-2-hydroxybenzenesulfonic acid	Allied	Buffalo, N. Y.[a]
	Nyanza	Ashland, Mass.
	Toms River Chem.	Toms River, N. J.
2-Amino-4-chloro-6-nitrophenol	Nyanza	Ashland, Mass.
o-Anisidine	Am. Color and Chem.	Lock Haven, Pa.
	Am. Aniline	Lock Haven, Pa.[a]
	du Pont	Deepwater, N. J.
	Monsanto	St. Louis, Mo.[a]
Benzaldehyde	Crompton and Knowles	Fair Lawn, N. J.
	Dow	Kalama, Wash.[a]
	Fritzsche	Clifton, N. J.[a]
	Kalama Chem.	Kalama, Wash.
	Monroe Chem.	Eddystone, Pa.
	F. Ritter	Los Angeles, Cal.[a]
	Stauffer	Edison, N. J.[a]
		Nixon, N. J.[a]
	Tenneco	Fords, N. J.[a]
		Garfield, N. J.
	UOP	East Rutherford, N. J.
	Velsicol	Chattanooga, Tenn.[a]
Bromobenzene	Dow	Midland, Mich.
	Velsicol	St. Louis, Mich.[a]
o-Bromofluorobenzene	Olin	Rochester, N. Y.
o-Chloroflurobenzene	Olin	Rochester, N. Y.
3-Chloro-4-fluoro-nitrobenzene	Olin	Rochester, N. Y.
3-Chloro-4-fluorophenol	Olin	Rochester, N. Y.
4-Chloro-2-nitorphenol	du Pont	Deepwater, N. J.[a]
	Maumee	St. Bernard, Ohio[a]
	Sherwin Williams	St. Bernard, Ohio[a]
Chloropentafluorobenzene	Whittaker	San Diego, Cal.[a]
2,4-Dibromofluorobenzene	Olin	Rochester, N. Y.

(continued)

TABLE 11 (continued)

Chemical	Producer	Location
3,4-Dichloroaniline	Blue Spruce	Bound Brook, N. J.
		Edison, N. J.[a]
	Chem. Insecticide	Metuchen, N. J.[a]
	du Pont	Deepwater, N. J.
	Martin Marietta	Sodyeco, N. C.[a]
	Monsanto	Luling, La.
		Sauget, Ill.[a]
o-Dichlorobenzene	Allied	Syracuse, N. Y.[a]
	Chem. Products	Cartersville, Ga.[a]
	Dover	Dover, Ohio[a]
	Dow	Midland, Mich.
	du Pont	Deepwater, N. J.[a]
	Hooker	Niagara Falls, N. Y.[a]
	Monsanto	Sauget, Ill.
	Montrose Chem.	Henderson, Nev.
	Neville Chem.	Sante Fe Springs, Cal.[a]
	Olin	McIntosh, Ala.[a]
	PPG	Natrium, W. Va.
	Solvent Chem.	Niagara Falls, N. Y.
		Malden, Mass.[a]
	Speciality Organics	Irwindale, Cal.
	Standard Chlorine	Delaware City, Del.
		Kearny, N. J.
3,4-Dichlorobenzaldehyde	Tenneco	Fords, N. J.
3,4-Dichlorobenzotrichloride	Tenneco	Fords, N. J.
3,4-Dichlorobenzotrifluoride	Tenneco	Fords, N. J.[a]
1,2-Dichloro-4-nitrobenzene	Blue Spruce	Bound Brook, N. J.
		Edison, N. J.[a]
	Chem. Insecticide	Metuchen, N. J.[a]
	Martin Marietta	Sodyeco, N. C.[a]
	Monsanto	Sauget, Ill[a]
	Plastifax	Gulfport, Miss.
3,4-Dichlorophenylisocyanate	Mobay Chem.	New Martinsville, S. C.
	Ott Chem.	Muskegon, Mich.[a]
3,4-Difluoroaniline	Olin	Rochester, N. Y.

(continued)

TABLE 11 (continued)

Chemical	Producer	Location
o-Difluorobenzene	Olin	Rochester, N. Y.
1,2-Dihydroxybenzene-3,5-disulfonic acid, disodium salt	Sterling Drug	New York, N. Y.[a]
2,5-Dihydroxybenzenesulfonic acid	Eastman Kodak	Rochester, N. Y.[a]
	Nease Chem.	State College, Pa.[a]
2,5-Dihydroxybenzenesulfonic acid, potassium salt	Nease Chem.	State College, Pa.[a]
2,4-Dinitrophenol	Martin Marietta	Sodyeco, N. C.
	Mobay	Bushy Park, S. C.
2,4-Dinitrophenoxyethanol	Hummel Chem.	Neward, N. J.[a] South Plainfield, N. J.
3,5-Dinitrosalicylic acid	Eastman Kodak	Rochester, N. Y.
	Hummel Chem.	Newark, N. J.[a] South Plainfield, N. J.[a]
	Salsbury Labs	Charles City, Iowa
Fumaric acid	Allied	Buffalo, N. Y.[a] Moundsville, W. Va.[a]
	Alberta Gas	Duluth, Minn.
	Hooker	Arecibo, P. R.
	Monsanto[b]	St. Louis, Mo.
	Petro-Tex	Houston, Tex.[a]
	Pfizer	Terre Haute, Ind.
	Reichhold	Morris, Ill.[a]
	Stepan Chem.	Fieldsboro, N. J.[a]
	Tenneco	Garfield, N. J.
	U. S. Steel	Neville Island, Pa.
Hexabromobenzene	Velsicol	St. Louis, Mich.
	Dover	Dover, Ohio[a]
Hexachlorobenzene	Hummel Chem.	Neward, N. J.[a] South Plainfield, N. J.[a]
	Stauffer	Louisville, Ky.[a]

(continued)

TABLE 11 (continued)

Chemical	Producer	Location
Hexafluorobenzene	PCR	Gainesville, Fla.
	Whittaker	San Diego, Cal.[a]
		Louisville, Ky.[a]
Maleic acid	Allied	Buffalo, N. Y.[a]
		Marcus Hook, Pa.
		Moundsville, W. Va.[a]
	Eastman Kodak	Rochester, N. Y.[a]
	Pfanstiehl Labs	Waukegan, Ill.
Maleic anhydride	Allied	Moundsville, W. Va.[a]
	Amoco	Joilet, Ill.
	Asland	Neal, W. Va.
	Chevron	Richmond, Cal.[a]
	Koppers	Bridgeville, Pa.
		Cicero, Ill.
	Petro-Tex	Houston, Tex.[a]
	Monsanto	St. Louis, Mo.
	Reichhold	Elizabeth, N. J.
		Morris, Ill.
	Standard Oil of Ind. (see Amoco above)	
	Tenneco	Fords, N. J.
	U.S. Steel	Neville Island, Pa.
o-Nitroanisole	du Pont	Deepwater, N. J.
	Monsanto	Sauget, Ill.[a]
		St. Louis, Mo.
2-Nitro-p-cresol	Sherwin Williams	Chicago, Ill.
	du Pont	Deepwater, N. J.[a]
o-Nitrophenol	Monsanto	Sauget, Ill.
	du Pont	Deepwater, N. J.
Pentabromochloro-cyclohexane	Dow	Midland, Mich.
Pentabromoethylebenzene	Hexcel	Sayreville, N. J.
Pentabromotoluene	White Chem.	Bayonne, N. J.

