

Hexahydro-spiro-di-*o*-xylylene (VII).—Spiro-di-*o*-xylylene (3 g.), Raney nickel (0.5 g.) and heptane (20 cc.) were sealed in a hydrogenation bomb that was pressured to 67 atm. Reaction was allowed to occur at room temperature for 3 days and then at 50° for an additional 15 hours. During this time about three equivalents of hydrogen was consumed as indicated by the decrease in pressure. The catalyst was separated by filtration and the filtrate was evaporated to dryness. The residual oil (3 g.) was purified by distillation at 0.6–0.8 mm. pressure (b.p. 115–120°, n_D^{25} 1.5558).

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 90.2; H, 9.8.

Comparison of its infrared spectrum (Fig. 1B) with that of spiro-di-*o*-xylylene indicated that the strong band at 11.2 μ attributed to *exo*-methylene double bond in Fig. 1A was gone and a new strong band at 7.2 μ associated with a methyl group was present instead. Its nuclear magnetic resonance data (Fig. 3B) confirms the structure for spiro-(5,5)-2,3-benz-6-methylundecane or (hexahydro-spiro-di-*o*-xylylene).

2,2'-Bis-(iodomethyl)-bibenzyl (Di-*o*-xylylene Di-iodide) (VIII).—Spiro-di-*o*-xylylene (1 g.) dissolved in CCl_4 (20 cc.) was added dropwise at room temperature to a solution of I_2 (1.3 g.) in CCl_4 (200 cc.). The color of the solution changed from that characteristic of iodine in CCl_4 to a brick red, which in turn slowly disappeared, forming a colorless solution. The solution was concentrated to 25 cc. by evaporation at room temperature under a stream of nitrogen. A white precipitate formed during the evaporation and this was removed by filtration. The impure product (2.2 g.) was recrystallized from CCl_4 and 2,2'-bis-(iodomethyl)-bibenzyl was obtained in the form of coarse white needles (m.p. 166–168°). The assigned structure was verified by the compound's nuclear magnetic resonance spectrum (τ values: 2.85 for aromatic C-H, 5.61 for H of ICH_2 group, 6.95 for H of ethylene group).

Anal. Calcd. for $C_{16}H_{16}I_2$: C, 41.58; H, 3.46; I, 54.93. Found: C, 41.6; H, 3.7; I, 54.9.

A sample of the 2,2'-bis-(iodomethyl)-bibenzyl (5 g.) dissolved in methanol (75 cc.) and zinc dust (5 g.) was caused

to react at reflux temperature for 1 hour. The excess zinc was removed by filtration. The mother liquor was concentrated to about 15 cc. whereupon the hydrocarbon crystallized from the cooled solution. The precipitate was recrystallized from a minimum amount of fresh methanol to give 1,2-di-*o*-tolylethane in the form of white crystals (m.p. 61–63°, mixed melting point with authentic sample 62–63°). The infrared spectra of the authentic sample and the derivative in question were identical.

2,2'-Bis-(bromomethyl)-bibenzyl (Di-*o*-xylylene Dibromide) (IX).—A solution of Br_2 (1 cc.) in CCl_4 (20 cc.) was added dropwise at -5° to spiro-di-*o*-xylylene (4 g.) dissolved in CCl_4 (50 cc.) until a slight excess of Br_2 remained, as indicated by the persistence of its characteristic color. The excess bromine was removed by bubbling a stream of nitrogen through the solution and then evaporating the solution to dryness. The residue was recrystallized from heptane at -15° and then from methanol. In this way, 2,2'-bis-(bromomethyl)-bibenzyl (IX) (2.6 g.) was obtained in the form of white needles (m.p. 139–140°, lit.²⁹ m.p. 137–138°). A sample (0.5 g.) was converted to the corresponding di-iodo compound by reaction at reflux temperature with KI in acetone. The product was recrystallized from CCl_4 to afford 2,2'-bis-(iodomethyl)-bibenzyl (VIII) in the form of white crystals (m.p. 163–165°). No depression in melting point was noted when these crystals were mixed with those of the diiodide sample prepared by addition of I_2 to spiro-di-*o*-xylylene.

Acknowledgments.—The author is indebted to Dr. J. J. McBrady for interpretation of the infrared spectra, Drs. F. A. Bovey and G. V. D. Tiers for interpretation of the nuclear magnetic resonance data, and the Analytical Section of the Minnesota Mining and Manufacturing Co., Central Research Laboratories, for elemental analyses and ultraviolet absorption data.

(29) E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 4281 (1953).

[CONTRIBUTION NO. 177 FROM THE CENTRAL RESEARCH LABORATORIES OF THE MINNESOTA MINING AND MANUFACTURING CO., ST. PAUL 15, MINN.]

