

*Anal.* Calcd. for  $C_8H_7N_3$ : C, 55.5; H, 4.08; N, 40.6. Found: C, 55.5; H, 4.02; N, 40.7.

**2,6,6-Tricyano-3,5,5-trimethyl-2-cyclohexen-1-one (XVII).**—Hydrolysis of IV as described by Coenen<sup>13</sup> give XVII, m.p. 126–127°, in 72% yield. The two following experiments were modeled after this preparation.

The infrared spectrum showed  $\lambda_{\max}^{KBr}$  4.47 (CN), 5.84 (C=O), and 6.19 (C=C)  $\mu$ .

**Methyl 1,3-Dicyano-4,6,6-trimethyl-2-oxo-3-cyclohexene-1-carboxylate (XXb).**—A mixture of 12.2 g. of IXb, 200 ml. of ethanol, 200 ml. of water and 10.5 ml. of concentrated hydrochloric acid was stirred at room temperature for 25.5 hr. The white solid was collected and washed with water to give 11.1 g. (90%) of XXb, m.p. 142.8–143.4°. The melting point was not raised when a sample was prepared for analysis by crystallization from an ethanol–water mixture.

The infrared spectrum showed  $\lambda_{\max}^{KBr}$  4.42 (w) (sat. CN), 4.45 (conj. CN), 5.74 (ester C=O), 5.89 (conj. ketone C=O), 6.17 (C=C)  $\mu$ .

*Anal.* Calcd. for  $C_{13}H_{14}N_2O_3$ : C, 62.9; H, 5.69; N, 11.3. Found: C, 62.9; H, 5.71; N, 11.4.

**Ethyl 1,3-Dicyano-4,6,6-trimethyl-2-oxo-3-cyclohexene-1-carboxylate (XXc).**—A mixture of 5.16 g. of IXc, 80 ml. of methanol, 80 ml. of water and 4.2 ml. of concentrated hydrochloric acid was

stirred at room temperature for 25 hr. The white solid that precipitated was collected, washed with water, and dried to give 4.85 g. (93%) of XXc, m.p. 108.2–109.1°. A sample prepared for analysis by crystallization from benzene–cyclohexene melted at 108.4°.

The infrared spectrum showed  $\lambda_{\max}^{KBr}$  4.45 (w) (sat. CN), 4.47 (conj. CN), 5.78 (ester C=O), 5.90 (conj. ketone C=O), 6.17 (C=C)  $\mu$ .

*Anal.* Calcd. for  $C_{13}H_{16}N_2O_3$ : C, 64.7; H, 6.20; N, 10.8. Found: C, 64.5; H, 6.20; N, 10.8.

**1-Amino-2-cyanocyclohexene (XI).**—A mixture of 30 g. of pimelonitrile, 400 ml. of toluene and 11 g. of sodium hydride dispersion (53% in oil) was heated under reflux for 17 hr. To the hot mixture was added successively 20 ml. of ethanol, 100 ml. of water and 15 ml. of acetic acid. The toluene layer was collected, washed with 150 ml. of water and filtered. The filtrate was reduced to a volume of 300 ml. by distillation and diluted while hot with 500 ml. of petroleum ether (b.p. 30–60°). The cooled solution was diluted to 1500 ml. with petroleum ether and refrigerated. The solid that crystallized was collected to give 20 g. of XI, m.p. 96.5–99.0°. A small sample prepared for spectral measurement by two crystallizations from methanol–water mixture melted at 98–99°.

The infrared spectrum showed  $\lambda_{\max}^{KBr}$  2.89, 2.92, 3.07, 4.57, 6.07, and 6.19  $\mu$ .

## The Chemistry of Xylylenes. XVIII. The Gas Phase Synthesis of $\alpha,\alpha'$ -Bistrichloromethyl-*p*-xylylene via Coaxial Pyrolysis of *p*-Xylene and Chloroform

L. A. ERREDE AND J. P. CASSIDY

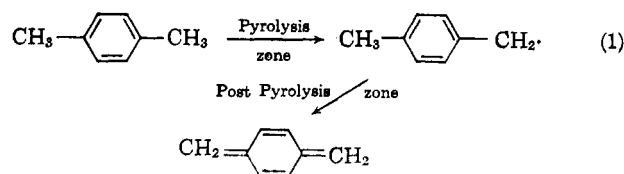
Contribution No. 234 from the Central Research Laboratories of the Minnesota Mining and Manufacturing Company,<sup>1</sup>

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Fast flowing streams of *p*-xylene and chloroform were pyrolyzed in separate concentric tubes. The resulting pyrolyzates were allowed to mix at a predetermined point downstream where coupling of the chlorocarbon and hydrocarbon radicals occurred to produce a mixture of products. The composition of reactive species in the respective gas streams changed with distance away from the point of generation *via* pyrolysis. Hence, the product distribution changed accordingly with the blend point. Thus, *p*-methylbenzyl chloride and  $\beta,\beta$ -dichloro-*p*-methylstyrene were isolated as major products when the two streams were made to blend within the pyrolysis zone, whereas *p*-methylbenzyl chloride and  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylylene were isolated as major products when the pyrolyzates were allowed to blend five inches beyond the pyrolysis zone.