(continued)

TABLE 11 (continued)

Chemical	Producer	Location
Pentachloroaniline	Olin	Rochester, N. Y.
Pentafluoroaniline	Whittaker	San Diego, Cal.[a]
o-Phenetidine	Am. Aniline	Lock Haven, Pa.[a]
	Monsanto	St. Louis, Mo.[a]
Phenol (from chlorobenzene)	Dow	Midland, Mich.[a]
	Hooker	North Tonawanda, N. Y.[a]
		South Shore, Ky.[a]
	Union Carbide	Marietta, Ohio[a]
1-Phenol-2-sulfonic acid, formaldehyde condensate	Allied	Buffalo, N. Y.
	Diamond Shamrock	Cedartown, Ga.[a]
	Rohm and Haas	Philadelphia, Pa.
Phenyl ether	Dow	Midland, Mich.
	Fritzsche	Clifton, N. J.[a]
	Monsanto	Chocolate Bayou, Tex.
Phthalic anhydride	Allied	Buffalo, N. Y.[a]
		Chicago, Ill.[a]
		El Segundo, Cal.
		Frankford, Pa.[a]
		Ironton, Ohio[a]
	BASF Wyandotte	Kearny, N. J.
	Chevron	Perth Amboy, N. J.[a]
		Richmond, Cal.
	Commonwealth Oil	Penuelas, P. R.[a]
	Conoco	Hebronville, Mass.[a]
	Exxon	Baton Rouge, La.
	W. R. Grace	Fords, N. J.[a]
	Hooker	Arecibo, P. R.
	Koppers	Bridgeville, Pa.
		Chicago, Ill.[a]
		Cicero, Ill.
	Monsanto	Bridgeport, N. J.
		Chocolate Bayou, Tex.[a]
		St. Louis, Mo.[a]
		Texas City, Tex.
	Reichhold	Azusa, Cal.[a]
		Elizabeth, N. J.[a]
		Morris, Ill.[a]
	Sherwin Williams	Chicago, Ill.[a]

(continued)

TABLE 11 (continued)

Chemical	Producer	Location
Phthalic anhydride (continued)	Stand. Oil Co. Cal. (see Chevron)	
	Stepan Chem.	Elwood, Ill. Millsdale, Ill[a]
	Union Carbide	Institute, W. Va.[a] South Charleston, S. C.[a]
	U.S. Steel	Neville Island, Pa.
	Witco Chem.	Chicago, Ill.[a] Perth Amboy, N. J.[a]
Picric acid	Allied	Buffalo, N. Y[a]
	du Pont	Deepwater, N. J.[a]
	Hummel Chem.	South Plainfield, N. J.[a]
	Martin Marietta	Sodyeco, N. C.
Sodium picrate	Hummel Chem.	South Plainfield, N. J.
	Martin Marietta	Sodyeco, N. C.[a]
	Northrop	Asheville, N. C.
Tetrabromophthalic anhydride	Velsicol	St. Louis, Mich.
1,2,4,5-Tetrachlorobenzene	Dover	Dover, Ohio[a]
	Dow	Midland, Mich.
	Hooker	Niagara Falls, N. Y.[a]
	Solvent Chem.	Malden, Mass.[a]
	Standard Chlorine	Delaware City, Del.
Tetrachlorophthalic anhydride	Hooker	Niagara Falls, N. Y.[a]
	Monsanto[b]	Bridgeport, N. J.
Tetrafluoro-m-phenylene-diamine	Whittaker	San Diego, Cal.[a]
Tribromobenzene	Velsicol	St. Louis, Mich.[a]
	Northrop	Asheville, N. C.
1,2,4-Trichlorobenzene	Chris Craft	Newark, N. J.[a]
	Dover	Dover, Ohio[a]
	Dow	Midland, Mich.
	Hooker	Niagara Falls, N. Y.[a]
	Neville Chem.	Sante Fe Springs, Cal.[a]
	Sobin Chems.	Neward, N. J.[a]
	Solvent Chem.	Malden, Mass.[a]
	Standard Chlorine	Delaware City, Del. Kearny, N. J.[a]
	Sun Chem.	Chester, S. C.[a]

(continued)

TABLE 11 (continued)

Chemical	Producer	Location
2,4,6-Trinitroresorcinol	Northrop Olin	Asheville, N. C. East Alton, Ill.

[a] No longer produced at this location.
[b] Possibly two plants.

TABLE 12. ALPHABETICAL LIST OF ORGANIC CHEMICAL PRODUCERS

Producer	Location	Chemical (class)
Aceto Chem. Co., Inc. 126-02 Northern Blvd. Flushing, N. Y. 11368 Arsynco, Inc. Subsid.	Carlstadt, N. J.	3,5-Dichlorosalicylic acid (II)
Alberta Gas Chems. Inc. Address not available	Duluth, Minn.	Fumaric acid (III)
Aldrich Chem. Co., Inc. 940 West St. Paul Ave. Milwaukee, Wis. 53233	Milwaukee, Wis.	2,4-Dichlorophenol (I)[a] 2,6-Dichlorophenol (I) 3,4-Dichlorophenol (I)
Allied Chem. Corp. Columbian Rd. and Park Ave. Morristown, N. J. 07960	Buffalo, N. Y.	3-Amino-5-chloro-2-hydroxybenzenesulfonic acid (III)[a] Fumaric acid (III)[a] Maleic acid (III)[a] 1-Phenol-2-sulfonic acid, formaldehyde condensate (III)[a] Phthalic anhydride (III)[a] Picric acid (III)[a]
	Chicago, Ill.	Phthalic anhydride (III)[a]
	El Segundo, Cal.	Phthalic anhdyride (III)
	Frankford, Pa.	Phthalic anhydride (III)[a]
	Ironton, Ohio	Phthalic anhydride (III)[a]
	Marcus Hook, Pa.	Maleic acid (III)
	Moundsville, W. Va.	Fumaric acid (III)[a] Maleic acid (III)[a] Maleic anhydride (III)[a]
	Syracuse, N. Y.	o-Dichlorobenzene (III)[a]
American Aniline Products, Inc. 25 McLean Blvd. P.O. Box 3063 Paterson, N. J. 07509 Owned by Pepi, Inc. 52% and Kopper Co., Inc., 48%	Lock Haven, Pa.	o-Anisidine (III)[a]
American Color and Chem. Corp. 11400 Westinghouse Blvd. P.O. Box 1688 Charlotte, N. C. 28201	Lock Haven, Pa.	o-Anisidine (III) 4-Chlororesorcinol (II)

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Amoco Chems. Corp. 200 E. Randolph Dr. Chicago, Ill. 60601 Affiliate of Standard Oil Co., Ind.	Joilet, Ill.	Maleic anhydride (III)
Arsynco	See Aceto	
Ashland Oil, Inc. 1409 Winchester Ave. P.O. Box 391 Ashland, Ky. 41101	Neal, W. Va.	Maleic anhdyride (III)
BASF Wyandotte Corp. 100 Cherry Hill Road Parisppany, N. J. 07054	Kearny, N. J.	Phthalic anhydride (III)
Blue Spruce Co. 1390 Valley Road Stirling, N. J. 07980	Bound Brook, N. J.	3,4-Dichloroaniline (III) 1,2-Dichloro-4-nitrobenzene (III)
	Edison, N. J.	3,4-Dichloroaniline (III)[a] 1,2-Dichloro-4-nitrophenol (III)[a]
Chemical Insecticide Corp. 30 Whitman Ave. Metuchen, N. J. 08840 No current address	Metuchen, N. J.	3,4-Dichloroaniline (III)[a] 1,2-Dichloro-4-nitrobenzene (III)[a]
Chemical Products Corp. 48 Atlanta Road Cartersville, Ga. 30120	Cartersville, Ga.	o-Dichlorobenzene (III)[a]
Chevron Chem. Co. 575 Market Street San Francisco, Cal. 94105 Subsid. Standard Oil Co. of Cal.	Richmond, Cal.	Maleic anhydride (III)[a] Phthalic anhydride (III)
	Perth Amboy, N. J.	Phthalic anhydride (III)[a]
Chris Craft Industry, Inc. 600 Madison Avenue New York, N. Y. See Montrose Chem.	Newark, N. J.	1,2,4-Trichlorobenzene (III)[a]

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Commonwealth Oil Refining Co., Inc. 245 Park Avenue New York, N. Y. 10017	Penuelas, P. R.	Phthalic anhydride (III)[a]
Continental Oil Co. (Conoco) Petrochemicals Dept. Saddle Brook, N. J. 07662	Hebronville, Mass.	Phthalic anhydride (III)[a]
Crompton and Knowles Corp. 345 Park Ave. New York, N. Y. 10022	Fair Lawn, N. J.	Benzaldehyde (III)
Diamond Shamrock Corp. 1100 Superior Ave. Cleveland, Ohio 44114	Cedartown, Ga.	1-Phenol-2-sulfonic acid, formaldehyde condensate (III)[a]
	Newark, N. J.	2,4-Dichlorophenol (I)[a]
Dover Chem. Corp. West 15th Street Dover, Ohio 44622 Affiliate of ICC Industries, Inc.	Dover, Ohio	o-Dichlorobenzene (III)[a] Hexachlorobenzene (III)[a] 1,2,4,5-Tetrachlorobenzene (III)[a] Tetrachlorobisphenol-A (II)[a] 1,2,4-Trichlorobenzene (III)[a]
Dow Chem. U.S.A. 2020 Dow Center Midland, Mich.	Kalama, Wash.	Benzaldehyde (III)[a]
	Midland, Mich.	o-Chlorophenol (II) 2-Chloro-4-phenylphenol (II) 2,4-Dibromophenol (I) o-Dichlorobenzene (III) 2,4-Dichlorophenol (I) Pentabromochlorocyclohexane (III) Phenol (III)[a,b] Phenyl either (III) Tetrabromobisphenol-A (II) 1,2,4,5-Tetrachlorobenzene (III) 2,4,6-Tribromophenol (I)[a] 1,2,4-Trichlorobenzene (III)

