reaction mixture by chromatography over Woelm alumina using pentane for elution led to recovery of 66 mg. of 4,12-dimethyl(2.2)metacyclophane and 1.0 mg. of pyrene.

Attempts to Effect Substitution on the Bridged Methylenes of IV.—The various experiments using N-bromosuccinimide, *t*-butyl hypochlorite, lead tetraacetate, cumene hydroperoxide and cuprous chloride, vanadium pentoxide and hydrogen peroxide, chromium trioxide and selenium dioxide are not described in detail since invariably the outcome was one of recovery of starting material or the formation of complex, tarry mixtures from which no useful products could be isolated.

[CONTRIBUTION NO. 176 FROM THE CENTRAL RESEARCH LABORATORIES, MINNESOTA MINING AND MANUFACTURING CO.' ST. PAUL, MINN.]

The Chemistry of Xylylenes. VIII. The Formation of Spiro-di-*o*-xylylene and Related Compounds[1]

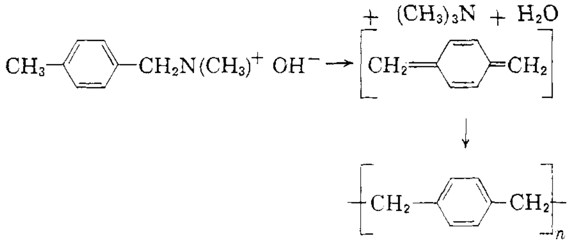
BY L. A. ERREDE

RECEIVED AUGUST 26, 1960

The Hofmann degradation of *o*-methylbenzyltrimethylammonium hydroxides at low pressure in a modified flow system is a convenient method for generating *o*-xylylene. *o*-Xylyl alcohol and bis-di-*o*-xylyl ether are formed as side products. Spiro-(5,5)-2,3-benz-6-methyleneundeca-7,9-diene (spiro-di-*o*-xylylene) is obtained in good yield when *o*-xylylene is warmed from −78° to room temperature. Cyclo-di-*o*-xylylene is also obtained in appreciable amount, but the ratio of the spiro to cyclic compounds is about 3 to 1. The spiro compound polymerizes at room temperature to high molecular weight poly-(*o*-xylylene). Spiro-di-*o*-xylylene reacts with I_2 or Br_2 to give the corresponding 2,2'-bis-(halomethyl)-bibenzyl, and it can be hydrogenated using Raney nickel catalyst to afford spiro-(5,5)-2,3-benz-6-methylundecane. It is suggested that the mechanism for addition of free radicals to spiro-di-*o*-xylylene involves attack at the *exo*-methylene group followed by aromatization to afford an *o*-substituted benzyl radical. This intermediate continues to react to give a variety of di-*o*-xylylene derivatives, depending upon the choice of experimental conditions.

Introduction

Fawcett, *et al.*,[2] have reported that poly-*p*-xylylenes and cyclo-di-*p*-xylylene were formed when *p*-methylbenzyltrimethylammonium hydroxide was decomposed in aqueous solution. They speculated that these products were formed from *p*-xylylene which is an extremely reactive molecule.[3] Other workers have also demonstrated[4,5] or postulated[6,7] the transient existence of xylylenes in related pyrolysis reactions.

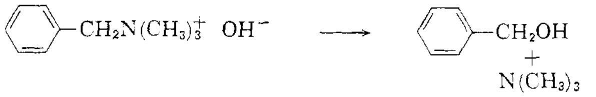


p-Xylylene, produced by fast flow pyrolysis of *p*-xylene in gas phase, can be isolated in solution by instantaneous condensation of the pyrolyzate in a cold solvent. Hence, it appeared probable to us that degradation of the appropriate quaternary hydroxide might be a convenient method for isolating a variety of xylylenes, if the procedure could be modified to enable removal of the transient intermediates from the reaction flask as fast as they are formed. Accordingly a flow technique was developed in our laboratory. It was only partially successful with *p*-xylylene, but it worked exceptionally well for *o*-xylylene.