An earlier investigation of the fast flow pyrolysis of *p*-xylene at low pressure has shown that thermal rupture of the C—H bond occurs in the pyrolysis zone to give *p*-methylbenzyl radicals that are dehydrogenated catalytically to give *p*-xylylene as the pyrolyzate travels away from the furnace.<sup>2,3</sup>



It was also demonstrated that *p*-methylbenzyl radicals and *p*-xylylene can be used selectively as reactive intermediates for gas phase synthesis of mono- and difunctional derivatives of *p*-xylene. The technique involves quenching the fast flowing pyrolyzate with a second stream of reactive intermediates at an ap-

propriate blend point. The proportion of mono- to difunctional derivatives obtained is a function of the corresponding ratio of *p*-methylbenzyl radicals to *p*-xylylene present at the point of mixing.

Similarly, fast flow pyrolysis of carbon tetrachloride at low pressure generates a stream of  $\text{CCl}_3\cdot$  and  $\text{Cl}\cdot$  that subsequently undergo coupling reactions to give  $\text{CCl}_2\text{CCl}_3$  and chlorine as the gas stream travels away from the pyrolysis zone.<sup>2</sup> When *p*-xylene and carbon tetrachloride were pyrolyzed in two separate concentric tubes and the resulting pyrolyzates allowed to blend at a predetermined point downstream, as shown in Fig. 1 of ref. 3, the products isolated were dependent upon the relative concentration of reactive species in the respective gas streams at the point of mixing. The approximate flow patterns for the hydrocarbon and chlorocarbon streams emanating from a common pyrolysis zone are shown in Fig. 1A and 1B. Thus, *p*-methylbenzyl chloride and  $\beta,\beta$ -dichloro-*p*-methylstyrene were isolated as the two major products of interaction (equations 2 and 3) when the two streams were allowed to blend at the exit point of the pyrolysis zone,<sup>2</sup> whereas *p*-xylylene dichloride was the major product of interaction (reaction 4) when the two fast flowing pyrolyzates were allowed to blend far downstream.<sup>3</sup>

(1) This work was carried out in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Company with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Company in March, 1957.

(2) L. A. Errede and J. P. Cassidy, Paper XVI, *J. Phys. Chem.*, **67**, 69 (1963).

(3) L. A. Errede and J. P. Cassidy, Paper XVII, *ibid.*, **67**, 73 (1963).

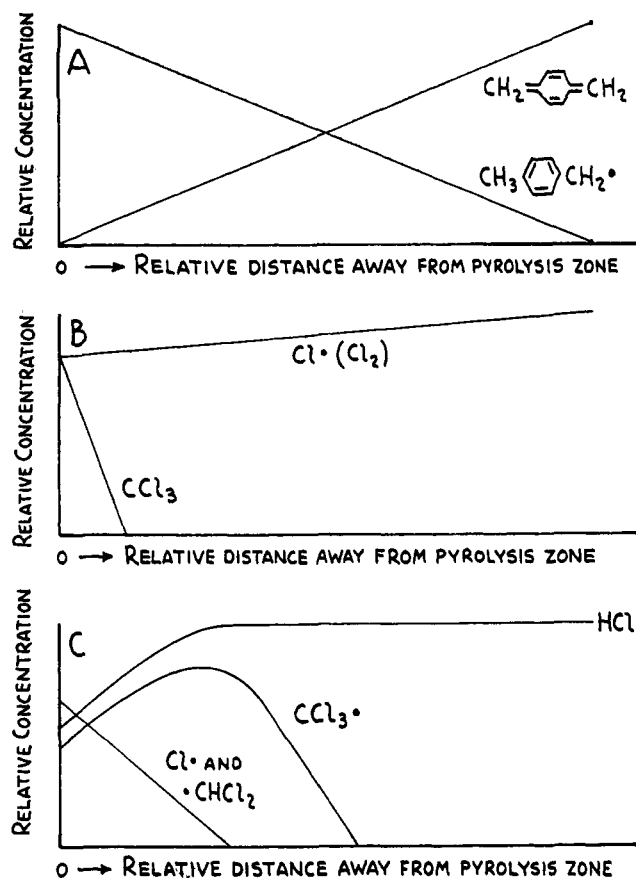
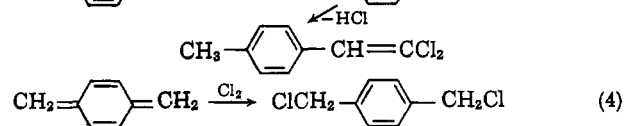
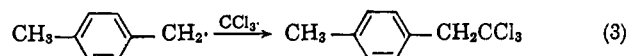
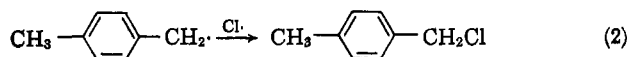