The Chemistry of Xylylenes. IX. The Copolymerization of *p*-Xylylene with Phosphorus Trichloride and Related Compounds^{2a}

BY L. A. ERREDE AND W. A. PEARSON^{2b}

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Phosphorus trichloride and *p*-xylylene copolymerize readily to produce high molecular weight poly-(*p*-xylylenephosphinic trichloride). The polymeric salt is converted easily to poly-(*p*-xylylenephosphinic chloride) which in turn can be hydrolyzed to the salt of the polymeric acid by treatment with aqueous base. Similarly, poly-*p*-xylylenephosphinic chloride can be converted to its corresponding ester or amide derivative by treatment with the appropriate reagent. Copolymers of *p*-xylylene are also produced with PBr_3 , PI_3 , $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$ but very little interaction occurs with $(C_6H_5)_3P$, $(CH_3)_3P$ and $(EtO)_3P$. Telomeric products are obtained with PCl_5 but not with $POCl_3$. The significance of these results with respect to the mechanism for addition of free radicals to trivalent phosphorus halides is discussed.

Introduction

It was reported in previous publications^{3–6} that *p*-xylylene (I) is an extremely reactive compound that behaves chemically as if it were a diradical.

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

(2) (a) Presented before the Polymer Division of The American Chemical Society at its 138th Meeting, September, 1960, held in New York. (b) Present address: St. Olaf College, Northfield, Minn.

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

(4) L. A. Errede and J. M. Hoyt, *ibid.*, **82**, 436 (1960).

(5) L. A. Errede and S. L. Hopwood, Jr., *ibid.*, **79**, 6507 (1957).

(6) L. A. Errede, R. S. Gregorian and J. M. Hoyt, *ibid.*, **82**, 5218 (1960).

Thus, reaction of *p*-xylylene at -78° with mono-radicals such as NO, NO_2 and DPPH or with molecules such as Cl_2 , Br_2 and $(SCN)_2$ affords the corresponding α, α' -disubstituted *p*-xylylene derivative,⁴ whereas reaction with diradicals such as O_2^5 or molecules such as SO_2^4 affords the corresponding one-to-one copolymers.

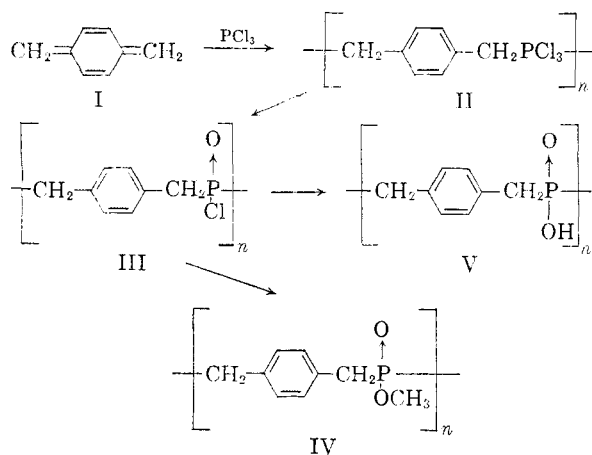
It was also reported^{7–10} that PCl_3 reacts readily with free radicals. For example, the addition of

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

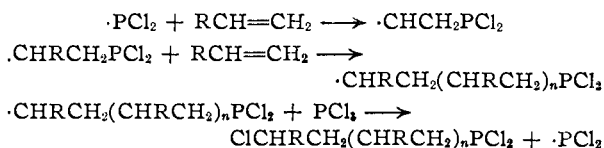
(8) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

(9) A. F. Childs and H. J. Coates, *Oil and Colour Chemists' Assoc.*, **42**, 612 (1959).

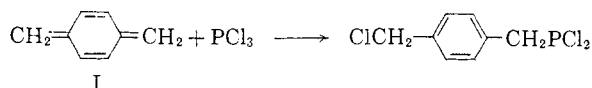
(10) P. C. Craft, *Quart. Revs.*, **12**, 341 (1958).



O₂ to PCl₃ or its solutions, gives POCl₃ in good yield.¹¹⁻¹³ If a hydrocarbon solvent is used, however, one also obtains an appreciable quantity of RP(O)Cl₂ owing to interaction of the free radical intermediates with the solvent. It was reported by Kharasch¹⁴ that chlorine abstraction occurs when olefins are caused to react with PCl₃ *via* free radical mechanism to afford telomers having -Cl and -PCl₂ end groups. It was postulated that this reaction involves a slightly modified Rice-Herzfeld¹⁵ chain mechanism. On the basis of these



observations it is reasonable to expect interaction of *p*-xylylene with PCl₃ to afford similar low molecular compounds. Actually copolymerization occurs



instead, and the one-to-one high molecular polymeric salt is obtained.

Results and Discussion

When a solution of *p*-xylylene and PCl₃ in hexane was warmed from -78° to room temperature, a finely divided precipitate was formed immediately. This material hydrolyzed readily with copious evolution of HCl. The chlorine to phosphorus ratio before drying was about 3 to 1 and its infrared spectrum was consistent with a linear structure of poly(*p*-xylylenephosphinic trichloride) (II). Two of the three chlorine atoms were removed easily when the hexene-saturated polymer was dried in air, yielding poly(*p*-xylylenephosphinic chloride) (III) as indicated by its infrared

(11) J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.*, **70**, 3880 (1948).