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
E.I. du Pont de Nemours and Co., Inc. 1007 Market Street Wilmington, Del. 19898	Deepwater, N. J.	o-Anisidine (III) 4-Chloro-2-nitrophenol (III)[a] 3,4-Dichloroaniline (III) o-Dichlorobenzene (III)[a] 2-Nitro-p-cresol (III)[a] o-Nitrophenol (III)[a] o-Nitroanisole (III)
Eastern Chem. Corp. Now Eastern Chem. Div. of Guardian Chem. Corp.	Pequannock, N. J.	Chlorohydroquinone (II)[a] 2,4,6-Tribromophenol (I)[a]
Eastman Kodak Co. 343 State Street Rochester, N. Y. 14650	Rochester, N. Y.	o-Bromophenol (II) Chlorohydroquinone (II) 2,5-Dihydroxybenzenesulfonic acid (III)[a] 2,5-Dinitrosalicylic acid (III) Maleic acid (III)[a]
Exxon Corp. 1251 Ave. of the Americas New York, N. Y. 10020	Baton Rouge, La.	Phthalic anhydride (III)
Fairmount Chem. Co., Inc. 117 Blanchard Street Newark, N. J. 07105	Newark, N. J.	2-Chloro-1,4-diethoxy-5-nitrobenzene (II)
Fritzsche Dodge and Olcott, Inc. 76 Ninth Ave. New York, N. Y. 10011	Clifton, N. J.	Benzaldehyde (III)[a] Phenyl ether (III)[a]
GAF Corp. 140 West 51st St. New York, N. Y. 10020	Rensselaer, N. Y.	2-Chloro-1,4-diethoxy-5-nitrobenzene (II) 5-Chloro-2,4-dimethoxyaniline (II) 4-Chlororesorcinol (II)
W. R. Grace and Co. 7 Hanover Square New York, N. Y. 10005	Fords, N. J.	Phthalic anhydride (III)[a]

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Great Lakes Chem. Corp. Hwy. 52, Northwest West Lafayette, Ind. 47906	El Dorado, Ark.	Decabromophenoxybenzene (I) Tetrabromobisphenol-A (II)
Guardian Chem. Corp. 230 Marcus Blvd. Hauppauge, N. Y. 11787	Hauppauge, N. Y.	Chlorohydroquinone (II)[a] 2,4,6-Tribromophenol (I)
Hexcel Corp. 11711 Dublin Blvd. Dublin, Cal. 94566	Sayreville, N. J.	Pentabromoethylbenzene (III)
Hooker Chem. Corp. 1900 St. James Pl. Houston, Tex. 77027 Subsid. Occidental Petroleum Corp.	Arecibo, P. R.	Furmaric acid (III) Phthalic anhydride (III)
	Niagara Falls, N. Y.	o-Dichlorobenzene (III)[a] Tetrachlorophthalic anhydride (III)[a] 1,2,4,5-Tetrachlorobenzene (III)[a] 1,2,4-Trichlorobenzene (III)[a]
	North Tonawanda, N. Y.	Phenol (III)[a,b]
	South Shore, Ky.	Phenol (III)[a,b]
Hummel Chem. Co., Inc. P.O. Box 250 South Plainfield, N. J. 07080	Newark, N. J.	2,4-Dinitrophenoxyethanol (III)[a] 3,5-Dinitrosalicylic acid (III)[a] Hexachlorobenzene (III)[a] Picric acid (III)[a]
	South Plainfield, N. J.	2,4-Dinitrophenoxyethanol (III) 3,5-Dinitrosalicylic acid (III)[a] Hexachlorobenzene (III)[a] Picric acid (III)[a] Sodium picrate (III)
ICC Industries See Solvent Chem.		
Inmont Corp. 1133 Ave. of the Americas New York, N. Y. 10036 (Subsid. of Carrier Corp.)	Carlstadt, N. J. NOTE: Carlstadt Plant listed under Interchemical Corp. which was acquired by Inmont Corp.	3,5-Dichlorosalicylic acid (III)[a]

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
International Minerals and Chem. Corp. IMC Plaza Libertyville, Ill. 60048	Newark, N. J.	1,2,4-Trichlorobenzene (III)[a]
Kalama Chem., Inc. The Bank of Cal. Center Suite 1110 Kalama, Wash. 98164	Kalama, Wash.	Benzaldehyde (III)
Kopper Co., Inc. Koppers Bldg. Pittsburgh, Pa. 15219	Bridgeville, Pa.	Maleic anhydride (III) Phthalic anhydride (III)
	Chicago, Ill.	Phthalic anhydride (III)[a]
	Cicero, Ill.	Maleic anhydride (III)[a] Phthalic anhdyride (III)
Martin Marietta Corp. 6801 Rockledge Dr. Bethesda, Md. 20034	Sodyeco, N. C.	2,6-Dibromo-4-nitrophenol (II)[a] 3,4-Dichloroaniline (III)[a] 1,2-Dichloro-4-nitrobenzene (III)[a] 2,4-Dinitrophenol (III) Picric acid (III) Sodium picrate (III)[a]
Maumee Chem. Co. Presumed to be acquired by Sherwin Williams Address not available	St. Bernard, Ohio	2,6-Debromo-4-nitrophenol (II)[a] 4-Chloro-2-nitrophenol (III)[a]
Mobay Chem. Co. Penn Lincoln Parkway West Pittsburgh, Pa. 15205	New Martinsville, W. Va.	3,4-Dichlorophenylisocyanate (III) 2,4-Dinitrophenol (III)
Monroe Chem. Co. Saville Ave. at 4th St. Eddystone, Pa. Subsid. of Kalama Chem., Inc. (see Kalama)	Eddystone, Pa.	Benzaldehyde (III)
Monsanto Co. 800 North Lindbergh Blvd. St. Louis, Mo. 63166	Bridgeport, N. J.	Phthalic anhydride (III) Tetrachlorophthalic anhydride (III)
	Chocolate Bayou, Tex.	Phenyl ether (III) Phthalic anhydride (III)[a]
	Luling, La.	3,4-Dichloroaniline (III)

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Monsanto (continued)	Sauget, Ill.	o-Chlorophenol (II) 3,4-Dichloroaniline (III)[a] o-Dichlorobenzene (III) 1,2-Dichlor-4-nitrobenzene (III)[a] 2,4-Dichlorophenol (I) o-Nitroanisole (III)[a] o-Nitrophenol (III)
	St. Louis, Mo.	o-Anisidine (III)[a] Fumaric acid (III) Maleic anhydride (III) o-Nitroanisole (III) o-Phenetidine (III)[a] Phthalic anhydride (III)[a]
	Texas City, Tex.	Phthalic anhydride (III)
Montrose Chem. Corp. of Cal. 2401 Morris Ave. P.O. Box E Union, N. J. 07083 (Jointly owned by Chris Craft Industries, Inc. and Stauffer Chem. Co.)	Henderson, Nev.	o-Dichlorobenzene (III)
Morton Chem. Co., Div. Morton-Norwich Products, Inc. 110 North Wacker Dr. Chicago, Ill. 60606	Ringwood, Ill.	3,5-Diiodosalicylic acid (II)[a]
Nease Chem. Co., Inc. P.O. Box 221 State College, Pa. 16801	State College, Pa.	2,5-Dihydroxybenzenesulfonic acid (III)[a] 2,5-Dihydroxybenzenesulfonic acid, potassium salt (III)[a]
Neville Chem. Co. Neville Island Pittsburgh, Pa. 15225	Sante Fe Springs, Cal.	o-Dichlorobenzene (III)[a] 1,2,4-Trichlorobenzene (III)[a]
Northrop Corp. 1800 Centruy Park, East Los Angeles, Cal. 90067	Asheville, N. C.	Sodium picrate (III) Tribromobenzene (III) 2,4,6-Trinitroresorcinol (III)