Fig. 1.—The flow pattern of reactive species produced *via* fast flow pyrolysis at low pressure. (A) pyrolyzed *p*-xylylene; (B) pyrolyzed carbon tetrachloride; (C) pyrolyzed chloroform. Figures represent relative concentration of reactive species in the fast flowing pyrolyzates as a function of distance from the end of the pyrolysis zone.



The existence of  $\text{CCl}_3\cdot$  in the chlorocarbon stream was not contemporary with the existence of *p*-xylylene in the hydrocarbon stream as shown in Fig. 1A and 1B. Obviously, co-existence of these two reactive species at the point of mixing is a mandatory requirement for formation of  $\alpha, \alpha'$ -bistrichloromethyl-*p*-xylylene. Since this requirement was not fulfilled adequately at any point along the dual pyrolysis system, it was impossible to isolate this derivative of *p*-xylylene.

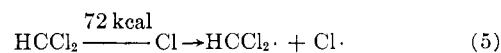
It was speculated, however, that  $\alpha, \alpha'$ -bistrichloromethyl-*p*-xylylene could be produced by co-axial pyrolysis of *p*-xylylene and chloroform since free radical abstraction of hydrogen from unreacted chloroform might afford a large amount of trichloromethyl radicals in the post pyrolysis zone as shown by the flow pattern in Fig. 1C. Accordingly, the products of interaction of pyrolyzed *p*-xylylene and pyrolyzed chloroform were investigated as a function of the choice of blend point.

## Results and Discussion

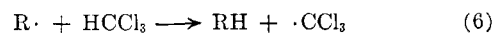
First, it was necessary to establish the magnitude of conversion and the type of reactive species produced when chloroform is subjected to the approximate conditions of fast flow pyrolysis that afford 10% conversion of *p*-xylylene to *p*-methylbenzyl radicals.<sup>3</sup> Hence, chloroform was pyrolyzed at 1005° and 2.5 mm. for 0.002-sec. residence time and the reaction products were isolated as described in the Experimental section. Sixty percent of the carbon atoms metered to the system were recovered as unchanged chloroform, 25% as  $\text{C}_2\text{Cl}_4$ , 4% as  $\text{C}_2\text{Cl}_6$ , 4% as  $\text{C}_2\text{Cl}_3\text{H}$ , 2% as carbon tetrachloride, leaving only 5% unaccounted for. A large quantity of hydrogen chloride (almost theoretical) was isolated but no molecular chlorine or hydrogen was detected. A very small amount of phosgene was also detected in the pyrolyzate, probably forming *via* reaction of  $\text{C}_2\text{Cl}_4$  with oxygen that leaked into the system during pyrolysis.

These products can be accounted for by assuming thermal rupture of the weakest bond in chloroform<sup>4</sup> followed by hydrogen abstraction, coupling of radicals and hydrogen chloride elimination as indicated by reactions 5–10.

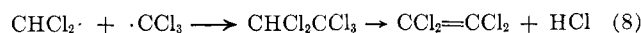
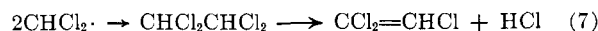
Thermal rupture



Hydrogen abstraction by  $\text{Cl}\cdot$  or  $\text{CHCl}_2\cdot$  (R·)

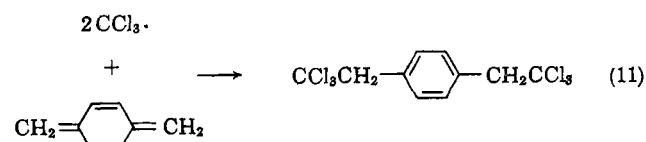


Coupling and HCl elimination



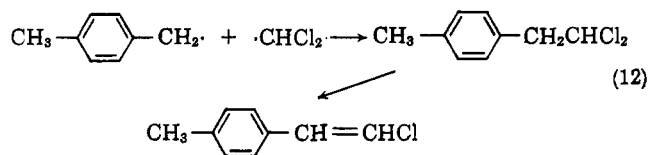
The hydrogen abstraction reactions represented by equation 6 would consume  $\text{Cl}\cdot$  and  $\cdot\text{CHCl}_2$  rapidly to keep the steady state concentration in the pyrolysis zone very low. On the other hand,  $\text{CCl}_3\cdot$  produced *via* hydrogen abstraction would attain a maximum just beyond the pyrolysis zone. The hydrogen chloride concentration would increase continuously to an amount that depends upon the pyrolysis conditions. Accordingly, the flow pattern of reactive species could be represented qualitatively as shown in Fig. 1C.