(12) L. Z. Soborovskii, Y. M. Zinovev and M. A. Englin, *Doklady Akad. Nauk, S.S.S.R.*, **67**, 293 (1949).

(13) A. F. Isbell and F. T. Wadsworth, *J. Am. Chem. Soc.*, **78**, 6042 (1956).

(14) M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **67**, 1864 (1945).

(15) F. O. Rice and K. F. Herzfeld, *ibid.*, **56**, 284 (1934).

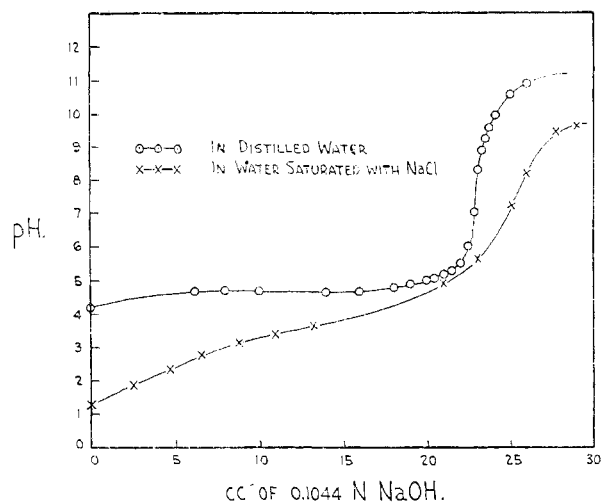


Fig. 2.—Titration curves for poly(*p*-xylylenephosphinic acid) (V).

spectrum. The elemental analysis indicated that the *p*-xylylene to POCl ratio was almost one to one.

The polymeric phosphinic chloride was converted to the corresponding polymeric ester IV by treatment with methanol. The product was only partly soluble in excess alcohol and the inherent viscosity of the methanol-soluble fraction was 0.288, indicating an appreciably high degree of polymerization. The insoluble polymer softened at about 150° and was pressed at this temperature into tough transparent films. No appreciable differences were noted in the infrared spectra, X-ray diffraction patterns, moldability and elemental analyses for the respective soluble and insoluble polymer fractions. Hence, it is believed that the insolubility of the latter was due to its higher degree of polymerization or cross linking rather than to a difference in chemical composition. Poly(*p*-xylylenephosphinic chloride) (III) was converted easily to the salt of the polymeric acid V by treatment with dilute aqueous sodium hydroxide. The soluble polymeric salt was not degraded by saponification at reflux temperature in 10% aqueous NaOH for 2 days; the corresponding polymeric acid V was precipitated as a gel when its solution was acidified with mineral acid. The polymer is a fairly strong acid and can be titrated conveniently with aqueous sodium hydroxide.

The neutralization equivalent and elemental analysis of the polymeric acid indicated that the *p*-xylylene to PO₂H ratio was almost one to one.

Poly(*p*-xylylenephosphinic chloride) (III) was converted to the corresponding amide by reaction with suitable amines such as hexamethylenediamine, aniline or *p*-aminophenol.

These results demonstrate that at low temperatures a benzyl radical adds directly to the phosphorus atom of PCl₃ to afford a phosphonyl radical which can couple with a hydrocarbon radical to give a stable molecule. The phosphonyl radical intermediate can also decompose to afford a monoalkyl derivative and Cl· (or ·PCl₂) *via* route a (or b) as shown in Fig. 3.

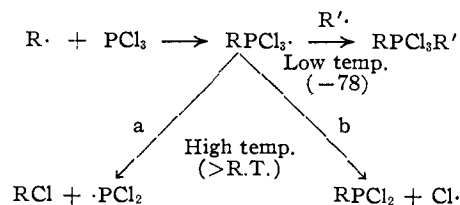


Fig. 3.

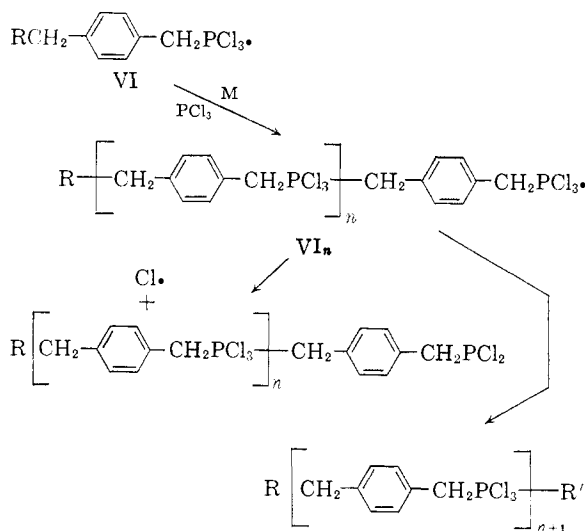
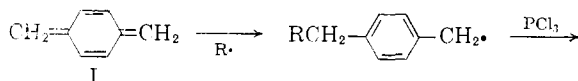


Fig. 4.