Results and Discussion

It was verified that poly-(*p*-xylylene) and cyclo-di-*p*-xylylene are formed in high yield and high conversion[2] when *p*-methylbenzyltrimethylammonium hydroxide is decomposed in aqueous solution, and that *p*-xylylene in very small amount is volatilized when the decomposition is carried out at low pressure. It was found, however, that the proportion of monomer collected in the cold trap was increased markedly if the aqueous quaternary hydroxide was metered into an evacuated system where rapid concentration occurred by evaporation followed by flash thermal degradation as described in the Experimental section. In this way the monomer collected in the cold trap represented about 20% of the hydroxide decomposed; the rest polymerized in the decomposition flask before it could be removed by flash distillation.

Closer examination of the reaction products obtained *via* decomposition of *p*-methylbenzyltrimethylammonium hydroxide indicated that appreciable amounts of *p*-methylbenzyl alcohol and bis-(*p*-methylbenzyl) ether were produced as well as poly-(*p*-xylylene) and cyclo-di-*p*-xylylene. The alcohol possibly was formed *via* an alternative route for decomposition of the quaternary base since it was reported by Groves and Greenaway[8] that decomposition of benzyltrimethylammonium hydroxide affords trimethylamine and benzyl alcohol as the major products. Bis-(*p*-methylbenzyl) ether



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[1] Presented before the Organic Chemistry Division of the American Chemical Society at its 138th Meeting, September, 1960, held in New York.

[2] (a) F. S. Fawcett, U. S. Patent 2,757,146; (b) British Patent 807,196; (c) H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

[3] (a) L. A. Errede and J. M. Hoyt, *ibid.*, **82**, 436 (1960); (b) L. A. Errede and B. F. Landrum, *ibid.*, **79**, 4952 (1957).

[4] M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

[5] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

[6] F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2826 (1954).

[7] J. Rosenberg, Ph.D. Thesis under the supervision of W. J. Bailey submitted to the Graduate Council of Wayne University, 1951.

[8] C. E. Groves and A. J. Greenaway, *J. Chem. Soc.*, **57**, 778 (1890).

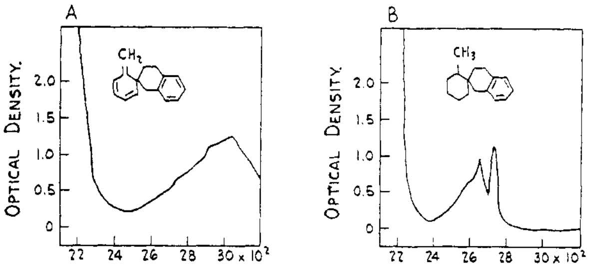


Fig. 1.—Ultraviolet absorption spectra of spiro-di-*o*-xylylene and hexahydro spiro-di-*o*-xylylene in isoöctane.

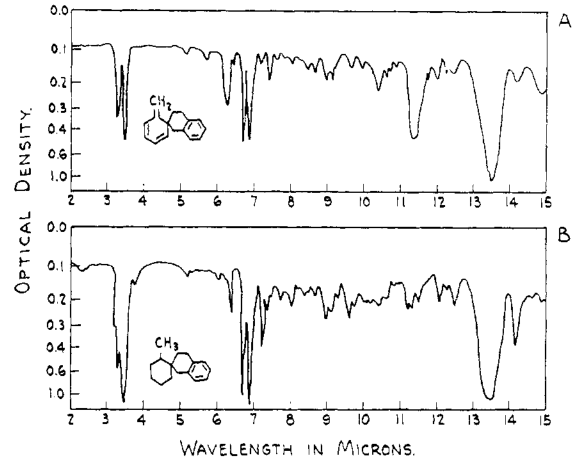
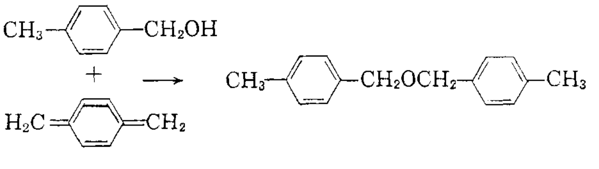


Fig. 2.—Infrared spectra of spiro-di-*o*-xylylene and hexahydro derivative.

most probably was formed *via* interaction of *p*-methylbenzyl alcohol with *p*-xylylene in the hot reaction flask since it is known that organic compounds with active hydrogen atoms add to *p*-xylylene at high temperature.[9]



