THE CHEMISTRY OF XYLYLENES. XVI. THE TRAPPING OF RADICALS IN GAS STREAMS BY MUTUAL QUENCH TECHNIQUES

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Fast flow co-pyrolysis of p-xylene and CCl$_4$ at low pressure affords a mixture having p-methylbenzyl chloride and β,β-dichloro-p-methylstyrene as its two major components. On the other hand, pyrolysis of p-xylene and carbon tetrachloride in separate coaxial tubes to give two pyrolyzate streams that blend at a point beyond the furnace affords a mixture having p-methylbenzyl chloride and p-xylylene dichloride as its two major components. It was shown that the products are formed via coupling of p-methylbenzyl radicals with chlorine and with trichloromethyl radicals and via reaction of p-xylylene with chlorine. The reactions of chlorocarbon radicals with p-xylene and hydrocarbon radicals with carbon tetrachloride in the quenched stream are relatively unimportant under the reaction conditions used in these experiments.

Introduction

Szwarc[2,3] has shown that p-methyl benzyl radicals (II) and p-xylylene (III) are formed sequentially when p-xylene is subjected to fast flow pyrolysis at low pressure.
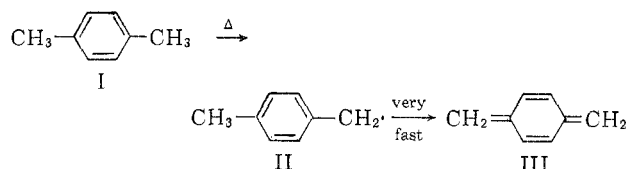
Attempts[4-6] have been made to convert these reactive intermediates to mono- and difunctional derivatives by pyrolysis of p-xylene with other thermolabile compounds or by mixing a second gas stream with the fast flowing p-xylene pyrolyzate as it leaves the furnace. It was reported[5] that "of all the materials used, only iodine reacted to yield a definite identified product, viz., p-xylylene diiodide, in significant quantities." p-Methylbenzyl halides, however, were isolated in small amounts when bromine and chlorine were used in lieu of iodine.[5] In other cases, little or no polymer was produced, indicating that some form of interaction might have occurred with the p-methylbenzyl and p-xylylene intermediates, but no isolable species were reported.[5]

The co-pyrolysis of carbon tetrachloride with p-xylene was studied in our Laboratories and the present paper reports some of the positive results obtained in that investigation.

Results and Discussion

It was reported[7] that fast flow pyrolysis of p-xylene at 1065°, 4 × 10^{-3} sec. residence time, and 4 mm. pressure converts 14% of the feed stock per pass to p-methylbenzyl radicals (II), about 80% of which are isolated as p-xylylene (III). When carbon tetrachloride was subjected to fast flow pyrolysis at about these same conditions, Cl$_2$, C$_2$Cl$_6$, C$_2$Cl$_4$, and C$_6$Cl$_6$ were isolated as the major products as shown in Table I.

These data are consistent with a stepwise formation of C$_6$Cl$_6$ from CCl$_4$ via reactions 1 to 4. A similar reaction scheme was postulated[8,9] to account for the formation of C$_6$F$_6$ via pyrolysis of CFBr$_3$.

$$CCl_4 \rightleftharpoons CCl_3\cdot + Cl\cdot \qquad (1)$$

$$2CCl_3\cdot \rightleftharpoons CCl_3CCl_3 \qquad (2)$$

$$CCl_3CCl_3 \rightleftharpoons CCl_2{=}CCl_2 + Cl_2 \qquad (3)$$

$$3CCl_2{=}CCl_2 \longrightarrow C_6Cl_6 + 3Cl_2 \qquad (4)$$

It has been shown by Dainton and Ivin[10] that pyrolysis of hexachloroethane leads to the formation of tetrachloroethylene in good yield; and it was shown in our Laboratory that appreciable amounts of hexachlorobenzene are produced when tetrachloroethylene is subjected to the relatively mild conditions of fast flow pyrolysis (Table I). Moreover, carbon tetra-

TABLE I
PYROLYSIS OF CHLOROCARBONS

Feed stock	T, °C.	t (sec.)	P (mm.)	CCl$_4$	CCl$_3$-CCl$_3$	CCl$_2$=CCl$_2$	C$_6$Cl$_6$
CCl$_4$	1005	0.003	2	73	7	20	0
CCl$_4$	1000	.005	4	48	6	45	0.6
CCl$_4$	1000	.015	10	..	..	..	14
CCl$_4$	1000	.03	30	..	..	..	49
CCl$_2$=CCl$_2$	1005	.01	3	..	..	55	39