If one superimposes this flow pattern on that established for fast flow pyrolysis of *p*-xylylene (Fig. 1A), one can readily anticipate the products of interaction as a function of blend point. Thus, the formation of  $\alpha, \alpha'$ -bistrichloromethyl-*p*-xylylene *via* coupling of  $\text{CCl}_3\cdot$  with *p*-xylylene should be at a maximum when the two pyrolysis streams are allowed to blend just beyond the furnace (reaction 11).

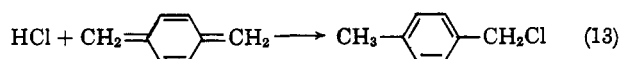


(4) L. A. Errede, *J. Phys. Chem.*, **64**, 1031 (1960).

If the blend point is located in the pyrolysis zone, one should obtain a mixture of *p*-methylbenzyl chloride, and  $\beta$ -chloro substituted styrenes *via* coupling of  $\text{Cl}\cdot$ ,  $\text{CHCl}_2\cdot$ , and  $\text{CCl}_3\cdot$  with *p*-methylbenzyl radicals followed by hydrogen chloride elimination at the high temperatures existing at the point of coupling (reactions 2, 3, and 12).



Eventually, hydrogen chloride and *p*-xylylene are the only reactive species in the chlorocarbon and hydrocarbon pyrolyzates. Hence, one should obtain *p*-methylbenzyl chloride as the major product *via* addition of hydrogen chloride to *p*-xylylene (reaction 13) when the two streams are allowed to blend a considerable distance beyond the pyrolysis zone. Although it has not



been demonstrated that reaction 15 occurs in the gas phase, it was demonstrated that it does occur readily when the gas stream is condensed in the low temperature trap.<sup>5</sup> The final product of interaction, therefore, would be the same regardless of where reaction occurs.

Accordingly, the pyrolysis system, shown schematically in Fig. 1 of ref. 3, was used for co-pyrolysis of *p*-xylylene and chloroform in two separate but concentric tubes. *p*-Xylene was metered to the evacuated system through the outer tube while chloroform was metered to the inner tube and the two pyrolyzates were allowed to blend at a predetermined point downstream. The distance to the blend point was increased with each successive pyrolysis. The data are summarized in Table I. The amount of *p*-xylene derivatives isolated, is equal to (or less than) the amount of *p*-methylbenzyl radicals produced pyrolytically as the gas stream travelled through the furnace. In an earlier study,<sup>3,6</sup> it was established that the fractional conversion of *p*-xylylene to *p*-methylbenzyl radicals (C) is given by

$$C = At \exp(-Bt) \quad (14)$$

where *t* is the residence time in seconds, *A* is the approximate rate constant for formation of *p*-methylbenzyl radicals, and *B* is the approximate rate constant for subsequent thermal destruction of the radicals. *A* and *B* are given by

$$A = 2.6 \times 10^{16} \exp(-83/RT) \quad (15)$$

$$B = 8.5 \times 10^{14} \exp(-80/RT) \quad (16)$$

Hence, the reported yield of each product was based on available *p*-methylbenzyl radicals produced pyrolytically as calculated by equations 14, 15, and 16.

The yields of *p*-methylbenzyl chloride,  $\beta,\beta$ -dichloro-*p*-methylstyrene, and  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene are shown in Fig. 2 as a function of the blend point, given in inches away from the end of the pyrolysis zone. It is noted that the pattern of reaction products is about as anticipated based on the earlier discussion.

(5) L. A. Errede, J. M. Hoyt, and R. S. Gregorian, *J. Am. Chem. Soc.*, **82**, 5224 (1960).

(6) L. A. Errede and F. DeMaria, *J. Phys. Chem.*, **66**, 2664 (1962).

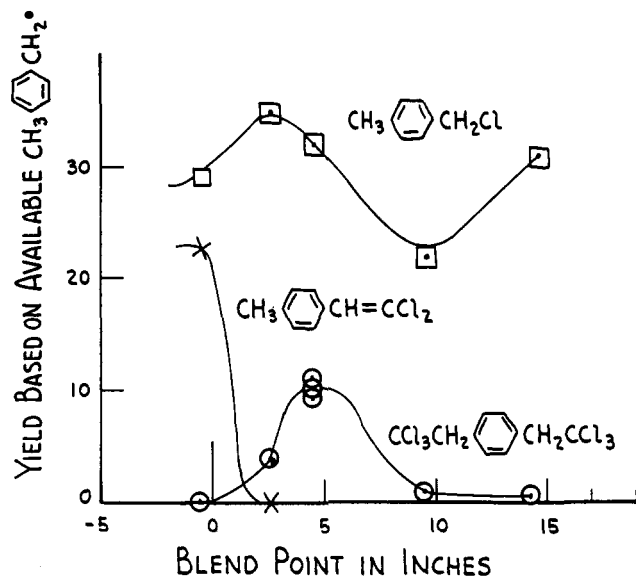


Fig. 2.—Yield of *p*-methylbenzyl chloride,  $\beta,\beta$ -dichloro-*p*-methylstyrene, and  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene as a function of blend point given in inches from the end of the pyrolysis zone.