The decomposition of *o*-methylbenzyltrimethylammonium hydroxide was considerably more interesting, since 80% of the *o*-xylylene produced thereby escaped from the reaction flask before it polymerized to non-volatile poly-(*o*-xylylene). A mixture of products was obtained as an oil when the condensate collected in the cold trap was warmed from −78° to room temperature. The oil was separated by chromatography into the following components: an unknown compound (61%), cyclo-di-*o*-xylylene (20%), bis-(*o*-methylbenzyl) ether (5%), a mixture of esters (4%) and *o*-methylbenzyl alcohol (2%). Material loss was 8%.

The unknown compound was an oil at room temperature. It solidified slowly when chilled to −20° and it remelted at −5 to 0°. It reacted readily with iodine and with potassium permanganate in acetone, decolorized solutions of diphenylpicrylhydrazyl and polymerized slowly at room temperature. Its elemental analysis and molecular weight indicated that the oil was a dimer of *o*-xylylene. Its ultraviolet absorption spectrum (Fig. 1A) indicated the presence of conjugate unsaturation. Its infrared spectrum (Fig. 2A) verified the presence of an *o*-xylylene unit and suggested the possible presence of an *exo*-methylene group. The nuclear magnetic resonance spectrum (Fig. 3A), interpreted by G. V. D. Tiers of this Laboratory, clearly showed the presence of the *exo*-methylene group as well as hydrogen atoms attached to *endo*-double bonds and to an *o*-xylylene unit. There are only three possible structures (I, II and III) that are consistent with these results.

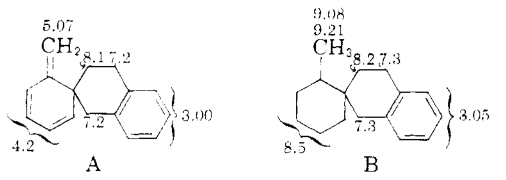
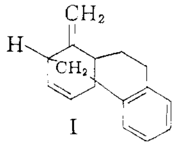
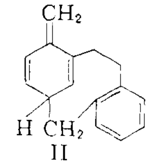


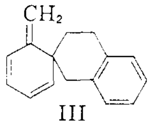
Fig. 3.—Data given in τ values as defined by G. V. D. Tiers.[24]



I



II



III

The nuclear magnetic resonance data favor structure III, since there is no peak in the range of 6.3 to 7.0 τ to account for a tertiary diallyl hydrogen as demanded in structures I and II. Moreover, the spiro structure III is completely strain free whereas the bicyclo structures I and II represent highly strained configurations as indicated by their respective Stuart molecular models. In fact the aliphatic bridges of the bicyclo structures had to be increased by an additional one or two methylene groups in order to assemble models homologous to I and II. On the basis of these results it was concluded that the compound in question is spiro-(5,5)-2,3-benz-6-methyleneundeca-7,9-diene (III) or more conveniently spiro-di-*o*-xylylene. An ultraviolet absorption peak of 2980 Å. was calculated for spiro-di-*o*-xylylene on the basis of the empirical method developed by Woodward.[10] This is in satisfactory agreement with the observed λ_{max} 3040 Å., ϵ 2558[11] (Fig. 1A). Ultraviolet absorption peaks at 3040 to 3130 Å. for *exo*-methylene cyclohexadienes have been reported by Eastham and Raaen[12] and by Van Eenam and Hauser.[13]

It is believed that the dimer, spiro-di-*o*-xylylene was formed when the monomeric *o*-xylylene, collected in the cold trap, was warmed from −78° to room temperature. Spiro-di-*o*-xylylene does

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

[10] L. F. Fieser and M. A. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 185.

[11] All values given are molar extinction coefficients.

[12] J. F. Eastham and V. F. Raaen, *Proc. Chem. Soc.*, 149 (1958).

[13] P. N. Van Eenam and C. R. Hauser, *J. Am. Chem. Soc.*, **79**, 5512 (1957).