The rate of decomposition increases with an increase in temperature. Hence, monoalkylphosphorus halides are the major products when reaction is carried out at room temperature or above. In the present case, the phosphonyl radical VI reacted at low temperature with *p*-xylylene (I), a pseudo-diradical, thereby regenerating a benzyl radical end-group which continued the copolymerization. Termination probably occurred eventually by decomposition of the phosphonyl radical or by coupling of free radical end-groups.

Kharasch, *et al.*,¹⁴ reported that PCl_3 reacts with olefinic monomers as described in the Introduction. Although his suggested mechanism is a logical assumption, it was never substantiated by proof that the product isolated was $Cl_2PCH_2CH_2RCl$ and not $ClCH_2CHRPCl_2$. It is suggested that reaction of PCl_3 with olefinic monomers might occur by addition of a hydrocarbon radical to the phosphorus atom to afford an unstable phosphonyl radical that continues to react in one of three ways as described for *p*-xylylene. In this case, however, decomposition of the phosphonyl radical intermediate occurs faster than addition to the olefinic monomer, since olefinic monomers are considerably less reactive toward free radicals than is *p*-xylylene. The higher temperatures (about 70–80°) required for reaction of PCl_3 with olefinic monomer also favor decomposition of the radical intermediate *via* route a or b as shown in Fig. 5.

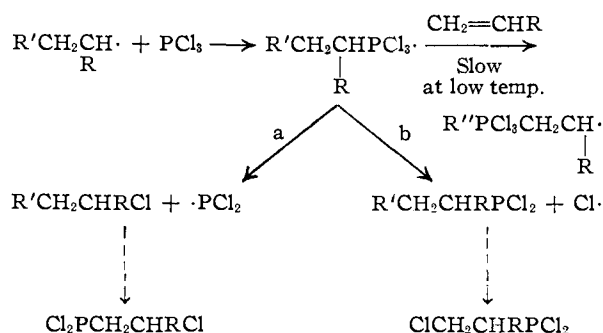


Fig. 5.

Hence, low molecular weight telomer is obtained as the major product. The possibility that some direct abstraction of chlorine atoms occurs at about 85° as postulated by Kharasch¹⁴ cannot be ruled out. It is doubtful, however, that its rate is comparable with addition of a radical to the phosphorus atom which is very facile, even at -78°. The relative rates of a (or its equivalent as postulated by Kharasch) and b can be established by quantitative determination of the $ClCH_2CHRPCl_2$ to Cl_2PCH_2CHRCI ratio in the product mixture, since the latter compound will be produced *via* a chain reaction involving $\cdot PCl_2$ as the chain carrier, whereas the former will be produced *via* a chain reaction involving $Cl \cdot$ as the chain carrier. It is intended that this phase of the problem be investigated at a future date.

Polymerization of *p*-xylylene with a wide variety of phosphorus compounds was investigated in order to establish the general limits of this reaction. It was found that copolymerization occurred at -78° with PBr_3 and with PI_3 . The yield of high molecular weight polymer as well as the amount of phosphorus incorporated in the polymer was markedly less than when the same reaction was carried out using PCl_3 . Moreover, a considerable amount of *p*-xylylene dihalide was isolated in each experiment. In another experiment, insoluble friable poly(*p*-xylylene) containing only 0.6% P was produced when copolymerization was attempted with PH_3 , and again the yield of polymer was low. These results appear to indicate the increased ease with which telomerization occurs when the X atoms of the PX_3 compound is I, Br or H. In this respect, it was reported⁷ that the ease with which an atom X is abstracted by a free radical R is in the order $I > H > Br > Cl > F$. The relative importance of the telomerization reaction in the present series of experiments appears to be in the same order. Hence, it is possible that both abstraction and addition might occur concurrently.

p-Xylylene copolymerized very readily at -78° with $C_6H_5PCl_2$ to afford high molecular weight poly-(*p*-xylylenephénylphosphonyl dichloride) (VII) in good yield. The polymeric salt was hydrolyzed to the corresponding polymeric phosphine oxide (VIII).

The inherent viscosity of a solution of the polymeric phosphine oxide VIII in acetic acid was 0.445 which indicates again an appreciably high molecular weight. The polymer was thermoplastic and could be pressed at 130° into tough transparent films.

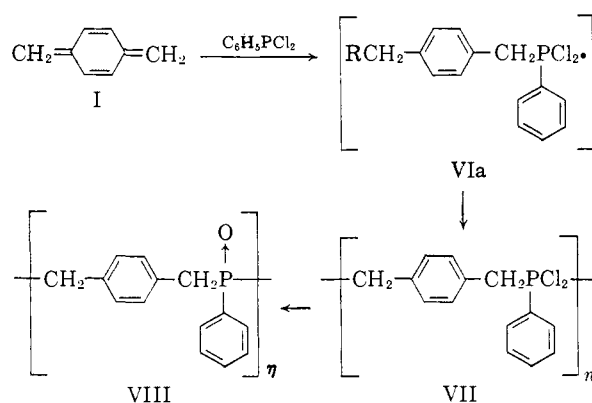


Fig. 6.

p-Xylylene was also copolymerized with $(C_6H_5)_2PCl$ to afford the corresponding polymeric salt. When the salt was hydrolyzed, however, a polymeric phosphine oxide was obtained and its infrared spectrum was similar to that of poly-(*p*-xylylenephénylphosphine oxide) (VIII). Apparently one of the hydrocarbon substituents as well as the chlorine atom was lost during the hydrolysis affording a polymeric phosphine oxide of rather complex structure.