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Northwest Industries (See Velsicol) G 300 Sears Tower Chicago, Ill. 60606		
Nyanza, Inc. 200 Sutton St. North Andover, Mass. 01721	Ashland, Mass	3-Amino-5-chloro-2-hydroxybenzenesulfonic acid (III) 2-Amino-4-chloro-6-nitrophenol (III)
Occidental Petroleum Corp. (See Hooker) 10889 Wilshire Blvd., Suite 1500 Los Angeles, Cal. 90024		
Olin Corp. 120 Long Ridge Road Stamford, Conn. 06904	East Alton, Ill. McIntosh, Ala. Rochester, N. Y.	2,4,6-Trinitroresorcinol (III)[a] o-Dichlorobenzene (III)[a] o-Bromofluorobenzene (III) o-Chlorofluorobenzene (III) 3-Chloro-4-fluoronitrobenzene (III) 2-Chloro-4-fluorophenol (I) 3-Chloro-4-fluorophenol (III) 2,4-Dibromofluorobenzene (III) 3,4-Difluoroaniline (III) o-Difluorobenzene (III) o-Fluoroanisole (II) Pentachloroaniline (III)
Ott Chem. Co. See Story Chem.		
PCR, Inc. P.O. Box 1466 Gainesville, Fla. 32602	Gainesville, Fla.	Hexafluorobenzene (III)
Petro-Tex Chem. Corp. 8600 Park Place Houston, Tex. 77017 Jointly owned by FMC Corp. and Tenneco, Inc.	Houston, Tex.	Fumaric acid (III)[a] Maleic anhydride (III)[a]

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Pfister Chem., Inc. Linden Avenue Ridgefield, N. J. 07657	Newark, N. J.	2-Chloro-1,4-diethoxy-5-nitrobenzene (II)[a] 5-Chloro-2,4-dimethoxyaniline (II)[a]
	Ridgefield, N. J.	5-Chloro-2,4-dimethoxyaniline (II)
Pfizer, Inc. 235 East 42nd St. New York, N. Y. 10017	Terre Haute, Ind.	Fumaric acid (III)
Plastifax, Inc. Indust. Seaway Blvd. P.O. Box 1056 Gulfport, Miss. 39501	Gulf Port, Miss.	1,2-Dichloro-4-nitrobenzene (III)
PPG Industries, Inc. One Gateway Center Pittsburgh, Pa. 15222	Natrium, W. Va.	o-Dichlorobenzene (III)
Reichhold Chems., Inc. RCI Bldg. White Plains, N. Y. 10603	Azusa, Cal.	Phthalic anhydride (III)[a]
	Elizabeth, N. J.	Maleic anhydride (III) Phthalic anhydride (III)[a]
	Morris, Ill.	Fumaric acid (III)[a] Maleic anhydride (III) Phthalic anhydride (III)[a]
Rhodia, Inc. 600 Madison Ave. New York, N. Y. 10022	Freeport, Tex.	2,4-Dichlorophenol (I)
F. Ritter and Co. 4001 Goodwin Ave. Los Angeles, Cal. 90039	Los Angeles, Cal.	Benzaldehyde (III)[a]
Rohm and Haas Co. Independence Mall West Philadephia, Pa. 19105	Philadelphia, Pa.	1-Phenol-2-sulfonic acid, formaldehyde condensate (III)
R.S.A. Corp. 690 Saw Mill River Road Ardsley, N. Y. 10502	Ardsley, N. Y.	Bromophenetole (II) o-Bromophenol (II) 2,6-Diiodo-4-nitrophenol (II) 3,5-Diiodosalicylic acid (II)[a] Pentabromophenol (I)[a] 2,4,6-Tribromophenol (I)[a]

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Salsbury Labs 2000 Rockford Road Charles City, Iowa 50616	Charles City, Iowa	3,5-Dinitrosalicyclic acid (III)
Sherwin Williams Co. 101 Prospect Ave. Cleveland, Ohio 44101	Chicago, Ill.	2-Nitro-p-cresol (III) Phthalic anhydride (III)[a]
	St. Bernard, Ohio	2,6-Dibromo-4-nitrophenol (II)[a] 4-Chloro-2-nitrophenol (III)[a]
Sobin Chems. Inc. See International Minerals and Chems. Corp.		
Solvent Chem. Co., Inc. 720 Fifth Avenue New York, N. Y. 10011 Affiliate if ICC Industries	Malden, Mass.	o-Dichlorobenzene (III)[a] 1,2,4,5-Tetrachlorobenzene (III)[a] 1,2,4-Trichlorobenzene (III)[a]
	Niagara Falls, N. Y.	o-Dichlorobenzene (III)
Specialty Organics, Inc. 5263 North Fourth St. Irwindale, Cal. 91706	Irwindale, Cal.	2,3-Dichlorophenol (I) 2,6-Dichlorophenol (I) o-Dichlorobenzene (III)
Standard Chlorine Chem. Co., Inc. 1035 Belleville Turnpike Kearny, N. J. 07032	Delaware City, Del.	o-Dichlorobenzene (III) 1,2,4,5-Tetrachlorobenzene (III) 1,2,4-Trichlorobenzene (III)
	Kearny, N. J.	o-Dichlorobenzene (III) 1,2,4-Trichlorobenzene (III)[a]
Standard Oil Co.(Cal.) (See Chevron) 575 Market St. San Francisco, Cal. 94105		
Standard Oil Co. (Ind.) (See Amoco) 910 South Michigan Ave. Chicago, Ill. 60605		
Standard Oil Co. (N.J.) (See Exxon)		

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
Stauffer Chem. Co. Westport, Conn. 06880	Edison, N. J.	Benzaldehyde (III)[a]
	Nixon, N. J.	Banzaldehyde (III)[a]
	Louisville, Ky.	Hexachlorobenzene (III)[a]
Stepan Chem. Co. Edens and Winnetka Rd. Northfield, Ill. 60093	Elwood, Ill.	Phthalic anhydride (III)[a]
	Fieldsboro, N. J.	Fumaric acid (III)[a]
	Millsdale, Ill.	Phthalic anhydride (III)[a]
Stering Drug Inc. 90 Park Avenue New York, N. Y. 10016	New York, N. Y.	1,2-Dihydroxy-3,5-disulfonic acid, disodium salt (III)[a]
Story Chem. Corp. 500 Agard Road Muskegon, Mich. 49445 Ott Chem. Co., Div.	Muskegan, Mich.	3,4-Dichlorophenylisocyanate (III)[a]
Sun Chem. Corp. Box 70 Chester, S. C. 29706	Chester, S. C.	1,2,4-Trichlorobenzene (III)[a]
Tenneco Chems. Co. Park 80 Plaza, West Saddle Brook, N. J. 07662 (Part of Tenneco, Inc.)	Fords, N. J.	Benzaldehyde (III)[a] 3,4-Dichlorobenzaldehyde (III) 3,4-Dichlorobenzotrichloride (III) 3,4-Dichlorobenzotrifluoride (III)[a] Maleic anhydride (III)
	Garfield, N. J.	Fumaric acid (III) Benzaldehyde (III)
Toms River Chem. Corp. P.O. Box 71 Toms River, N. J. 08753 (80% Ciba-Geigy and 20% Sandoz AG)	Toms River, N. J.	3-Amino-5-chloro-2-hydroxybenzenesulfonic acid (III)
Transvaal, Inc. Marshall Road P.O. Box 69 Jacksonville, Ark. 72076 (Subsid. of Vertac)	Jacksonville, Ark.	2,4-Dichlorophenol (I)
Union Carbide Corp. 270 Park Avenue New York, N. Y. 10017	Marietta, Ohio	Phenol (III)[a,b]

(continued)

TABLE 12 (Continued)

Producer	Location	Chemical (class)
UOP, Inc. Ten UOP Plaza Algonquin and Mt. Prospect Roads Des Plaines, Ill. 60016	East Rutherford, N. J.	Benzaldehyde (III)
U.S. Steel Corp. Sixth and Grant Pittsburgh, Pa. 15230	Neville Island, Pa.	Fumaric acid (III)
		Maleic anhydride (III)
		Phthalic anhydride (III)
Velsicol Chem. Corp. 341 East Ohio St. Chicago, Ill. 60611 (Subsid. of Northwest Industries, Inc.)	Beaumont, Tex.	4-Bromo-2,5-dichlorphenol (I)
		2,5-Dichlorophenol (I)
	Chattanooga, Tenn.	Benzaldehyde (III)[a]
	St. Louis, Mich.	Hexabromobenzene (III)[a]
		Pentabromophenol (I)[a]
		Tetrabromobisphenol-A (II)
		Tetrabromophthalic anhydride (III)
		Tribromobenzene (III)[a]
		2,4,6-Tribromophenol (I)[a]
Vertac, Inc. (See Transvaal) 2414 Clark Tower Memphis, Tenn. 38137		
White Chem. Corp. P.O. Box 278 Bayonne, N. J. 07002	Bayonne, N. J.	2,4-Dibromophenol (I)
		Pentabromophenol (I)
		Pentabromotoluene (III)
		2,4,6-Tribromophenol (I)
Whittaker Corp. 10880 Wilshire Blvd. Los Angeles, Cal. 90024	San Diego, Cal.	Hexafluorobenzene (III)[a]
		Pentafluoroaniline (III)[a]
		Chloropentafluorobenzene (III)[a]
		Tetrafluoro-m-phenylenediamine (III)[a]
Witco Chem. Corp. 277 Park Avenue New York, N. Y. 10017	Chicago, Ill.	Phthalic anhydride (III)[a]
	Perth Amboy, N. J.	Phthalic anhydride (III)[a]

[a] No longer produced at this location.