(% Carbon atoms of feed stock isolated as)

chloride was converted to hexachlorobenzene in high conversion by increasing the severity of the pyrolysis conditions. These experiments demonstrate that thermal degradation of carbon tetrachloride is more facile than that of p-xylene under the same pyrolysis conditions. This is consistent with the relative bond strengths of the weakest links in the respective molecular structures [D(CCl$_3$—Cl) = 69 kcal.; D(CH$_3$-C$_6$H$_4$CH$_2$—H) = 77 kcal.].[11] Hence we were reasonably sure that co-pyrolysis of p-xylene with CCl$_4$ would afford a more than adequate amount of chlorine and chlorocarbon radical fragments (via reaction 1) to accommodate the hydrocarbon radicals produced from p-xylene.

Accordingly, an approximately equimolar gas mixture of p-xylene and carbon tetrachloride was pyrolyzed

(1) This work was carried out in the laboratories of the M. W. Kellogg Co. The data were acquired by Minnesota Mining and Mfg. Co. with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Co. in March, 1957.
(2) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).
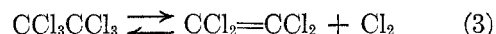(3) M. Levy, M. Szwarc, and J. Thrussell, *ibid.*, **22**, 1904 (1954).
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(8) Y. Desirant, *Bull. Classe Sci., Acad. Roy. Belg.*, [5] **41**, 759 (1955).
(9) M. Hellman, E. Peters, W. J. Plummer, and L. A. Wall, *J. Am. Chem. Soc.*, **79**, 5654 (1957).
(10) F. S. Dainton and K. J. Ivin, *Trans. Faraday Soc.*, **46**, 295 (1950).
(11) L. A. Errede, *J. Phys. Chem.*, **64**, 1031 (1960).

TABLE II

THE PYROLYSIS OF p-XYLENE AND CARBON TETRACHLORIDE AT 1000° AND 5 MM. FOR 0.005 SEC.[a]

Pyrolysis stream	Non-pyrolyzed quench stream	Blend point[b]	p-Xylene to CCl₄ ratio[c]	% Conversion to interaction products[d]			
				p-CH₃C₆H₄CH=CCl₂	p-CH₃C₆H₄CH₂Cl	p-ClCH₂C₆H₄CH₂Cl	Others
p-Xylene and CCl₄	None	−20	1/1.1	3.7	4.7	0	3.2[e]
p-Xylene and CCl₄	None	4.5	1/1.2	0	5.4	1.5	3.9[f]
p-Xylene	CCl₄	4.5	1/0.65	0	0	0	[g]
CCl₄	p-Xylene	4.5	1/0.32	0	0.03	0	0.04[h]

[a] These conditions are known to cause 11% conversion of p-xylene to p-methylbenzyl radicals (L. A. Errede and F. DeMaria, *J. Phys. Chem.*, **66**, 2664 (1962)) which are isolated subsequently as various products.[7] [b] Blend point in inches away from the end of the pyrolysis zone. [c] Molar ratio. [d] Based on moles of p-xylene metered to the system. [e] Calculated as p-xylyl equivalents with 0.7 Cl atom per unit. Average molecular weight was 631; % Cl = 17.2. Infrared spectrum indicated this product to be a mixture of alkylated aromatics. [f] Calculated as p-xylyl equivalents as $(C_8H_6Cl_{0.7})_n$ having an average molecular weight of ca. 2000. [g] Five % isolated as poly-(p-xylylene) and 5% as the usual low molecular weight products of p-xylene pyrolysis.[7] [h] 2-Chloro-p-xylene.