In this series of experiments,  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene was produced in maximum amount when the blend point was set at 5 inches beyond the pyrolysis zone. Since the formation of *p*-xylylene from *p*-methylbenzyl radicals is a function of the geometry of the post-pyrolysis zone,<sup>3</sup> it is conceivable that the maximum point varies with the design of the pyrolysis system.

The assigned structure of  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene was verified by its elementary analysis and molecular weight which indicated an empirical formula of  $\text{C}_{10}\text{H}_8\text{Cl}_6$ . No halogen was alpha to the phenyl group as indicated by a negative test for active halogen using silver nitrate in alcohol. The compound contained no olefin unsaturation as indicated by negative tests for unsaturation using potassium permanganate in acetone, and bromine in carbon tetrachloride. The infrared spectrum of the compound was consistent with the assigned structure. Two equivalents of hydrogen chloride were eliminated when the compound was treated with sodium methoxide in methanol. The elementary analysis and molecular weight of the resultant compound indicated an empirical formula of  $\text{C}_{10}\text{H}_6\text{Cl}_4$ . Its infrared and ultraviolet absorption spectra were consistent with the structure of  $\beta,\beta,\beta',\beta'$ -tetrachloro-*p*-di-vinylbenzene. Oxidation of the di-vinylbenzene derivative with potassium permanganate in acetone gave terephthalic acid which was identified by conversion to its dimethyl ester. These reactions, as outlined in Fig. 3, prove that the compound isolated in maximum amount at blend point 5 inches away from the pyrolysis zone is  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene.

Although  $\beta$ -chloro-*p*-methylstyrene was not isolated, it is possible that the compound was formed as anticipated by reaction 12 and was decomposed during the separation procedure, or it may simply have been present as one of the components in the relatively large portion of unresolved residue.

It was demonstrated that abstraction of a hydrogen atom from chloroform by *p*-methylbenzyl radicals to afford  $\cdot\text{CCl}_3$  was not an important contribution to

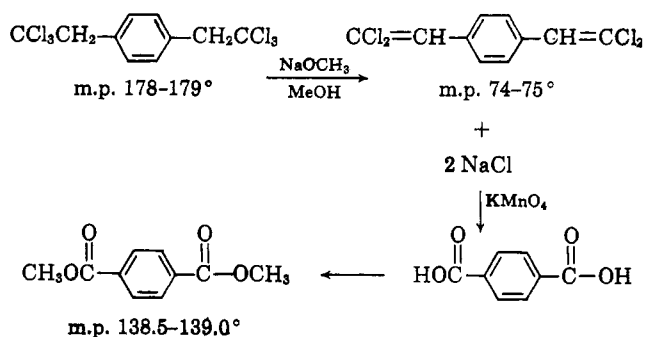


Figure 3

the reaction products. Thus, a stream of pyrolyzed *p*-xylene was quenched at one inch beyond the pyrolysis zone with a nonpyrolyzed stream of chloroform. The major product (60%) was poly(*p*-xylylene). The usual low molecular weight products of *p*-xylene pyrolysis (40%) were also obtained as an oil that contained only 0.3% chlorine.

### Experimental

**Pyrolysis of Chloroform.**—Chloroform (5.5 moles) was metered at the rate of 0.046 mole/min. to the pyrolysis system (shown in Fig. 1 of ref. 7) evacuated at 2.5-mm. pressure. Pyrolysis was effected at 1005° for  $2 \times 10^{-3}$  sec. residence time and the pyrolyzate was collected in 4 l. of hexane kept at  $-78^\circ$ . A second trap cooled with liquid nitrogen was used in series to collect gases that escaped condensation in the first one. The liquid nitrogen trap was warmed to room temperature and the gas stream evolved was passed through 3 l. of 1 *N* aqueous sodium hydroxide. The trap system was swept with nitrogen and the aqueous solution was back titrated with 0.5 *N* hydrochloric acid. The result showed that 1.5 moles hydrochloric acid were collected in the liquid nitrogen trap. An additional 0.2 mole was recovered from the Dry Ice trap using a similar procedure.