[b] From chlorobenzene.

TABLE 13. FORMER LOCATIONS OF ORGANIC CHEMICAL PRODUCTION

Producer	Location	Chemical (class)
Aldrich	Milwaukee, Wisc.	2,4-Dichlorophenol (I)
Allied	Buffalo, N. Y.	3-Amino-5-chloro-2-hydroxybenzenesulfonic acid (III) Fumaric acid (III) Maleic acid (III) 1-Phenol-2-sulfonic acid, formaldehyde condensate (III) Phthalic anhydride (III)
	Chicago, Ill.	Phthalic anhydride (III)
	Frankford, Pa.	Phthalic anhydride (III)
	Ironton, Ohio	Phthalic anhydride (III)
	Moundsville, W. Va.	Fumaric acid (III) Maleic acid (III) Maleic anhydride (III)
	Syracuse, N. Y.	o-Dichlorobenzene (III)
Am. Aniline	Lock Haven, Pa.	o-Anisidine (III)
Blue Spruce	Edison, N. J.	3,4-Dichloroaniline (III) 1,2-Dichloro-4-nitrobenzene (III)
Chem. Insecticide	Metuchen, N. J.	3,4-Dichloroaniline (III) 1,2-Dichloro-4-nitrobenzene (III)
Chem. Products	Cartersville, Ga.	o-Dichlorobenzene (III)
Chevron	Richmond, Cal. Perth Ambay, N. J.	Maleic anhydride (III) Phthalic anhydride (III)
Chris Craft	Newark, N. J.	1,2,4-Trichlorobenzene (III)
Commonwealth Oil	Penuelas, P. R.	Phthalic anhydride (III)
Conoco	Hebronville, Mass.	Phthalic anhydride (III)
Dover	Dover, Ohio	o-Dichlorobenzene (III) Hexachlorobenzene (III) 1,2,4,5-Tetrachlorobenzene (III) Tetrachlorobisphenol-A (II) 1,2,4-Trichlorobenzene (III)
Diamond Shamrock	Cedartown, Ga.	1-Phenol-2-sulfonic acid, formaldehyde condensate (III)
Dow	Midland, Mich.	Phenol[a] (III) 2,4,6-Tribromophenol (I)

(continued)

TABLE 13 (Continued)

Producer	Location	Chemical (class)
Dow (continued)	Kalama, Wash.	Benzaldehyde (III)
du Pont	Deepwater, N. J.	4-Chloro-2-nitrophenol (III) o-Dichlorobenzene (III) 2-Nitro-p-cresol (III) o-Nitrophenol (III)
Eastern Chem. (currently Eastern Chem. Div. of Guardian)	Pequannock, N. J.	Chlorohydroquinone (II) 2,4,6-Tribromophenol (I)
Eastman Kodak	Rochester, N. Y.	2,5-Dihydroxybenzenesulfonic acid (III) Maleic acid (III)
Fritzsche	Clifton, N. J.	Benzaldehyde (III) Phenyl ether (III)
W. R. Grace	Fords, N. J.	Phthalic anhydride (III)
Guardian	Hauppauge, N. Y.	Chlorohydroquinone (II)
	Pequannock, N. J.	Chlorohydroquinone (II) 2,4,6-Tribromophenol (I)
Hooker	Niagara Falls, N. Y.	o-Dichlorobenzene (III) Tetrachlorophthalic anhydride (III) 1,2,4,5-Tetrachlorobenzene (III) 1,2,4-Trichlorobenzene (III)
	North Tonawanda, N. Y.	Phenol[a] (III)
	South Shore, Ky.	Phenol[a] (III)
Hummel Chem.	Newark, N. J.	2,4-Dinitrophenoxyethanol (III) 3,5-Dinitrosalicylic acid (III) Hexachlorobenzene (III) Picric acid (III)
	South Plainfield, N. J.	3,5-Dinitrosalicylic acid (III) Hexachlorobenzene (III) Picric acid (III)
Inmont (formerly Interchemical Corp.)	Carlstadt, N. J.	3,5-Dichlorosalicylic acid (III)

(continued)

TABLE 13 (Continued)

Producer	Location	Chemical (class)
Koppers	Chicago, Ill.	Phthalic anhydride (III)
	Cicero, Ill.	Maleic anhydride (III)
Martin Marietta	Sodyeco, N. C.	2,6-Dibromo-4-nitrophenol (II)
		3,4-Dichloroaniline (III)
		1,2-Dichloro-4-nitrobenzene (III)
		Sodium picrate (III)
Monsanto	Chocolate Bayou, Tex.	Phthalic anhydride (III)
	Saugett, Ill.	3,4-Dichloroaniline (III)
		1,2-Dichloro-4-nitrobenzene (III)
		o-Nitroanisole (III)
	St. Louis, Mo.	o-Anisidine (III)
		o-Phenetidine (III)
		Phthalic anhydride (III)
Morton Chem.	Ringwood, Ill.	3,5-Diiodosalicylic acid (II)
Nease Chem.	State College, Pa.	2,5-Dihydroxybenzenesulfonic acid (III)
		2,5-Dihydroxybenzenesulfonic acid and potassium salt (III)
Neville Chem.	Santa Fe Springs, Cal.	o-Dichlorobenzene (III)
		1,2,4-Trichlorobenzene (III)
Olin	East Alton, Ill.	2,4,6-Trinitroresorcinol (III)
	McIntosh, Ala.	o-Dichlorobenzene (III)
Petro-Tex	Houston, Tex.	Fumaric acid (III)
		Maleic anhydride (III)
Pfister	Newark, N. J.	2-Chloro-1,4-diethoxy-5-nitrobenzene (II)
		5-Chloro-2,4-dimethoxyaniline (II)
Reichhold	Azusa, Cal.	Phthalic anhydride (III)
	Elizabeth, N. J.	Phthalic anhydride (III)
	Morris, Ill.	Fumaric acid (III)
		Phthalic anhydride (III)
F. Ritter	Los Angeles, Cal.	Benzaldehyde (III)

(continued)

TABLE 13 (Continued)

Producer	Location	Chemicals (class)
R.S.A.	Ardsley, N. Y.	3,5-Diiodosalicyclic acid (II) Pentabrompphenol (I) 2,4,6-Tribromophenol (I)
Sherwin Williams	St. Bernard, Ohio	2,6-Dibromo-4-nitrophenol (II) 4-Chloro-2-nitrophenol (III) Phthalic anhydride (III)
Sobin Chems. (currently International Minerals and Chems. Corp.)	Newark, N. J.	1,2,4-Trichlorobenzene (III)
Solvent Chem.	Malden, Mass.	o-Dichlorobenzene (III) 1,2,4,5-Tetrachlorobenzene (III) 1,2,4-Trichlorobenzene (III)
Standard Chlorine	Kearny, N. J.	1,2,4-Trichlorobenzene (III)
Stauffer	Edison, N. J.	Benzaldehyde (III)
	Louisville, Ky.	Hexachlorobenzene (III)
	Nixon, N. J.	Benzaldehyde (III)
Stepan Chem.	Fieldsboro, N. J.	Fumaric acid (III)
	Millsdale, Ill.	Phthalic anhydride (III)
Sterling Drug	New York, N. Y.	1,2-Dihydroxy-3,5-disulfonic acid, disodium salt (III)
Story Chem.	Muskegon, Mich.	3,4-Dichlorophenylisocyanate (III)
Sun Chem.	Chester, S. C.	1,2,4-Trichlorobenzene (III)
Tenneco	Fords, N. J.	3,4-Dichlorobenzotrifluoride (III)
Union Carbide	Marietta, Ohio	Phenol[a] (III)
Velsicol	Chattanooga, Tenn. St. Louis, Mich.	Benzaldehyde (III) Hexabromobenzene (III) Pentabromophenol (I) Tribromobenzene (III) 2,4,6-Tribromophenol (I)

(continued)

TABLE 13 (Continued)

Producer	Location	Chemicals (class)
Whittaker	San Diego, Cal.	Hexafluorobenzene (III) Pentafluoroaniline (III) Chloropentafluorobenzene (III) Tetrafluoro-m-phenylenediamine (III)
Witco	Chicago, Ill.	Phthalic anhydride (III)
	Perth Amboy, N. J.	Phthalic anhydride (III)

[a] From chlorobenzene.