at 1005°, 0.003 sec. residence time, and 5 mm. pressure. Poly-(p-xylylene) was not obtained in the condensate nor was it possible to isolate any difunctional derivative of p-xylylene, such as p-xylylene dichloride, despite all efforts to do so. On the other hand, p-methylbenzyl chloride (IV) and β,β-dichloro-p-methylstyrene (VI) were isolated in about equal amounts as the major products (see Table II). p-Methylbenzyl chloride (IV) would form via reaction of p-methylbenzyl radical with chlorine or chlorine atoms; β,β-dichloro-p-methylstyrene (VI) could form via coupling of p-methylbenzyl radical with trichloromethyl radical to afford the corresponding β,β,β-trichloroethyltoluene (V) which then could split out HCl. The β,β-dichloro-p-methylstyrene was identified
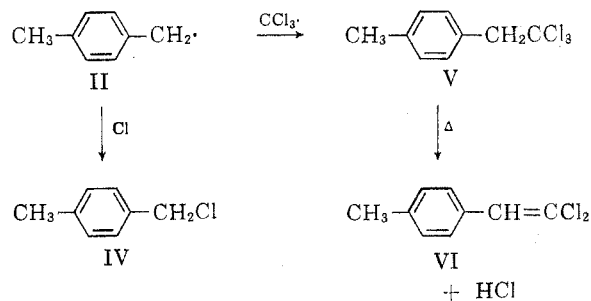


by elementary analysis, n.m.r., infrared spectral analysis, and by oxidation to p-toluic acid as described in the Experimental section.

Apparently, coupling with chlorine and trichloromethyl radicals occurred faster than dehydrogenation of p-methylbenzyl radicals to afford p-xylylene, since no difunctional derivative of the latter intermediate was isolated. It was speculated that difunctional derivatives might be obtained if the compounds were pyrolyzed in separate gas streams and then made to blend after a sufficient time was allowed for p-xylylene molecules to form in the hydrocarbon stream.

Accordingly, p-xylene and carbon tetrachloride were pyrolyzed in concentric tubes at 1000° and the resultant pyrolyzates were mixed downstream. The more thermolabile chlorocarbon was metered through the inner tube and the hydrocarbon through the outer tube. Confluence was allowed to occur at a point 4.5 in. beyond the pyrolysis zone and the resultant gas mixture was condensed in hexane kept at −78°. Again no polymer was formed, but this time the major products of interaction were p-methylbenzyl chloride (IV) and p-xylylene dichloride (VIII). No β,β,β-trichloroethyltoluene nor bis-trichloromethyl-p-xylylene was isolated, indicating that the trichloromethyl

radicals had been consumed in the chlorocarbon stream via reactions 1 and 2 before mixing had occurred. The isolation of p-xylylene dichloride, however, indicated that p-xylylene might have formed in the hydrocarbon stream after it left the pyrolysis zone and then reacted with Cl₂ at the blend point.

$$CH_2=\!\!\!\!\bigcirc\!\!\!\!=CH_2 \quad \longrightarrow \quad ClCH_2-\!\!\!\!\bigcirc\!\!\!\!-CH_2Cl \qquad (5)$$
$$+ \ Cl_2$$
VII   VIII
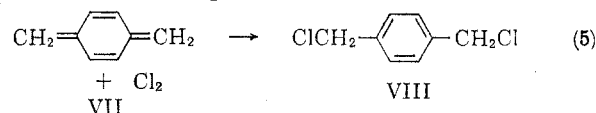
It was probable that some of the products of interaction might have formed by attack of hydrocarbon radicals on carbon tetrachloride or by attack of Cl₂ and CCl₃· on p-xylene. To check this possibility, a stream of p-xylene was pyrolyzed in the usual way and then mixed with a stream of non-pyrolyzed carbon tetrachloride at the same blend point used in the previous experiments. The confluent stream was collected at −78° in a cold solvent. The resultant solution was warmed to room temperature and poly-(p-xylylene) was obtained in good yield as described previously.[12,13] Neither the polymer nor the low molecular weight products of p-xylene pyrolysis[7] contained chlorine, indicating that little or no interaction of the pyrolyzed hydrocarbon stream occurred with non-pyrolyzed CCl₄.

In the next experiment, a stream of carbon tetrachloride was pyrolyzed and then mixed with a large excess of non-pyrolyzed p-xylene at the same blend point. A considerable amount of the usual products of CCl₄ pyrolysis was isolated but only minute amounts of p-methylbenzyl chloride and 2-chloro-p-xylene were obtained, indicating that very little interaction (relative to co-pyrolysis) of the two gas streams had occurred. Actually, the traces of p-methylbenzyl chloride and 2-chloro-p-xylene isolated in this experiment may have formed in solution when the condensate rich in p-xylene and chlorine was warmed from −78° to room temperature.