Triphenylphosphine, however, did not react appreciably with *p*-xylylene at -78° . High molecular weight poly-(*p*-xylylene) containing less than 0.1% P was obtained instead. The experiment was repeated using tris-(*p*-chlorophenyl)-phosphine and again poly-(*p*-xylylene) containing only 0.4% P was obtained. The yield of polymer, however, was somewhat low. Similar results were realized with trimethylphosphine, tri-*n*-butylphosphine, triethyl phosphite, dimethyl hydrogen phosphite and tris-(β -chloroethyl) phosphite as summarized in Table I.

TABLE I

COPOLYMERIZATION OF *p*-XYLYLENE WITH PHOSPHORUS COMPOUNDS^a

Phosphorus compd.	% P in polymer	Calcd. ratio <i>p</i> -xylylene to P	Yield insol. polymer, %
PCl_3	14.6 ^b	1.3	100
$C_6H_5PCl_2$	11.0 ^c	1.5	100
$(C_6H_5)_2PCl$	7.3	3	20
PBr_3	5.0 ^d	5	45
PI_3	4.3 ^d	7	40
PH_3 ^e	0.6 ^f	50	50
$P(CH_3)_3$.6 ^f	50	25
$(p\text{-ClC}_6\text{H}_4)_3P$.4 ^f	70	75
$(CH_3O)_2PH$.27 ^f	100	100
$P(OCH_2CH_2Cl)_3$.19 ^f	200	75
$(EtO)_3P$.09 ^f	300	100
$(C_6H_5)_3P$.08 ^f	400	100
$(n\text{-Bu})_3P$.08 ^f	400	70

^a Two equivalents of phosphorus compound used per equivalent *p*-xylylene. ^b Polymer analyzed as the phosphorus chloride. ^c Polymer analyzed as one to one mixture of the dichlorophosphine and the phosphine oxide. ^d Polymer analyzed as the phosphoric acid. ^e About 1 mole of PH_3 used per mole of *p*-xylylene. ^f Polymer analyzed as $-(C_6H_5)_n-$.

Interaction of *p*-xylylene with phosphorus oxychloride does not occur significantly. Thus, insoluble poly-(*p*-xylylene) containing only 0.4%

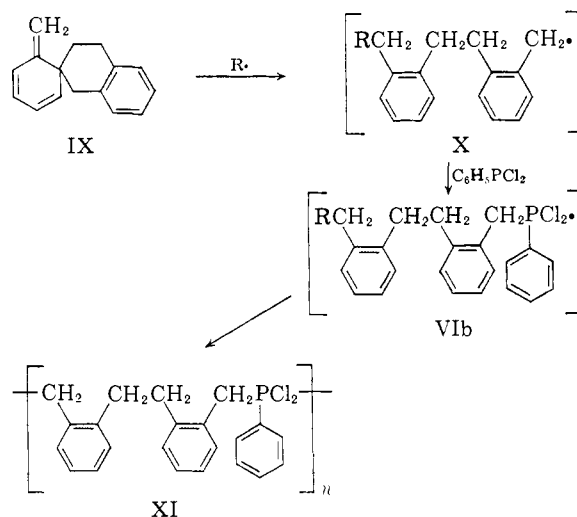


Fig. 7.

Cl and 0.12% P was produced in almost 100% yield when *p*-xylylene was allowed to polymerize in the presence of twofold molar excess $POCl_3$. On the other hand, PCl_5 reacted readily with *p*-xylylene affording predominantly low molecular weight soluble products that were hydrolyzed easily by cold dilute aqueous NaOH. This reaction, however, could have occurred ionically since *p*-xylylene is known to react readily with Lewis acids,¹⁶ or it could have occurred *via* reaction with PCl_3 and Cl_2 formed as the result of dissociation of PCl_5 .

An alkylphenyl dichlorophosphonyl radical intermediate (VIa) should be considerably more thermally stable than the corresponding alkyl trichlorophosphonyl radical intermediate VI owing to the increased possibility for electronic interaction with the phenyl group attached to the phosphorus atom. This point of view is substantiated by the results obtained when $C_6H_5PCl_2$ was caused to react at room temperature or above with monomers such as spiro-di-*o*-xylylene (IX)¹⁷ or butadienes,¹⁸ both of which are considerably less reactive than *p*-xylylene. It was shown that a free radical intermediate adds to the *exo*-methylene group of spiro-di-*o*-xylylene (IX), causing the molecule to open up to afford a linear di-*o*-xylyl radical (X) that continues the polymerization. It was observed that a low molecular weight copolymer XI was produced when spiro-di-*o*-xylylene was allowed to polymerize at room temperature in $C_6H_5PCl_2$.