TABLE 14. PRODUCERS OF PESTICIDE CHEMICALS, CLASSES I AND II

Chemical	Producer	Location
Class I		
Bifenox	Mobil	Mt. Pleasant, Tenn.
Chloranil	Arapahoe	Boulder, Colo.[a]
	Uniroyal	Naugatuck, Conn.[a]
2,4-D and esters and salts	Amchem	Ambler, Pa. Fremont, Cal. St. Joseph, Mo.
	Chemical Insecticide Corp.	Metuchen, N. J.[a]
	Chempar	Portland, Ore.[a]
	Diamond Shamrock	Newark, N. J.[a]
	Dow	Midland, Mich.
	Fallek-Lankro	Tuscaloosa, Ala.
	Guth Chem.	Hillside, Ill.[a]
	Imperial	Shenandoah, Iowa
	Miller Chem.	Whiteford, Md.[a]
	Monsanto	Sauget, Ill.[a]
	PBI-Gordon	Kansas City, Kans.
	Rhodia	N. Kansas City, Mo.[a] Portland, Ore. St. Joseph, Mo. St. Paul, Minn.[a]
	Riverdale	Chicago Hgts., Ill.
	Thompson Chem.	St. Louis, Mo.[a]
	Thompson-Hayward	Kansas City, Kans.
	Transvaal	Jacksonville, Ark.
	Woodbury	Orlando, Fla.[a]
2,4-DB and salts	Amchem	Ambler, Pa.
	Rhodia	N. Kansas City, Mo.[a] Portland, Ore. St. Joseph, Mo. St. Paul, Minn.[a]
Dicamba	Velsicol	Beaumont, Tex. Chattanooga, Tenn.[a]
Dicapthon	American Cyanamid	Warners, N. J.[a]
Dichlofenthion	Mobile	Charleston, S. C.[a] Mt. Pleasant, Tenn.[a]

(continued)

TABLE 14 (continued)

Chemical	Producer	Location
Dimethylamine salt of dicamba	PBI-Gordon	Kansas City, Kans.
Disul Sodium (Sesone)	Amchem	Ambler, Pa.[a] Fremont, Cal.[a] Linden, N. J.[a] St. Joseph, Mo.[a]
	GAF	Linden, N. J.[a]
	Union Carbide	Institue and S. Charleston, W. Va.[a]
2,4-DP	Rhodia	Portland, Ore.
	Transvaal	Jacksonville, Ark.
Erbon	Dow	Midland, Mich.[a]
Hexachlorophene	Givaudan	Clifton, N. J.
Isobac 20	Givaudan	Clifton, N. J.
Nitrofen	Rohm and Haas	Philadelphia, Pa.
Pentachlorophenol (PCP) and salts	Dow	Midland, Mich.
	Merck	Hawthorne, N. J.[a]
	Monsanto	Sauget, Ill.
	Reichhold	Tacoma, Wash.
	Sonford Chemical	Port Neches, Tex.[a]
	Vulcan Matls.	Wichita, Kans.
Ronnel	Dow	Midland, Mich.
Silvex and esters and salts	Dow	Midland, Mich.
	Guth Chemical	Hillside, Ill.[a]
	Millmaster Onyx	Berkeley Hgts., N. J.[a]
	Riverdale	Chicago Hgts., Ill.
	Thompson-Hayward	Kansas City, Kans.
	Transvaal	Jacksonville, Ark.
2,4,5-T and esters and salts	Amchem	Ambler, Pa. Fremont, Cal. St. Joseph, Mo.
	Chemical Insecticide Corp.	Metuchen, N. J.[a]
	Chempar	Portland, Ore.[a]

(continued)

TABLE 14 (continued)

Chemical	Producer	Location
2,4,5-T and esters and salts (continued)	Diamond Shamrock Dow Guth Chemical Hercules Millmaster Onyx PBI-Gordan Riverdale Thompson Chemical Thompson-Hayward Transvaal	Newark, N. J.[a] Midland, Mich. Hillside, Ill.[a] Brunswick, Ga.[a] Berkeley Hgts., N. J.[a] Kansas City, Kans. Chicago Hgts., Ill. St. Louis, Mo.[a] Kansas City, Kans. Jacksonville, Ark.
2,3,4,6-Tetrachlorophenol	Dow Sonford	Midland, Mich. Port Neches, Tex.[a]
2,4,5-Trichlorophenol and salts	Chemical Insecticide Corp. Diamond Shamrock Dow GAF Hercules Hooker N. Eastern Pharmacy Transvaal	Metuchen, N. J.[a] Newark, N. J.[a] Midland, Mich. Linden, N. J.[a] Brunswick, Ga.[a] Niagara Falls, N. Y.[a] Verona, Mo.[a] Jacksonville, Ark.
2,4,6-Trichlorophenol	Dow	Midland, Mich.
Class II		
o-Benzyl-p-chlorophenol	Monsanto Reichhold	Sauget, Ill. Tacoma, Wash.
Bromoxynil and esters	Amchem Rhodia	Ambler, Pa. Portland, Ore. St. Joseph, Mo.
Carbophenothion	Stauffer	Cold Creek, Ala.[a] Henderson, Nev.
Chlorothalonil	Diamond Shamrock	Greens Bayou, Tex.
DCPA	Diamond Shamrock	Greens Bayou, Tex.
Dichlone	Aceto FMC Uniroyal	Flushing, N. Y.[a] Middleport, N. Y. Nangatuck, Conn.[a]

(continued)

TABLE 14 (continued)

Chemical	Producer	Location
Dinitrobutylphenol, ammonium salt	Dow	Midland, Mich.
4,6-Dinitro-o-cresol and sodium salt	Blue Spruce	Bound Brook, N. J.
Ioxynil	Amchem	Fremont, Cal.[a]
	Rhodia	Portland, Ore.[a]
Lindane	Hooker	Niagara Falls, N. Y.
	Prentiss	Newark, N. J.
MCPA and derivatives	Diamond Shamrock	Newark, N. J.[a]
	Dow	Midland, Mich.
	Fallek-Lankro	Tuscaloosa, Ala.
	Guth Chemical	Hillside, Ill.[a]
	Monsanto	Nitro, W. Va.[a]
	Rhodia	Portland, Ore.
MCPB	Amchem	Ambler, Pa. Fremont, Cal. St. Joseph, Mo.
	Dow	Midland, Mich.[a]
	Monsanto	Sauget, Ill.[a]
	Rhodia	Portland, Ore. St. Joseph, Mo.
Mecoprop	Cleary	Somerset, N. J.
	Fallek-Lankro	Tuscaloosa, Ala.
	Morton Chem.	Ringwood, Ill.[a]
	PBI-Gordon	Kansas City, Kans.
	Rhodia	Portland, Ore. St. Joseph, Mo.
Parathion	American Cyanamid	Warners, N. J.[a]
	American Potash	Hamilton, Miss.[a] Los Angeles, Cal.[a]
	Monsanto	Anniston, Ala.
	Stauffer	Mt. Pleasant, Tenn.[a]
	Velsicol	Bayport, Tex.[a]
PCNB	Monsanto	Sauget, Ill.[a]
	Olin	Leland, Miss. McIntosh, Ala. Rochester, N. Y.[a]

(continued)

TABLE 14 (continued)

Chemical	Producer	Location
Pipecolinopropyl-3,4-dichlorobenzoate	Eli Lilly	Lafayette, Ind.
Piperalin	Eli Lilly	Indianapolis, Ind.[a] Lafayette, Ind.
Propanil	Blue Spruce Eagle River Monsanto Sobin Chemical	Bound Brook, N. J. Helena, Ark. Luling, La.[a] Newark, N. J.
Tetradifon	FMC	Baltimore, Md.[a]
2,3,6-Trichlorobenzoic acid	Amchem	Ambler, Pa. Fremont, Cal. St. Joseph, Mo.
	du Pont	Deepwater, N. J.[a]
	Tenneco	Fords, N. J.[a]
2,3,6-Trichlorophenyl acetic acid and sodium salt	Amchem	Ambler, Pa. Fremont, Cal. St. Joseph, Mo.
	Tenneco	Fords, N. J.[a]
Triiodobenzoic acid	Amchem Mallinckrodt	Ambler, Pa. Raleigh, N. C.[a]

[a] No longer produced at this location.