These results (summarized in Table II) indicate that the products of interaction were produced almost entirely by coupling of the radical fragments. It appeared probable that the pyrolyzed hydrocarbon and chlorocarbon streams were serving one another as mutual radical quenches. These results suggested that this technique might be used to help elucidate the mechanism of p-xylylene formation from p-methylbenzyl radicals as described in another publication.[14]

(12) L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, **79**, 4952 (1957).
(13) L. A. Errede, R. S. Gregorian, and J. M. Hoyt, *ibid.*, **82**, 5218 (1960).
(14) L. A. Errede and J. P. Cassidy, *J. Phys. Chem.*, **67**, 73 (1963).

Experimental

Pyrolysis of CCl₄.—Pyrolysis of carbon tetrachloride was carried out using the apparatus shown in Fig. 1 of ref. 12 according to the procedure described previously for the pyrolysis of p-xylene.[7,12,13] The system was evacuated to the desired pressure and the furnace was adjusted to afford the desired maximum temperature and temperature profile. About 10 moles of carbon tetrachloride was metered at the rate of ca. 0.04 mole/min. to the evacuated system through a calibrated capillary. Pyrolysis occurred in a 1-in. i.d. quartz tube. The pyrolysis zone (i.e., the distance along the tube through which the gas was no less than 50° below its maximum temperature) was about 5 in. long. The pyrolyzate was collected in heptane (3 l.) kept at −78° so that the chlorine condensed therein would be converted to chloroheptanes. A smaller liquid nitrogen trap was used in series with the large Dry Ice trap. At the end of the pyrolysis, the cold traps were warmed to room temperature. The resultant solutions were combined. The solvent and volatile product of pyrolysis were separated by distillation at atmospheric pressure to afford four fractions: (1) b.p. 77–117°; (2) b.p. 117–127°; (3) b.p. 140–148°; and (4) residue. Fractions 1 to 3 were analyzed by means of a mass spectrometer. Fraction 1 was a mixture of n-heptane, tetrachloroethane, and carbon tetrachloride. Fraction 2 was essentially all tetrachloroethane, and fraction 3 was a mixture of chloroheptanes. The residue was a mixture of hexachloroethane and hexachlorobenzene. The former was separated from the latter by leaching the residue with methanol. Hexachloroethane crystallized in the form of white platelets (m.p. 181–183°) from the hot concentrated alcohol extract.

Anal. Calcd. for C₂Cl₆: C, 10.15; Cl, 89.84; mol. wt. 236.8. Found: C, 10.14; Cl, 90.1; mol. wt. 221.

The methanol insoluble residue was recrystallized from hot CCl₄ and hexachlorobenzene was obtained in the form of fine white needles (m.p. 224–226°).

Anal. Calcd. for C₆Cl₆: C, 25.29; Cl, 74.69; mol. wt. 284.8. Found: C, 25.19; Cl, 74.36; mol. wt. 269.

Pyrolyses were repeated at 2, 4, 10, and 30 mm. pressures and the data are summarized in Table I. Although the amount of chloroheptanes obtained in these experiments indicated that most of the chlorine produced pyrolytically was converted to chloroheptanes and HCl in the condenser, the results were by no means quantitative. Hence, one pyrolysis was repeated at 1000°, 4 mm. pressure, and 0.005 sec. residence time and the pyrolyzate of CCl₄ (10 moles) was collected in a one to one mixture of CCl₄ and HCCl₃ kept at −78°. The cold traps (−78° and −190°) were warmed to room temperature and the chlorine contained therein was passed through an aqueous solution of KI. A slow stream of N₂ was used to remove the last traces of Cl₂ from the cold traps and this gas stream was led into a fresh KI solution. A total of 4.9 moles of I₂ was liberated as determined by titration with sodium thiosulfate. This amount represents about 25% of the chlorine metered to the system as CCl₄, which agrees well with the amount of Cl₂ anticipated (24%) from products isolated in previous similar runs.

Pyrolysis of Tetrachloroethylene.—Tetrachloroethylene (1.54 moles) was metered at the rate of 0.009 mole/min. to the pyrolysis system evacuated to 3.3 mm. The gas stream was pyrolyzed at 1005° for 0.014 sec. residence time in the pyrolysis zone of the 1-in. i.d. quartz tube and the pyrolyzate was condensed in a Dry Ice–acetone trap. The condensate was separated by distillation at atmospheric pressure and 0.86 mole of C₂Cl₄ was recovered, leaving 0.12 mole of non-volatile impure hexachlorobenzene (m.p. 205–215°) which after one recrystallization from hexane was obtained as fine white needles (m.p. 222–224°).