Mass spectrometric analysis of a sample of the chloroform pyrolyzate in hexane indicated that the solution contained 3.3 moles of chloroform, 0.7 mole of  $\text{C}_2\text{Cl}_4$ , 0.1 moles  $\text{C}_2\text{Cl}_3\text{H}$ , and a trace of phosgene. This solution was separated by distillation at atmospheric pressure to give three major fractions: (1) 3.0 kg., b.p.  $65-72^\circ$  (this fraction was a hexane solution that contained 3.0 moles of chloroform, 0.12 mole of carbon tetrachloride and 0.06 mole of  $\text{C}_2\text{Cl}_3\text{H}$  as indicated by mass spectrometric analysis); (2) 91 g., b.p.  $120-121^\circ$  (this fraction was  $\text{C}_2\text{Cl}_4$  as indicated by its boiling point and infrared spectrum); (3) 48 g. residue. This residue was dissolved in methanol and the solution was chilled to  $-78^\circ$  to yield 23 g.  $\text{CCl}_3\text{CCl}_3$  in the form of white platelets (m.p.  $181-183^\circ$ ). The mother liquor was evaporated to dryness leaving a mixture of  $\text{C}_2\text{Cl}_4$  and  $\text{C}_2\text{Cl}_6$  as residue (15 g.).

In order to prove the presence of phosgene, aniline (150 cc.) was added to fraction 1. Aniline hydrochloride (4 g.) precipitated immediately and was removed by filtration. The mother liquor was allowed to remain overnight at room temperature and a white solid (2.5 g.) separated from solution. This precipitate was recrystallized from methanol to give diphenylurea in the form of white needles (m.p.  $239-240^\circ$ ; no depression when mixed with an authentic sample). The infrared spectrum of this sample was also identical with that of the authentic compound.

Thus, 5.5 moles of chloroform was metered to the pyrolysis system and 3.3 moles of the carbon atoms were recovered as starting material, 1.4 moles as  $\text{C}_2\text{Cl}_4$ , 0.2 mole as  $\text{C}_2\text{Cl}_3\text{H}$ , 0.2 mole as  $\text{C}_2\text{Cl}_6$ , 0.1 mole as carbon tetrachloride, and a trace as phosgene leaving 0.3 mole unaccounted for.

To determine whether hydrogen or chlorine were produced in this reaction, the pyrolysis was repeated on a microscale using a closed system that was purged with nitrogen and then evacuated to 1 mm. Chloroform (1.5 g.) was pyrolyzed at  $920^\circ$  and 1 mm. for approximately 0.01-sec. residence time and the products were collected in a micro cold trap kept at  $-78^\circ$ . No pressure rise was noted, indicating the absence of non-condensable gases such

as hydrogen. The gases in this system at 1-mm. pressure were collected by means of a Toepler pump. Mass spectrometric analysis indicated that this gas sample was a mixture of chloroform,  $\text{C}_2\text{Cl}_4$ , and nitrogen.

**Coaxial Pyrolysis of *p*-Xylene and Chloroform.**—The apparatus shown schematically in Fig. 1 of ref. 3 was used for the coaxial pyrolysis of *p*-xylene and chloroform. A given quantity of *p*-xylene was metered to the system at a predetermined rate through the outer concentric tube (1-in. i.d.), while a second quantity of chloroform was metered to the system through the inner concentric tube (7-mm. i.d. and 9-mm. o.d.). The two streams were pyrolyzed coaxially and then allowed to blend at a predetermined point as indicated in Table I. The mixture of pyrolyzates was collected in hexane kept at  $-78^\circ$  and the resultant solution was warmed to room temperature after termination of the pyrolysis. The excess solvent was removed by rapid evaporation at 60-mm. pressure and  $100^\circ$ . The residue was evaporated to constant weight at  $100^\circ$  under a stream of nitrogen at atmospheric pressure.

The dark oil obtained as residue was stored at room temperature for several days during which time dark needle-like crystals formed throughout the viscous solution. The crystals were removed by filtration and the mother liquor was dissolved in hexane (1 l. of hexane/200 g. of product). The solution was chilled to  $-78^\circ$  and a grey solid precipitated. This material was combined with the crystals separated previously. The solid was washed with hexane, dried and purified by vacuum sublimation (1-mm. pressure) at  $100^\circ$ . The sublimate was recrystallized from methanol and the compound was obtained in the form of dense white needles (m.p.  $178-179^\circ$ ). The compound did not decolorize potassium permanganate in acetone nor did it react with bromine in carbon tetrachloride indicating the absence of olefinic bonds. The compound was insoluble in cold concentrated sulfuric acid and sulfonation occurred at higher temperature to afford water soluble products. The compound gave a positive test for chlorine but gave a negative test for active halogen using alcoholic silver nitrate, indicating that the chlorine atoms were not alpha to the phenyl ring. The infrared spectrum in Nujol (medium or strong bands 6.62, 7.04, 8.37, 8.98, 9.73, 10.70, 11.43, 12.47, 13.60, and 14.30  $\mu$ , plus usual Nujol absorptions) was consistent with the anticipated structure of  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene, and the elementary analysis was consistent with the empirical formula for this compound.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_8\text{Cl}_2$ : C, 35.23; H, 2.37; Cl, 62.46; mol. wt., 340.9. Found: C, 35.1; H, 2.02; Cl, 62.4; mol. wt., 337.