TABLE 15. ALPHABETICAL LIST OF PESTICIDE CHEMICAL PRODUCERS

Producer	Location	Chemical (class)
Aceto Chemical Co., Inc.	Flushing, N. Y.	Dichlone (II)[a]
Alco Standard Corp. (See Miller Chem.)		
Amchem Products, Inc. Brookside Ave. P.O. Box 33 Ambler, Pa. 19002 (Subsid. of Union Carbide)	Ambler, Pa.	2,4-D and esters and salts (I) 2,4-DB and salts (I) Disul sodium (I)[a] 2,4,5-T and esters and salts (I) Bromoxynil and esters (II) MCPB (II) 2,3,6-Trichlorobenzoic acid and salt (II) Triiodobenzoic acid (II)
	Fremont, Cal.	2,4-D and esters and salts (I) Disul sodium (I)[a] 2,4,5-T and esters and salts (I) Ioxynil (II)[a] MCPB (II)[a] 2,3,6-Trichlorobenzoic acid (II) 2,3,6-Trichlorophenyl acetic acid, sodium salt (II)
	Linden, N. J.	Disul sodium (I)[a]
	St. Joseph, Mo.	2,4-D and esters and salts (I) Disul sodium (I)[a] 2,4,5-T and esters and salts (I) MCPB (II) 2,3,6-Trichlorobenzoic acid (II) 2,3,6-Trichlorophenyl acetic acid, sodium salt (II)
American Cyanamid Co. Berdan Ave. Wayne, N. J. 07470	Warners, N. J.	Dicapthon (I)[a] Parathion (II)[a]
American Potash and Chem. Corp. Kerr-McGee Chem. Corp. Kerr-McGee Center Oklahoma City, Okla. 73125	Hamilton, Miss.	Parathion (II)[a]
	Los Angeles, Cal.	Parathion (II)[a]

(continued)

TABLE 15 (Continued)

Producer	Location	Chemical (class)
Arapahoe Chem. Div. Syntex Corp. 3401 Hillview Ave. Palo Alto, Cal. 94304	Boulder, Col.	Chloranil (I)[a]
Blue Spruce Co. Stirling, N. J. 07980	Bound Brook, N. J.	4,6-Dinitro-o-cresol and sodium salt (II) Propanil (II)
Chemical Insecticide Corp. 30 Whitman Ave. Metuchen, N. J. 08840 (1971 address)	Metuchen, N. J.	2,4-D and esters and salts (I)[a] 2,4,5-T and esters and salts (I)[a] 2,4,5-Trichlorophenol (I)[a]
Chempar Chem. Co., Inc. (Address not available)	Portland, Ore.	2,4-D and esters and salts (I)[a] 2,4,5-T and esters and salts (I)[a]
W. A. Cleary 1049 Somerset St. Somerset, N. J. 08873	Somerset, N. J.	Mecoprop (II)
Diamond Shamrock Corp. 1100 Superior Ave. Cleveland, Ohio 44114	Greens Bayou, Tex.	Chlorothalonil (II) DCPA (II)
	Newark, N. J.	2,4-D and esters and salts (I)[a] 2,4,5-T and esters and salts (I)[a] 2,4,5-Trichlorophenol and salts (I)[a] MCPA (II)[a]
Dow Chemical U.S.A.	Midland, Mich.	2,4-D and esters and salts (I) Dinitrobutylphenol ammonium salt (II) Erbon (I)[a] MCPA and derivatives (II) MCPB (II)[a] Pentachlorophenol and salts (I) Ronnel (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I) 2,4,5-Trichlorophenol (I) 2,4,6-Trichlorophenol (I)

(continued)

TABLE 15 (Continued)

Producer	Location	Chemical (class)
E.I. du Pont de Nemours and Co., Inc. 1007 Market Street Wilmington, Del. 19898	Deepwater, N. J.	2,3,6-Trichlorobenzoic acid and salts (II)[a]
Eagle River Chemicals, Co. Helena, Ark. 72342 (Subsid. of Vertac, Inc.)	Helena, Ark.	Propanil (II)
Eli Lilly and Co. 740 S. Alabama St. Indianapolis, Ind. 96206	Indianapolis, Ind. Lafayette, Ind.	Piperalin (II)[a] Pipecolinopropyl-3,4-dichlorobenzoate (II) Piperalin (II)
FMC Corp. One Illinois Center 200 East Randolph Dr. Chicago, Ill. 60601	Baltimore, Md.	Tetradifon (II)[a]
	Middleport, N. Y.	Dichlone (I)
Fallek-Lankro Corp. P.O. Box H Tuscaloosa, Ala. 35401 (Joint venture of Fallek Chem. Corp. and Lankro Chem. Group Ltd. [UK])	Tuscaloosa, Ala.	2,4-D and esters and salts (I) MCPA and derivatives (II) Mecoprop (II)
GAF Corp. 140 West 51st St. New York, N. Y. 10020	Linden, N. J.	Disul sodium (I)[a] 2,4,5-Trichlorophenol and salts (I)[a]
Givaudan Corp. 100 Delawanna Ave. Clifton, N. J. 07014 (Affiliate of L. Givaudan and Cie [Switz.])	Clifton, N. J.	Hexachlorophene (I) Isobac 20 (I)
Guth Chemical Co. P.O. Box 302 Naperville, Ill.	Hillside, Ill.	2,4-D and esters and and salts (I)[a] Silvex and esters and salts (I)[a] 2,4,5-T and esters and salts (I)[a] MCPA (II)[a]
Gulf Oil Corp. (See Millmaster Onyx)		

(continued)

TABLE 15 (Continued)

Producer	Location	Chemical (class)
Hercules, Inc. 910 Market St. Wilmington, Del. 19899	Brunswick, Ga.	2,4,5-T and esters and salts (I)[a] 2,4,5-Trichlorophenol and salts (I)[a]
Hooker Chemical Corp. 1900 St. James Pl. Houston, Tex. 77027 (Subsid. of Occidental Petroleum Corp.)	Niagara Falls, N. Y.	2,4,5-Trichlorophenol and salts (I)[a] Lindane (II)
Imperial, Inc. West 6th and Grass Sts. Shenandoah, Iowa	Shenandoah, Iowa	2,4-D and esters and salts (I)
Mallinckrodt, Inc. 675 Brown Road P.O. Box 5840 St. Louis, Mo. 63134	Raleigh, N. C.	Triiodobenzoic acid (II)[a]
Merck and Co., Inc. 126 East Lincoln Ave. Rahway, N. J. 07065	Hawthorne, N. J.	Pentachlorophenol and salts (I)[a]
Miller Chem. and Fertz. Corp. Subsid of Alco Standard Corp. Valley Forge, Pa. 19481	Whiteford, Md.	2,4-D and esters and salts (I)[a]
Millmaster Onyx Group 99 Park Ave. New York, N. Y. 10016 (Part of Gulf Oil Corp.)	Berkeley Hgts., N. J.	Silvex and esters and and salts (I)[a] 2,4,5-T and esters and salts (I)[a]
Mobil Chem. Co. Phosphorus Div. P.O. Box 26638 Richmond, Va. 23261 (Div. of Mobil Corp.)	Charleston, S. C. Mt. Pleasant, Tenn.	Dichlofenthion (I)[a] Bifenox (I) Dichlofention (I)[a]
Monsanto Co. 800 North Lindbergh Blvd. St. Louis, Mo. 63166	Anniston, Ala. Luling, La. Nitro, W. Va. Sauget, Ill.	Parathion (II) Propanil (II)[a] MCPA (II)[a] 2,4-D and esters and salts (I)[a]

(continued)

TABLE 15 (Continued)

Producer	Location	Chemical (class)
Monsanto Co. (continued)		Pentachlorophenol and salts (I) o-Benzyl-p-chlorophenol (II) MCPB (II)[a] PCNB (II)[a]
Morton Chem. Co. Div. of Morton-Norwich Products, Inc. 110 North Wacker Dr. Chicago, Ill. 60606	Ringwood, Ill.	Mecoprop (II)[a]
North Eastern Pharmaceutical and Chem. Co. P.O. Box 270 Stamford, Conn. 06904	Verona, Mo.	2,4,5-Trichlorophenol and salts (I)[a]
Occidental Petroleum Corp (See Hooker)		
Olin Corp. 120 Long Ridge Rd. Stanford, Conn. 06904	Leland, Miss. McIntosh, Ala. Rochester, N. Y.	PCNB (II) PCNB (II) PCNB (II)[a]
PBI-Gordon Corp. 300 South Third St. Kansas City, Kans. 66118	Kansas City, Kans.	Dimethylamine salt of dicamba (I) 2,4,5-T and esters and salts (I) Mecoprop (II)
Prentiss Drug and Chem. Co., Inc. 363 Seventh Ave. New York, N. Y. 10001	Newark, N. J.	Lindone (II)
Reichhold Chemicals, Inc. RCI Building White Plains, N. Y. 10603	Tacoma, Wash.	Pentachlorophenol and and salts (I) o-Benzyl-p-chlorophenol (II)
Rhodia, Inc. 600 Madison Ave. New York, N. Y. 10022 (Subsid. of Rhone-Poulenc SA [France])	N. Kansas City, Mo. Portland, Ore.	2,4-D (I)[a] 2,4-DB (I)[a] Ioxynil (II)[a] 2,4-D (I) 2,4-DB (I)