Co-pyrolysis of p-Xylene and Carbon Tetrachloride.—p-Xylene (12.1 moles) and carbon tetrachloride (13.9 moles) were metered to the pyrolysis system through separate calibrated capillaries at the rate of 0.035 and 0.040 mole/min., respectively. The two gas streams were mixed within the 1-in. i.d. quartz tube where co-pyrolysis occurred at 1005° and 4.7 mm. for 0.003 sec. residence time. The pyrolyzate was collected in 4.0 l. of hexane kept at −78°. The resultant solution was warmed to room temperature. No polymer formed, indicating the absence of any residual p-xylylene in the gas stream when it reached the condenser. The solvent of the clear solution was removed by rapid evaporation at 60 mm. and 100° in a solvent evaporator. The liquid was metered through the top of the evacuated apparatus. The volatile components were vaporized as the liquor

cascaded down the steam heated column, and were removed through an overhead side arm. The non-volatile components were collected in a receiving flask at the bottom of the reactor. A previous trial run using a synthetic mixture showed that virtually all the hexane and xylene are removed in this way with only a negligible loss (<1%) of p-methylbenzyl chloride, β,β-dichloro-p-methylstyrene, and p-xylylene chloride. The last traces of p-xylene were removed by evaporation under a stream of N₂. The residue (291 g.) was a dark oil that contained 28.6% chlorine. This was dissolved in 1 l. of hexane and the resulting solution was chilled to −78° in an attempt to cause precipitation of any p-xylylene dichloride that might have been present. No precipitate was obtained, indicating that very little if any of this compound was present since the solubility of p-xylylene dichloride in 1 l. of similar solutions at −78° is less than 1 g. The hexane was removed by evaporation and the residue was separated by distillation at 1.0 mm. pressure. Four major fractions were obtained: (1) 80 g., amber oil, b.p. 40–46°; m.p. −2° to 0°; (2) 82 g., b.p. 65–79°; m.p. 28–30°; (3) 39 g., amber oil, b.p. 100–120°; and (4) 50 g., residue which did not distil below 200°.

Fraction 1 gave a strong positive test for active halogen using alcoholic AgNO₃. The infrared spectrum of this fraction was about the same as that of p-methylbenzyl chloride (IV) and this assignment was supported by elementary analysis.

Anal. Calcd. for C₈H₉Cl: C, 68.38; H, 6.40; Cl, 25.26; mol. wt. 140.5. Found: C, 68.7; H, 5.82; Cl, 25.3; mol. wt. 141.

A sample of the chloride was converted to the corresponding nitrile by treatment with NaCN in methanol–water solution. Subsequent hydrolysis and acidification yielded p-tolylacetic acid which, after one recrystallization from hexane was obtained in the form of white flat needles (m.p. 86–88°; no depression when mixed with authentic sample).

Fraction 2 was recrystallized from MeOH at −78° and β,β-dichloro-p-methylstyrene (VI) was obtained in the form of tiny white platelets (m.p. 32.0–32.5°) having a characteristic licorice-like odor. The assigned structure was verified by its infrared spectra in Nujol (strong bands at 6.23, 7.90, 11.07, 11.60, 12.00, 12.47, 13.25, 14.13, and 14.85 μ), n.m.r. spectrum [τ values 7.68 for CH₃, 3.25 for olefinic CH, 2.63 and 2.90 (A-B type peak) for aromatic CH], and by elemental analysis.

Anal. Calcd. for C₉H₈Cl₂: C, 57.77; H, 4.33; Cl, 37.90; mol. wt. 187.1. Found: C, 57.5; H, 4.01; Cl, 38.0; mol. wt. 184.

A sample of the compound was oxidized by KMnO₄ in acetone to give p-toluic acid (m.p. 176–177°; no depression when mixed with authentic sample).