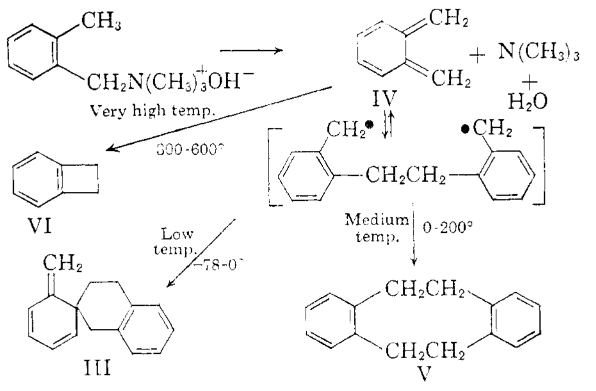
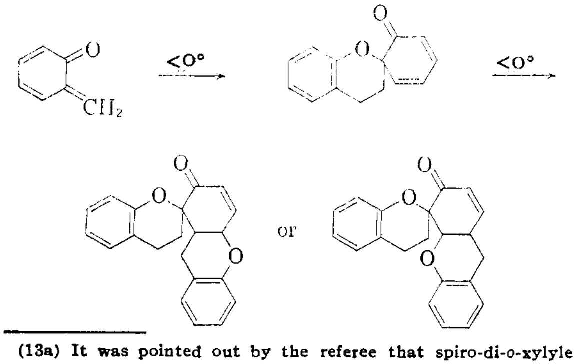


Fig. 4.

not distil below 125° when the pressure is as low as 3 mm., whereas the temperature of the distillate passing up through the short condenser of the hot decomposition reaction flask during the decomposition of quaternary hydroxide was about 30° at 15–20 mm. The distillate was collected as a solid cake. The entrapped *o*-xylylene molecules were "liberated" when the ice cake was melted by warming to room temperature. The monomer molecules then coupled forming di-*o*-xylylene-diradical intermediates which cyclized easily to afford either cyclo-di-*o*-xylylene (V) of spiro-di-*o*-xylylene (III).[13a]

Apparently the formation of the spiro compound is favored at low temperature (<0°) and the formation of cyclo-compound V is favored at high temperature, since the major product of dimerization obtained by others[2,3,5,7] who caused the *o*-xylylene intermediate (IV) to react at elevated temperature was always cyclo-di-*o*-xylylene (V). In this respect, Cava[5,14b] has reported that benzocyclobutene (VI) was formed when *o*-xylylene was produced as an intermediate in gas phase at very high temperature (600°), whereas a mixture of the benzocyclobutene and cyclo-di-*o*-xylylene was obtained when *o*-xylylene was produced as an intermediate in solution at lower temperature (300°). Gardner, *et al.*,[15] also reported that a mixture of heterocyclic spiro compounds was formed when impure *o*-quinone methide, prepared by fast flow pyrolysis of *o*-methoxymethylphenol and subsequent condensation of the pyrolyzate at −190°, was made to react by warming the mixture from −140° to room temperature.



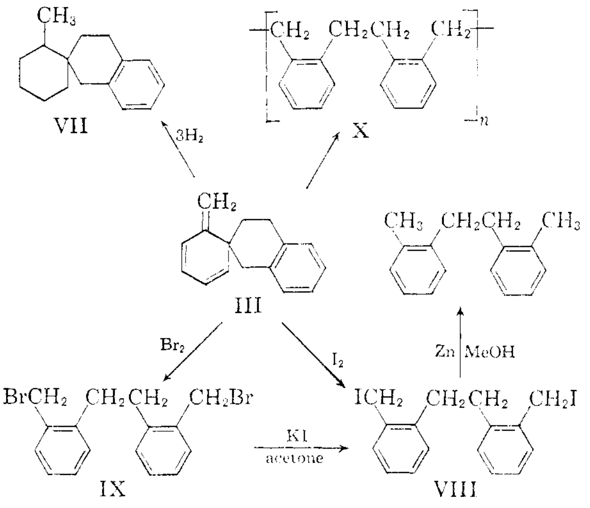
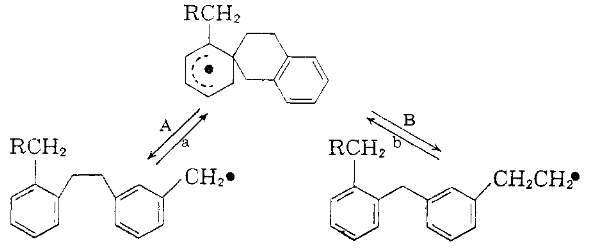


Fig. 5.