Several years after completion of this work the assigned structure was also verified in the laboratories of the Minnesota Mining and Manufacturing Company by n.m.r. analysis ( $\tau$  values<sup>8</sup>: 6.07 for  $\text{CH}_2$  and 2.57 for aromatic C-H).

The hexane mother liquor, from which  $\alpha,\alpha'$ -bistrichloromethyl-*p*-xylene was separated by filtration, was evaporated to dryness. The residue was separated by vacuum distillation as described previously for copyrolysis of *p*-xylene with carbon tetrachloride.<sup>2,3</sup> The separation was not clean cut and often the composition in each distillation fraction was determined by infrared or mass spectrometric analysis.

The distance from the pyrolysis zone to the blend point was increased in a series of experiments that are summarized in Table I. The residue after distillation represented a major portion of the reaction products, but attempts to separate this mixture further were not successful. Occasionally small amounts of new products were isolated in individual runs. These compounds, however, were only partly characterized as indicated in Table I.

**Pyrolyzed *p*-Xylene Quenched with Nonpyrolyzed Chloroform.**—A stream of *p*-xylene (5.3 moles) was pyrolyzed at  $1000^\circ$  and 6 mm. for 0.005-sec. residence time. These are pyrolysis conditions known to afford 6% conversion *p*-xylene to *p*-methylbenzyl radicals.<sup>3,9</sup> The pyrolyzate was quenched with nonpyrolyzed chloroform (9.6 moles) at a point 7 inches downstream where the temperature was only  $500^\circ$ . The resultant gas mixture was collected in 2 l. of hexane kept at  $-78^\circ$ . Poly(*p*-xylylene) (13 g.) was produced when the solution was warmed to room temperature. The polymer was removed by filtration. Virtually all the chloroform was recovered in the mother liquor as indicated by mass spectrometric analysis of an aliquot sample. The soluble products of pyrolysis were recovered from the mother

(7) L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, **79**, 4952 (1957).

(8) N.m.r. values refer to the system of G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

TABLE I  
PRODUCTS OBTAINED *via* COAXIAL PYROLYSIS OF *p*-XYLENE AND CHLOROFORM AS A FUNCTION OF BLEND POINT

Pyrolysis conditions			Feed stock		Estimated amount		Products <sup>a</sup> isolated, g.								
<i>T</i> , °C.	<i>t</i> , sec.	<i>P</i> , mm.	<i>p</i> -Xylene, g.	Chloroform, g.	Blend point <sup>b</sup>	<i>p</i> -Methylbenzyl produced, <sup>c</sup> g.	1	2	3	4	5	6	7	8	9
1000	0.01	6.8	437	1251	14.5	44	18	0	0.5	1	15	17	—	—	<sup>d</sup>
1005	.009	4.2	525	1394	9.5	58	17	0	0	1.5	23	15	0.5	5	—
1000	.005	2.5	365	810	4.5	22	9.4	0	0	8.5	10	16	2	—	<sup>e</sup>
1000	.005	5.0	1491	2074	4.5	89	—	—	—	28	—	—	—	—	—
1000	.006	3.3	621	1266	4.5	43	—	—	—	15	—	—	—	—	—
1005	.01	4.8	356	836	2.5	41	19	0	0	5	21	41	1	—	—
1005	.007	4.7	1287	1847	1.5	109	—	—	—	1	—	—	—	—	—
1005	.01	3.7	401	1047	-0.5	46	18	19	0	0	18	36	—	—	—
1010	.006	3.3	453	1135	-10	36 <sup>f</sup>	20	26	0	0	60	57	—	—	—