Fraction 3 was dissolved in methanol and chilled to −78°, causing 13 g. of 1,2-di-p-tolylethane to crystallize from solution in the form of white platelets (m.p. 74–76°, no depression when mixed with authentic sample). The infrared spectrum of this product was identical with that of an authentic sample.[7] The methanol mother liquor was evaporated to constant weight (26 g.) and the residue was redistilled under vacuum. The infrared spectrum of the distillate indicated that this was a mixture composed mostly of alkylated diphenylmethanes[7] with a small amount of 1,4-di-p-tolylethane. A routine qualitative test for chlorine (sodium fusion followed by AgNO₃) indicated the presence of chlorine in only trace amounts.

Fraction 4 was not separated further. The infrared spectra of this fraction indicated that it was a complex mixture of alkylated aromatics. The average molecular weight was 631, as determined by freezing point depression of cyclohexane, and it contained 17.2% chlorine, which corresponds roughly to about 0.6 chlorine atom per xylyl unit.

In summary, co-pyrolysis of 12.1 moles of p-xylene and 13.9 moles of CCl₄ gave 0.57 mole of p-methylbenzyl chloride, 0.44 mole of β,β-dichloro-p-methylstyrene, 0.35 mole of p-methylbenzyl equivalents isolated as 1,4-di-p-tolylethane or diphenylmethanes, and 0.40 mole of p-methylbenzyl equivalents isolated as ill-defined partially chlorinated non-distillable residue.

Pyrolysis of p-Xylene and Carbon Tetrachloride in Separate Coaxial Streams.—The pyrolysis system shown in Fig. 1 of ref. 12 was modified such that the internal thermowell (no. 17) was replaced by an open quartz tube (3-mm. i.d., 7-mm. o.d.) through which the chlorocarbon stream was metered for pyrolysis. The temperature was measured by an external thermocouple that traveled parallel to the quartz pyrolysis tube between the tube and the furnace. The open end of the inner tube extended

1.5 in. beyond the furnace to a point where the temperature was about 600°, at a point 4.5 in. beyond the pyrolysis zone where the temperature was above 990 to 1040° at its center. The system was evacuated to 4.5 mm. and p-xylene (7.6 moles) was metered through the outer concentric tube at the rate of 0.032 mole/min., while carbon tetrachloride (8.8 moles) was metered through the inner concentric tube at the rate 0.037 mole/min. Pyrolysis occurred independently in the two concentric tubes for 5×10^{-3} and 4×10^{-4} sec. residence time, respectively, and confluence occurred at the blend point 1 in. beyond the furnace, where the temperature was about 600°. The resultant gas mixture was collected in 4 l. of hexane kept at −78° (no. 7). The resultant solution was warmed to room temperature and the excess solvent was removed by rapid evaporation at 60 mm. pressure and 100° as described previously, and the non-volatile products of interaction were collected as residue. The pyrolysis experiment was repeated three more times so that totals of 30.5 moles of p-xylene and 35.2 moles of CCl_4 were passed through the outer and inner concentric tubes, respectively, to afford a total of 684 g. of non-volatile mixture of reaction products.

The residues were combined and then dissolved in 3.4 l. of hexane. The resultant solution was chilled to −78° and p-xylylene dichloride (77 g.) precipitated in the form of grayish crystals (m.p. 90–95°). A sample was recrystallized from methanol to afford this compound as white crystals that melted at 95–97°. The compound was characterized further by reaction with NaCN in aqueous ethanol to give p-xylylene dicyanide (m.p. 95.5–96.5°). The dicyanide then was hydrolyzed in aqueous NaOH to the salt of p-phenylenediacetic acid. Acidification with mineral acid afforded the free acid (m.p. 243–245°). The melting points and infrared spectra of the p-xylylene dichloride and its subsequent derivatives were identical with those of authentic samples.