Spiro-di-*o*-xylylene was hydrogenated at 67 atm. using Raney nickel as catalyst, and about three equivalents of molecular hydrogen was consumed. The infrared spectrum (Fig. 2B) of the hydrogenated compound indicated that the *exo*-methylene double bond (strong band at 11.2 μ, Fig. 2A) was converted to a CH_3 group (strong band at 7.2 μ, Fig. 2B). Its ultraviolet absorption spectrum (Fig. 1B) λ_{max} isoöctane 2660 Å.(ε 582) and 2730 Å.(ε 720) was similar to that of *o*-xylene (λ_{max} isoöctane 2630 and 2710 Å.) and 1,2-bis-*o*-tolylethane (λ_{max} isoöctane 2640 and 2702 Å.). Its elemental analysis was consistent with the empirical formula $C_{16}H_{22}$ and its nuclear magnetic resonance spectrum (Fig. 3B) confirmed the anticipated structure of spiro-(5,5)-2,3-benz-6-methylcyclane (VII).

When spiro-di-*o*-xylylene was made to react with I_2 or Br_2, the corresponding 2,2′-bis-(halomethyl)-bibenzyl (VIII) or (IX) was obtained in good yield. When the spiro compound was warmed to room temperature or above, either in bulk or in solution, polymerization occurred, affording the high molecular weight poly-(*o*-xylylene) (X).

The driving force in these reactions is the tendency of spiro-di-*o*-xylylene to undergo aromatization. Apparently the most accessible point of attack is at the terminal methylene group. Free radical addition occurs at this site, followed by rupture of the spiro-bridgehead, affording an aromatic nucleus and an alkyl radical end group. Actually the spiro-bridgehead can rupture in one of two ways, (A) to give a benzyl radical or (B) to give a β-arylethyl radical.



[13a] It was pointed out by the referee that spiro-di-o-xylylene and cyclo-di-o-xylylene could also form at the moment of condensation.

[14] (a) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958); (b) M. P. Cava and A. A. Deana, *ibid.*, **81**, 4267 (1959).

[15] P. D. Gardner, H. Sarrafizadeh R., and R. L. Brandon, *ibid.*, **81**, 5515 (1959).

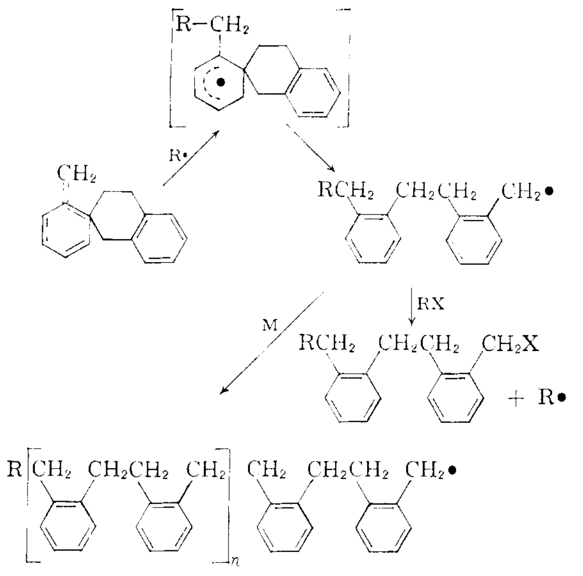
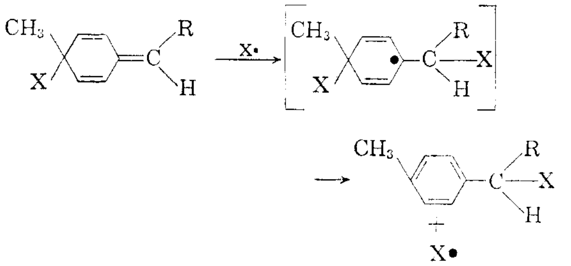


Fig. 6.