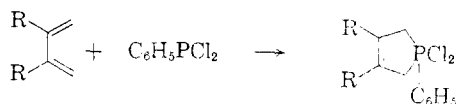
When the experiment was repeated using PCl_3 , the major product was an oil having an average molecular weight of only about 530. Moreover, growing chains of poly-(*o*-xylylene) could only be extended by one or two units when the "living" polymer-monomer solution was dissolved in PCl_3 . Additional evidence for the stabilizing effect of a phenyl group attached to a phosphonyl radical is found in the work of McCormack¹⁸ who observed

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

(17) L. A. Errede, *ibid.*, **83**, 949 (1961).

(18) W. B. McCormack, U. S. Patents 2,663,736; 2,663,737; 2,663,738 (1953); also 2,671,077-2,671,080 (1954).

that $C_6H_5PX_2$ and butadienes react at about 40° to afford the corresponding heterocyclic phenylphosphorus dichloride Diels-Alder adduct. Telo-



meric products,^{7,9,13} which McCormack referred to as "interpolymers" were obtained when the reaction was initiated by monoradicals. The analogous reactions of butadienes with PCl_3 , however, were not reported.

The copolymerization of pseudo-diradicals with PCl_3 represents a novel approach to formation of linear polymers with P incorporated in the chain¹⁹ and to the preparation of C-P bonds in general, for which there are relatively few examples.⁷⁻¹⁰

Experimental

Poly-(*p*-xylylenephosphinic trichloride) (II) and Poly-(*p*-xylylenephosphinic chloride) (III).—A cold (-78°) solution of *p*-xylylene (0.3 mole) in toluene (4.5 l.) was prepared as described in previous publications.⁵⁻⁸ Phosphorus trichloride (0.5 mole) was added and the resultant solution was warmed to room temperature. A finely divided precipitate was formed throughout the solution. The mixture was separated by filtration using a closed system to ensure exclusion of air and moisture. The filtered cake was washed thoroughly with 4 l. of hexane. A sample of the hexane-saturated polymeric salt was analyzed immediately for chloride and phosphorus and the results (6.3% Cl, 2.0% P) corresponded to a Cl to P ratio of 2.8 to 1. Its infrared spectrum showed a very weak absorption band at 8.1μ indicating the presence of only a trace amount of P→O.

The hexane-saturated poly-*p*-xylylenephosphinic trichloride (II) was dried by evaporation in air to afford 43 g. of poly-(*p*-xylylenephosphinic chloride) (III) in the form of a very fine off-white powder. Its elemental analysis (8.0% Cl, 10.6% P) corresponded to a Cl to P ratio of 0.7 to 1, and a *p*-xylylene to POCl ratio of 2.1/1. In other experiments in which the two compounds were allowed to react at -78° for several days before being warmed to room temperature, the phosphorus content of the polymer was as high as 14.6%, corresponding to a ratio of *p*-xylylene to POCl of 1.3 to 1. Its infrared spectra verified the presence of *p*-xylylene (strong bands at 11.7, 7.1, 6.6 and 3.4μ) and the presence of P→O (strong band at 8.1μ). A small band at 10.5μ indicated that some hydrolysis of PCl to POH had occurred.

In another experiment the hexane-saturated polymeric salt was dried under vacuum and then exposed to atmospheric oxygen for only about a minute. Its elemental analysis (12.5% Cl, 11.7% P) again indicated a Cl to P ratio of about 1 to 1, and its infrared spectrum was identical with that of poly-(*p*-xylylenephosphinic chloride) described earlier.

Poly-(methyl *p*-xylylenephosphinate) (IV).—Poly-(*p*-xylylenephosphinic chloride) (III) (20 g.) which contained 9.8% P was added to methanol (1 l.) at room temperature. The mixture was stirred for 1 hr. and then the finely divided suspension was allowed to settle overnight. The mixture was separated by filtration, and the insoluble residue (12.5 g.) was washed with methanol. The soluble polymer (5 g.) was recovered from the mother liquor by addition to 3 l. of water, and the rubbery mass obtained was dried overnight in a vacuum oven kept at 80° . Its elemental analysis (70.9% C, 6.8% H, 10.3% P, 1.0% Cl) corresponds approximately to $[(C_8H_8)_{2.3}POCH_3]_n$. The phosphorus content of the insoluble polymer was 10.4%. The infrared spectra of the insoluble and soluble polymers were identical and similar to that of the parent polymeric phosphinic

chloride, except for the presence of a strong band at 9.7μ , characteristic of a phosphorus ester group. The X-ray diffraction patterns of the soluble and insoluble polymeric ester were also identical, showing haloes at 4.76 and 3.92 \AA . The inherent viscosity of the methanol-soluble polymer was 0.288. The polymers softened at about 150° and could be pressed at this temperature and 100 atm. into clear transparent films. The specimens made from the insoluble polymer were considerably tougher than those made from the soluble portion. The polymer did not support combustion.