<sup>a</sup> 1, CH<sub>3</sub>⌡CH<sub>2</sub>Cl; 2, CH⌡CH=CCl<sub>2</sub>; 3, ClCH<sub>2</sub>⌡CH<sub>2</sub>Cl; 4, Cl<sub>3</sub>CCH<sub>2</sub>⌡CH<sub>2</sub>CCl<sub>3</sub>; 5, mixture of 1,2-di-*p*-tolylethane and methylated diphenylmethanes; 6, residue mixture chlorocarbons and hydrochloro carbons; 7, C<sub>2</sub>Cl<sub>6</sub>; 8, C<sub>6</sub>Cl<sub>6</sub>; and 9 miscellaneous products isolated and only partially characterized. <sup>b</sup> Measured in inches away from the end of the pyrolysis zone. <sup>c</sup> Estimation based on calculated conversion of *p*-xylene to *p*-methylbenzyl radicals as a function of pyrolysis conditions. <sup>d</sup> 0.5 g., m.p. 86–88°, b.p. = 145° at 3 mm., % C = 23.9, % Cl = 75.9; % H = 0.46; Infrared spectrum indicated that product might be a highly conjugated or aromatic compound. <sup>e</sup> 0.6 g., m.p. 111–113°, % C = 51.5; % H = 3.7; % Cl = 44.6; mol. wt. = 634. Infrared spectrum indicates the presence of *p*-xylene and CCl<sub>3</sub> groups. <sup>f</sup> Weight of products obtained far exceeded that anticipated on the basis of earlier work relating conversion as a function of temperature and residence time (see *b* above). Indicates considerable interaction in the pyrolysis zone.

liquor by distillation at atmospheric pressure. The residue (20 g.), after separation of *p*-xylene (b.p. 138°), was a mixture of the usual low molecular weight products of *p*-xylene pyrolysis.<sup>9</sup> Elementary analysis indicated that this residue contained 0.3% chlorine.

***β,β,β',β'*-Tetrachloro-*p*-divinylbenzene.**—*α,α'*-Bistrichloromethyl-*p*-xylene (0.716 g.; 0.0021 mole) was dissolved in methanol (25 cc.). Sodium methoxide (1.5 g.) was added and the mixture was warmed on a steam bath for 0.5 hr. The reaction mixture was diluted with cold water (100 cc.) and the insoluble product was removed by filtration. The amount of chloride ion present in the aqueous mother liquor was determined by gravimetric analysis. The results showed that 0.0039 equivalent of chlorine (0.139 g.) was produced. Thus, about two moles of hydrogen chloride were eliminated per mole of starting material.

The product was recrystallized from a methanol water solution to yield the compound in the form of pearl-like platelets (m.p. 74–75°). The infrared spectrum (strong bands at 11.02, 11.44, 12.15, and 12.68 μ) is consistent with the anticipated

structure of *β,β,β',β'*-tetrachloro-*p*-divinylbenzene. The elemental analysis is consistent with the empirical formula for this compound.

*Anal.* Calcd. for C<sub>10</sub>H<sub>6</sub>Cl<sub>4</sub>: C, 44.84; H, 2.42; Cl, 52.96. Found: C, 45.2; H, 2.02; Cl, 53.0.

Several years after completion of this work, the assigned structure of this compound was also verified in the laboratories of the Minnesota Mining and Manufacturing Company by n.m.r. analysis ( $\tau$  values: 2.46 for aromatic C–H and 3.18 for vinyl C–H<sup>8</sup>).

A sample of *β,β,β',β'*-tetrachloro-*p*-divinylbenzene (1.5 g.) was oxidized at reflux temperature in 100 cc. of acetone saturated with potassium permanganate. The solvent was removed by evaporation. The manganese dioxide was dissolved in aqueous hydrochloric acid and the residue was leached with hot acetone. The acid residue (0.25 g.) was fused with phosphorus pentachloride (1 g.) and the melt was poured into methanol (5 cc.). The ester was precipitated by addition to excess water and then recrystallized from a water-methanol solution to yield dimethyl terephthalate in the form of long white needles (m.p. 138.5–139.0°); no depression with an authentic sample.

(9) L. A. Errede and J. P. Cassidy, *J. Am. Chem. Soc.*, **82**, 3653 (1960).

## Oxidation of Phenols with Cupric Salts

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Cupric salts of carboxylic acids oxidize phenols to produce products coupled at vacant *ortho* and *para* positions in a manner characteristic of single electron oxidizing agents. Disubstituted phenols (*ortho*, *para*) eliminate the possibility of direct polymer formation and are especially useful for the preparation of dimers.

The susceptibility of phenols to oxidation is well known. This characteristic has been a major obstacle in processes for the preparation of phenol itself by the direct oxidation of benzene with air. On the other hand, a number of more highly substituted phenols are of industrial importance as antioxidants because of their sensitivity to oxidizing agents and ability to terminate chain reactions. A considerable number of papers have appeared dealing with details of the mechanism of this reaction.<sup>1</sup>

A large number of oxidizing agents have been used with various phenols.<sup>1b</sup> The first step appears to involve the extraction of the phenolic hydrogen atom. The resulting phenoxy radical undergoes a complex series of reactions, the nature of which depends on the phenol itself, the oxidizing agent, and various conditions of reaction. Usually a mixture of products are formed with prominent yields of intractable resins.

(1) For leading references see (a) V. K. Ingold, *Chem. Rev.*, **61**, 563 (1961); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).