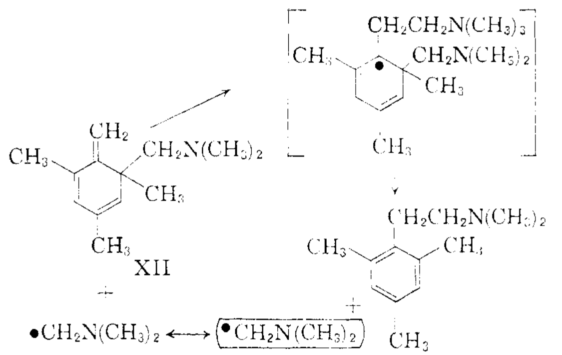
Since reaction A involves rupture of the weaker bond,[16] it occurs faster than reaction B. Moreover, the benzyl radical intermediate, owing to electronic interaction with the aromatic ring, is more stable than the β-arylethyl radical. Hence, reformation of the spiro-radical *via* b is faster than *via* a. The net result is that intermolecular reaction occurs almost exclusively *via* the benzyl radical intermediate; continued addition of *spiro*-di-*o*-xylylene to the benzyl radical end group affords high molecular weight polymer.

A similar mechanism was proposed by Bird and Cookson[17] to explain the von Auwers rearrangement[18,19] of "semi-benzenes" (*exo*-methylenecyclohexadienes). The results obtained when *exo*-methylenecyclohexadieneamines are caused to undergo thermal rearrangements, are also consistent with this mechanism. Hauser and Van Eenam[13] have reported that β-mesityl-ethyldimethylamine (XI) was obtained in 83% yield when their *exo*-methylenecyclohexadieneamine (XII) was caused to rearrange at 150°.



where X is $CHCl_2$ or CCl_3 and R is CO_2H or H

Apparently the cyclic-radical intermediate undergoes rupture at the weaker C–C bond of the two *gem*-substituents to afford the more stable free radical fragment that serves as the chain carrier. In some cases the weaker bond can be established by comparison of appropriate bond dissociation energy data reported in the literature[20–23] or calculated bond dissociation energy data using simple equations that relate bond strength and molecular structure.[16]



XII

XI

Experimental[24]

p- and o-Methylbenzyltrimethylammonium Bromides.—*p*-Methylbenzyl bromide (300 g.) dissolved in ether (3 l.) was charged to a 5-liter round-bottom flask fitted with a reflux condenser, an inlet tube and a stirrer. The ether solution was agitated vigorously at room temperature as a slow stream of trimethylamine was metered to the system at a point above the level of the liquid. Reaction was continued for 3 hours during which time the quaternary salt separated as a finely divided white precipitate. This was removed by filtration, washed with ether and dried to afford 384 g. (97% of theory) of *p*-methylbenzyltrimethylammonium bromide. The salt was recrystallized from a solution of ethyl acetate and methanol and was obtained in the form of white needles (m.p. 101.5–102.5°).[2]

The procedure was repeated using *o*-methylbenzy bromide, and *o*-methylbenzyltrimethylammonium bromide (m.p. 213–214°) was obtained in 100% yield.

Anal. Calcd. for $C_{11}H_{18}NBr$: C, 54.12; H, 7.41; N, 5.73; Br, 32.74. Found: C, 54.1; H, 7.4. N, 5.69; Br, 32.9, 32.5.

Preparation of Aqueous Quaternary Hydroxide Solution.—*p*-Methylbenzyltrimethylammonium bromide (277 g.) was dissolved in 350 cc. of water. This solution was added to 200 g. of Ag_2O suspended in 350 cc. of water. The resulting heterogeneous mixture was caused to react at 55° for 5 hours, before it was separated by centrifugation and subsequent decantation. The clear amber solution was concentrated under vacuum at 60° until the appearance of insoluble poly-(*p*-xylylene). At this point the solution was 2.5 molar with respect to quaternary base as indicated by titration of an aliquot with standard acid solution. Aqueous solutions of *o*-methylbenzyltrimethylammonium hydroxide (2.5 molar) were also prepared in this way.