Poly-(*p*-xylylenephosphinic acid) (V).—Poly-*p*-xylylenephosphinic chloride (III) (15 g.) of 11.7% phosphorus content was digested in hot dilute aqueous NaOH (3%) for 2 days. The mixture was separated by filtration and 5.4 g. insoluble polymer was recovered. The clear solution gave a light blue fluorescence when irradiated with ultraviolet light. The mother liquor was acidified with dilute HNO_3 and the soluble polymer was reprecipitated as a highly swollen gel. The reprecipitated polymer was dried to a friable powder (6.5 g.). Its elemental analysis (14.6% P, 0.1% Cl) and neutralization equivalent (215) indicated that the product had a *p*-xylylene to PO₂H ratio of 1.4 to 1. The percentage chlorine and neutralization equivalent did not decrease when the polymer was again treated at reflux temperature with 10% aqueous sodium hydroxide for an additional 2 days. The infrared spectrum of the polymeric acid showed a strong band at 10.5μ and a broad absorption through the 2.8–5.0 μ region indicative of the POH group, a strong band at 8.05μ for P→O and a strong band at 11.8μ indicative of *p*-substituted xylene.

The polymer can be used as an ion exchange resin. Divalent and trivalent metal ions are retained rather tenaciously, even when treated with concentrated HCl.

Poly-(*p*-xylylenephosphonium dichloride) (VII).—*p*-Xylylene (0.25 mole) and phenyldichlorophosphine (0.45 mole) were allowed to react at -78° in heptane (4.5 l.) for 4 days. The reaction products were recovered as described previously. A sample of the hexane-saturated salt was analyzed for Cl and P. The results (2.3% Cl and 1.0% P) corresponded to a Cl to P ratio of 2 to 1. The infrared spectrum of the hexane-saturated salt showed no band that could be attributed to P→O absorption. The salt was dried in air and 65 g. of impure poly-(*p*-xylylenephosphonium dichloride) (VII) was obtained as an off-white powder. Its infrared spectrum was consistent with its assigned structure (absorption bands at 11.7μ for *p*-xylylene, 13.5 and 14.5μ for phenyl). A small but broad absorption at 3–5 μ plus weak absorption at 10.2μ indicated the presence of some POH, and a weak band at 8.1μ indicated that the presence of some P→O owing to hydrolysis of PCl_2 . The elemental analysis (9.2% P and 7.6% Cl) corresponds to a *p*-xylylene to P ratio of about 1.6 to 1 and a chlorine to phosphorus ratio of 0.72 to 1.

Although similar results were realized with diphenylchlorophosphine, only high molecular weight poly-(*p*-xylylene) containing 0.08% P was obtained when *p*-xylylene was polymerized in the presence of 2 mole equivalents of triphenylphosphine. In another experiment tris-(*p*-chlorophenyl)-phosphine (m.p. $103-104^\circ$), prepared from PI_3 and *p*-chlorophenylmagnesium bromide according to the procedure of Mann and Chaplin,²⁰ was tried in place of $(C_6H_5)_3P$ and again essentially poly-(*p*-xylylene) was obtained, although the phosphorus content incorporated in the polymer had increased to 0.4%.

Poly-(*p*-xylylenephosphine oxide) (VIII).—Poly-(*p*-xylylenephosphonium dichloride)(VII) (10 g.) prepared as described above was leached with dilute NaOH and then digested at reflux temperature in glacial acetic acid (1 l.) for 24 hours. A small amount of insoluble polymer (1 g.) was removed by filtration. The mother liquor was added dropwise to water (2 l.) and 7 g. of polymer was recovered as a white powder. Its elemental analysis (11.0% P, 0.13% Cl) corresponds to a *p*-xylylene to $C_6H_5P=O$ ratio of about 1.5 to 1. A strong band at 8.1μ indicative of P→O, was present in its infrared spectrum. (Bands at 13.5 and 14.4μ for phenyl; strong bands at 3.33, 3.45, 6.6, 7.1, 11.7μ for *p*-xylylene were also present.) Its X-ray diffraction pattern showed sharp haloes at 4.6 and 4.2 \AA . The inherent viscosity of the soluble polymer in glacial acetic acid was 0.445. The

(19) V. V. Korshak, G. S. Koelsnikov and B. A. Zhubanov, *Izvest. Akad. Nauk. S.S.S.R. (Otdel. Khim.)*, 618 (1958).

(20) F. G. Mann and E. J. Chaplin, *J. Chem. Soc.*, 527 (1937).

polymer softened above 140° and could be pressed at this temperature into tough transparent flexible films. Transparent films could be cast from solution.

In another experiment, 18.5 g. (0.08 mole) of diphenylchlorophosphine (b.p. 170–172° (3mm.)), prepared by heating 52.4 g. of triphenylphosphine and 35.8 g. of phenyldichlorophosphine at 300° for 12 hours, was added at –78° to 0.09 mole of *p*-xylylene in 4.5 l. of toluene. Only 1.6 g. of polymer (7.32% P) was isolated when the mixture was warmed to room temperature. After the active chloride was removed by hydrolysis, the infrared spectrum of the resulting product was very similar to that of poly-(*p*-xylylenephénylphosphine oxide) (VIII).