The hexane mother liquor from which p-xylylene dichloride was removed by filtration was evaporated to dryness under a stream of nitrogen. The residue was separated by distillation at 1.5 mm. and the following fractions were isolated: (1) 231 g. of p-methylbenzyl chloride, b.p. 54–60°, m.p. −2 to 0°; (2) 5 g. of amber oil, b.p. 85–100°. The sample was dissolved in hot methanol and then chilled to room temperature to afford 1.1 g. of p-xylylene dichloride, m.p. 97–98°. The solute in the mother liquor was recovered by evaporation to dryness. The infrared spectrum of this residue indicated that it was mostly a mixture of diarylmethanes and 1,2-di-p-tolylethane. (3) An amber oil (154 g.), b.p. 100–126° at 1–2 mm. This oil was dissolved in methanol and chilled to −78° to afford 20 g. of di-p-tolylethane (m.p. 74–76°). The solute was recovered from the mother liquor by evaporation to dryness. The amber residue was the usual mixture of diarylmethanes and 1,2-di-p-tolylethane.[7] (4) A non-distillable residue (150 g.). The elemental analysis (19.1% Cl; 4.70% H; and 74.8% C) of this fraction corresponds to an average empirical formula of $(C_8H_6Cl_{0.7})_n$. Its average molecular weight was ca. 2000. An attempt was made to separate the dark oily residue by liquid chromatography using a 6-ft. column filled with 4 lb. of Al_2O_3. The column was developed with hexane as described previously.[7] Ill-defined tars were obtained in each eluted fraction and only trace amounts of cyclic-tri-p-xylylene and 1,4-bis-(2-p-tolylethyl)-benzene were isolated.

Thus the pyrolysis of 30.5 moles of p-xylene and 35.2 moles of CCl_4 in two concentric streams that blended at a point 4.5 in. beyond the pyrolysis zone produced 1.65 moles of p-methylbenzyl chloride, 0.45 mole of p-xylylene dichloride, 1.46 moles of p-methylbenzyl equivalents isolated as diarylmethanes and 1,2-di-p-tolylethane, and 1.18 moles of ill-defined non-volatile residue whose average empirical formula was $(C_8H_6Cl_{0.7})_n$.

Pyrolyzed CCl_4 Quenched with Non-pyrolyzed p-Xylene.—The pyrolysis system shown in Fig. 1 of ref. 12 was modified such that manometer 8 and stopcock 9 were replaced by a 7 mm. quartz tube that extended to within 1 in. of the furnace. Provisions were made so that p-xylene could be metered into the system through this tube. The system was evacuated to 10 mm. and 1.8 moles of CCl_4 was metered to the system through vaporizer no. 15, at the rate of 0.026 mole/min., while 5.6 moles of p-xylene was being metered to the system at the other end at the rate of 0.08 mole/min. Pyrolysis of CCl_4 occurred at 1000° for 0.015 sec. and the chlorocarbon pyrolyzate was quenched with non-pyrolyzed p-xylene at a point 4.5 in. away from the pyrolysis zone. The gas mixture was collected in cold (−78°) heptane (4 l.). The resulting solution was warmed to room temperature and the excess solvent was separated by rapid evaporation at 60 mm. and 100° as described previously to afford 32 g. of non-volatile residue. This residue was dissolved in hot methanol and hexachlorobenzene (19 g.) crystallized in the form of white needles (m.p. 205–210°) when the solution was cooled to room temperature. The methanol mother liquor was separated by distillation at 1.5 mm. to give 5 g. of distillate (b.p. 50–70°) which was a mixture of p-methylbenzyl chloride (ca. 2 g.) and 2-chloro-p-xylene (ca. 3 g.) as indicated by infrared analysis and mass spectrometric analysis. The non-volatile residue (5 g., b.p. > 100° at 1.5 mm.) was essentially hexachlorobenzene as indicated by its infrared spectrum.

Pyrolyzed p-Xylene Quenched with Non-pyrolyzed CCl_4.—The pyrolysis system shown in Fig. 1 of ref. 12 was modified as described previously for the pyrolysis of CCl_4 and subsequent quench with non-pyrolyzed p-xylene. The system was evacuated to 4.5 mm. p-Xylene (6.4 moles) was metered at the rate 0.035 mole/min. into the system and pyrolyzed at 1100° for 6×10^{-3} sec. The hydrocarbon pyrolyzate was quenched at a point 4.5 in. away from the pyrolysis zone with non-pyrolyzed CCl_4 entering (at 0.023 mole/min.) through the inlet at the other end of the pyrolysis system. The gas mixture was collected in 3.5 l. of hexane kept at −78°. The resulting clear solution was warmed to room temperature and poly-(p-xylene) precipitated throughout the flask. This was removed by filtration to give 33 g. of dry polymer that contained no chlorine. The solvent of the mother liquor was separated by rapid evaporation at 60 mm. and 100° as described previously. The non-volatile residue (29 g.) also contained no chlorine and was a mixture of the usual products of p-xylene pyrolysis[7] as indicated by infrared analysis. The distillate was a mixture of hexane, carbon tetrachloride, p-xylene, and some toluene, as indicated by infrared analysis.