(continued)

TABLE 15 (Continued)

Producer	Location	Chemical (class)
Rhodia, Inc. (cont.)		2,4-DP (I) Bromoxynil and esters (II) MCPA and derivatives (II) MCPB (II) Mecoprop (II)
	St. Joseph, Mo.	2,4-D and esters and salts (I) 2,4-DB and salts (I) Bromoxynil and esters (II) MCPA and derivatives (II) MCPB (II) Mecoprop (II)
	St. Paul, Minn.	2,4-D and esters and salts (I)[a] 2,4-DB (I)[a]
Riverdale Chemicals, Inc. 220 E. 17th St. Chicago Hgts., Ill. 60411	Chicago Hgts., Ill.	2,4-D and esters and salts (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I)
Sobin Chemicals, Inc. International Minerals and Chem. Corp. IMC Plaza Libertyville, Ill. 60048	Newark, N. J.	Propanil (II)[a]
Sonford Chem. Co. Pure-Atlantic Hwy. Port Neches, Tex. 77651	Port Neches, Tex.	Pentachlorophenol and salts (I)[a] 2,3,4,6-Tetrachlorophenol (I)[a]
Stauffer Chemical Co. Westport, Conn. 06880	Cold Creek, Ala.	Carbophenothion (II)[a]
	Henderson, Nev.	Carbophenothion (II)
	Mt. Pleasant, Tenn.	Parathion (II)[a]
Syntex Corp. (See Arapahoe)		
Tenneco Chemicals Co. Park 80 Plaza West Saddle Brook, N. J. 07662 (Part of Tenneco, Inc.)	Fords, N. J.	2,3,6-Trichlorobenzoic acid and salts (II)[a] (2,3,6-Trichlorophenyl) acetic acid and sodium salt (II)[a]
Thompson Chemicals Corp. 3028 Locust St. St. Louis, Mo. 63103	St. Louis, Mo.	2,4-D and esters and salts (I)[a] 2,4,5-T and esters and salts (I)[a]

(continued)

TABLE 15 (Continued)

Producer	Location	Chemical (class)
Thompson-Hayward Chem. Co. 5200 Speaker Rd. P.O. Box 2383 Kansas City, Kans. 66110 (Subsid of North American Philips Corp.)	Kansas City, Kans.	2,4-D and esters and salts (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I)
Transvaal, Inc. Marshall Rd. P.O. Box 69 Jacksonville, Ark. 72076 (Subsid. Vertac, Inc.)	Jacksonville, Ark.	2,4-D and esters and salts (I) 2,4-DP (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I) 2,3,4,6-Tetrachlorophenol (I) 2,4,5-Trichlorophenol and salts (I)
Union Carbide Corp. 270 Park Ave. New York, N. Y. 10017 (See also Amchem)	Institute and South Charleston, W. Va.	Disul sodium (I)[a]
Uniroyal, Inc. 1230 Ave. of the Americas New York, N. Y. 10020	Naugatuck, Conn.	Chloranil (I)[a] Dichlone (II)[a]
Velsicol Chemical Corp. 341 East Ohio St. Chicago, Ill. 60611 (Subsid. of Northwest Industries, Inc.)	Bayport, Tex. Beaumont, Tex.	Parathion (II)[a] Dicamba (I)
Vertac, Inc. (See Transvaal and Eagle River)		
Vulcan Materials Co. P.O. Box Birmingham, Ala. 35223	Wichita, Kans.	Pentachlorophenol and salts (I)
Woodbury Chemicals Subsid. of Comutrix Corp. 8373 N. E. 2nd Ave. Miami, Fla. 33138	Orlando, Fla.	2,4-D and esters and salts (I)

[a] No longer produced at this location.

TABLE 16. FORMER PESTICIDE PRODUCTION LOCATIONS

Producer	Location	Chemical (class)
Aceto	Flushing, N. Y.	Dichlone (II)
Amchem	Ambler, Pa.	Disul Sodium (I) 2,3,6-Trichlorobenzoic acid and salts (II)
	Fremont, Cal.	Disul Sodium (I) Ioxynil (II) MCPB (II)
	Linden, N. J.	Disul Sodium (I)
	St. Joseph, Mo.	Disul Sodium (I)
American Cyanamid	Warners, N. J.	Dicapthon (I) Parathion (II)
American Potash	Hamilton, Miss.	Parathion (II)
Arapahoe	Boulder, Col.	Chloranil (I)
Chem. Insecticide Corp.	Metuchen, N. J.	2,4-D and esters and salts (I) 2,4,5-T and esters and salts (I) 2,4,5-Trichlorophenol and salts (I)
Chempar	Portland, Ore.	2,4-D and esters and salts (I) 2,4,5-T and esters and salts (I)
Diamond Shamrock	Newark, N. J.	2,4,5-T and esters and salts (I) 2,4,5-Trichlorophenol and salts (I) MCPA (II)
Dow	Midland, Mich.	Erbon (I) MCPB (II)
du Pont	Deepwater, N. J.	2,3,6-Trichlorobenzoic acid and salts (II)
Eli Lilly	Indianapolis, Ind.	Piperalin (II)
FMC	Baltimore, Md.	Tetradifon (II)
GAF	Linden, N. J.	Disul Sodium (I) 2,4,5-Trichlorophenol and salts (I)

(continued)

TABLE 16 (Continued)

Producer	Location	Chemical (class)
Guth Chem.	Hillside, Ill.	2,4-D and esters and salts (I) Silvex and esters and salts (I) 2,4,5-T and esters and salts (I) MCPA (II)
Hercules	Brunswick, Ga.	2,4,5-T and esters and salts (I) 2,4,5-Trichlorophenol and salts (I)
Hooker	Niagara Falls, N. Y.	2,4,5-Trichlorophenol and salts (I)
Mallinckrodt	Raleigh, N. C.	Triiodobenzoic acid (II)
Merck	Hawthorne, N. J.	Pentachlorophenol and salts (I)
Miller Chem.	Whiteford, Md.	2,4-D and esters and salts (I)
Millmaster Onyx	Berkeley Hgts., N. J.	Silvex and esters and salts (I) 2,4,5-T and esters and salts (I)
Mobil	Charleston, S. C.	Dichlorofenthion (I)
Monsanto	Luling, La. Nitro, W. Va. Sauget, Ill.	Propanil (II) MCPA (II) 2,4-D and esters and salts (I) MCPB (II) PCNB (II)
Morton	Ringwood, Ill.	Mecoprop (I)
N. Eastern Pharm.	Verona, Mo.	2,4,5-Trichlorophenol and salts (I)
Olin	Rochester, N. Y.	PCNB (II)
Rhodia	N. Kansas City, Mo.	2,4-D and esters and salts (I) 2,4-DB and salts (I)
	Portland, Ore.	Ioxynil (II)
	St. Paul, Minn.	2,4-D and esters and salts (I) 2,4-DB and salts (I)

(continued)

TABLE 16 (Continued)

Producer	Location	Chemical (class)
Sobin Chem.	Newark, N. J.	Propanil (II)
Sonford	Port Neches, Tex.	Pentachlorophenol and salts (I) 2,3,4,6-Tetrachlorophenol (I)
Stauffer	Cold Creek, Ala.	Carbophenothion (II)
Tenneco	Fords, N. J.	2,3,6-Trichlorobenzoic acid and salts (II) (2,3,6-Trichlorophenyl) acetic acid (II)
Thompson Chem.	St. Louis, Mo.	2,4-D and esters and salts (I) 2,4,5-T and esters and salts (I)
Union Carbide	Institute and South Charleston, W. Va.	Disul Sodium (I)
Uniroyal	Naugatuck, Conn.	Chloranil (I) Dichlone (II)
Velsicol	Bayport, Tex. Chattanooga, Tenn.	Parathion (II) Dicamba (I)
Woodbury	Orlando, Fla.	2,4-D and esters and salts (I)

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16. ABSTRACT

Chemical reaction mechanisms by which dioxins may be formed are reviewed, particularly those likely to occur within commercially significant processes. Various routes of formation are identified in addition to the classical route of the hydrolysis of trichlorophenol. Basic organic chemicals and pesticides with a reasonable potential for dioxin byproduct contamination are surveyed as to current and past producers and production locations.

Classifications are presented both for general organic chemicals and for pesticides that indicate likelihood of dioxin formation. Conditions are noted that are most likely to promote dioxin formation in various processes.

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