Reaction of *p*-Xylylene with PCl₅.—Phosphorus pentachloride (0.25 mole) was added at –78° to 0.10 mole of *p*-xylylene in toluene (3.5 l.). After 7 days the reaction mixture was warmed to room temperature and 2 g. of polymer was removed by filtration. The mother liquor was evaporated to dryness. The residue (37 g.) was dissolved in ether and extracted with dilute aqueous NaOH. The ether layer was evaporated to dryness, leaving a mixture of the usual neutral products of *p*-xylene pyrolysis²¹ as residue (16 g.). The dark aqueous NaOH solution was acidified and a dark heavy oil (10 g.) settled to the bottom. This was separated by decantation. The oil contained 7.1% P and 3.1% Cl. Its molecular weight determined by the

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

method of Neumeyer²² was about 1100. Its infrared spectrum is consistent with randomly chlorinated poly-(*p*-xylylenephosphonic acid) (no distinct absorptions 11–15 μ , strong band at 3.4 and 6.7 μ) having PO₂H₂ end-groups (broad absorption 3–5 and 10–10.5 μ).

The dark, almost black, oil (5 g.) was dissolved in methanol (30 cc.) and the solution was added to FeCl₃ (3 g.) dissolved in MeOH (20 cc.). Water was added dropwise until the color of the solution became reddish-orange characteristic of FeCl₃ in methanol. A brown-black precipitate (0.9 g., 6.6% P, 7.8% Fe) formed with each drop and this was separated by filtration. The remaining polymer was precipitated from the clear reddish-orange mother liquor by addition of an equal volume of water. When dry, the product was a pale yellow powder (4.9 g., 7.0% P, 0.8% Fe). The material did not melt below 300° and was soluble in aqueous NaOH but not in methanol, acetone or toluene.

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(22) J. J. Neumeyer, *Anal. Chim. Acta*, **20**, 523 (1959).

[CONTRIBUTION NO. 189 FROM THE CENTRAL RESEARCH LABORATORIES OF THE MINNESOTA MINING AND MANUFACTURING CO., ST. PAUL 19, MINN.]

The Chemistry of Xylylenes. XI. Some Reactions of *spiro*-Di-*o*-xylylene that Occur via Cationic Intermediates

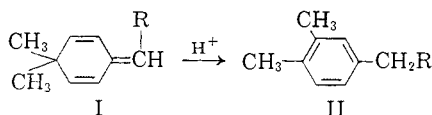
BY L. A. ERREDE

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Despite the ease with which *spiro*-di-*o*-xylylene undergoes reaction *via* free radical mechanism, it will react ionically in the presence of Lewis acids. Proton addition occurs at the *exo*-methylene group producing a carbonium ion intermediate that rearranges by aromatization to afford a *o*-(β -*o*-tolylethyl)-benzyl carbonium ion. The fate of this ion is dependent upon its environment. Thus, di-*o*-xylyl halides, esters, ethers and alkylated phenols were obtained when the carbonium ion was produced in the presence of the appropriate reagent. Poly-(*o*-xylylene) was obtained when an acid catalyst was added to a concentrated solution of *spiro*-di-*o*-xylylene in hexane; 1-methyldibenzo[*a,d*]cyclohepta-1,4-diene was obtained *via* intramolecular aromatic substitution when the ionic reaction was carried out in dilute solution. *spiro*-Di-*o*-xylylene and formaldehyde were copolymerized to afford the corresponding polymeric ether.

Introduction

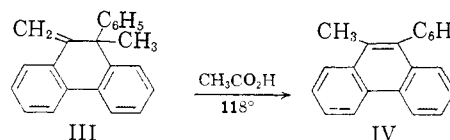
exo-Methylenecyclohexadienes^{1–6} are known to rearrange in acidic media to afford a variety of aromatic compounds. Thus, von Auwers and Ziegler reported¹ that 1-methylene-4,4-dimethylcyclohexadiene-2,5 and related compounds (I) rearrange ionically to give the corresponding 1,2-dimethyl-4-alkylbenzenes (II).



Shriner and Giepel reported² that 9,10-dihydro-9-methyl-10-methylene-9-phenylphenanthrene (III) rearranges in acetic acid at reflux temperature to give 9-methyl-10-phenylphenanthrene⁷ in 80%

- (1) K. von Auwers and K. Ziegler, *Ann.*, **425**, 217 (1921).
- (2) R. L. Shriner and L. Giepel, *J. Am. Chem. Soc.*, **79**, 227 (1957).
- (3) C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 5512 (1957).
- (4) C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 5520 (1957).
- (5) C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 6277 (1957).
- (6) C. R. Hauser and D. N. Van Eenam, *ibid.*, **79**, 6280 (1957).
- (7) C. K. Bradsher, L. Rapaport and P. Anderson, *ibid.*, **68**, 2153 (1946).

yield, but the fate of the expelled CH₃ substituent was not established. Hauser and Van



Eenam reported^{3–6} that *exo*-methylenecyclohexadienamines (V) rearrange readily in acidic solvents to give a mixture of compounds VI and VII, the relative ratio of which is dependent upon the acid strength of the reaction medium.