Decomposition of p-Methylbenzyltrimethylammonium Hydroxide.—A low pressure (5–20 mm.) distillation apparatus was modified in such a way as to enable the aqueous solution of *p*-methylbenzyltrimethylammonium hydroxide to be metered into the system at the rate of 1–3 cc./min. through the top of a steam jacketed column. The solution was concentrated rapidly as it flowed downward through the column and the concentrate fell dropwise into a 1-liter round-bottom flask kept at 200–250°. In this way decomposition of the quaternary base occurred almost instantaneously and the products of reaction (xylylenes, trimethylamine and water) were flash distilled out of the hot chamber through a wide bore gooseneck adapter kept at room temperature. The gas stream was condensed in a cold trap kept at −78°.

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

(17) C. W. Bird and R. C. Cookson, *J. Org. Chem.*, **24**, 441 (1959).

(18) K. von Auwers, *Ber.*, **44**, 588 (1911).

(19) K. von Auwers and K. Ziegler, *Ann.*, **425**, 217 (1921).

(20) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(21) H. H. Sehon and M. Szwarc, *Ann. Rev. Phys. Chem.*, **8**, 439 (1957).

(22) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed. Butterworth's Scientific Publications, London, 1958.

(23) N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. I, Princeton Univ. Press, Princeton, N. J., 1958.

(24) Melting points reported here are uncorrected and the τ values for nuclear magnetic resonance data refer to the system of G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1152 (1958).

Usually about 1.3 moles quaternary base in 0.5 liter of solution were decomposed over a period of 5–8 hours. The apparatus was equilibrated to atmospheric pressure and room temperature and the reaction mixture was neutralized with dilute HCl. The insoluble products in the hot and cold flasks were recovered by filtration, and the total weight of products isolated indicated that decomposition of the quaternary base was 90% complete. Most of the reaction products (about 80%) were recovered from the high-temperature flask. About 60% of this was soluble in acetone and a white precipitate (about 5% of the solubles) was formed when this solution was chilled to −78°. The precipitate was recrystallized from MeOH and was obtained in the form of white platelets (m.p. 63.5°). The material was identified as bis-(*p*-methylbenzyl) ether by its m.p., its infrared spectrum (strong bands at 3.3–3.5, 7.60, 7.18, 9.0, 9.76 and 12.58 μ), its nuclear magnetic resonance spectrum (τ values: 2.93 for aromatic C–H, 5.64 for CH_2O and 7.69 for CH_3) and its elemental analysis.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.1; H, 8.1.

A small sample of the ether was oxidized by $K_2Cr_2O_7$ in acetic acid affording *p*-toluic acid (m.p. 179°).

The acetone mother liquor, from which some of the bis-(*p*-methylbenzyl) ether was recovered as described above, was evaporated to dryness, leaving a residue that was a mixture of low molecular weight polymerization product of *p*-xylylene,[25] bis-(*p*-methylbenzyl) ether and *p*-methylbenzyl alcohol, as indicated by its infrared spectrum.

The acetone-insoluble portion (40% of the original mixture in the high temperature flask) was leached with hot benzene, dissolving about one-fourth of the product. The solubles were recovered by evaporation to dryness. The infrared spectrum of this residue indicated that this was mostly cyclo-di-*p*-xylylene.[25]

About 75% of the product isolated in the low temperature trap was identified as insoluble high molecular weight poly-(*p*-xylylene) by its infrared and X-ray diffraction spectra. The acetone-soluble portion (about 25%) was a mixture of bis-(*p*-methylbenzyl) ether, *p*-methylbenzyl alcohol and some low molecular weight products of *p*-xylylene polymerization as indicated by its infrared spectrum.

Decomposition of *o*-Methylbenzyltrimethylammonium Hydroxide and Identification of the Reaction Products.—*o*-Methylbenzyltrimethylammonium hydroxide (about 1.3 moles) dissolved in 0.5 liter of water was decomposed as described above. Only 20% of the total products of reaction remained in the high temperature flask. This was dissolved in a minimum amount of hot benzene and then reprecipitated as a plastic mass by dropwise addition to a tenfold volume of methanol. The product was identified as poly-(*o*-xylylene) by its infrared spectrum (strong absorption bands at 3.3–3.5, 6.3, 6.8, 7.0 and 13.3 μ) and its nuclear magnetic resonance spectrum (τ values: 3.14 for aromatic H and 7.34 for CH_2). Its X-ray diffraction pattern showed diffuse haloes at 3.65 and 5.10 Å. The inherent viscosity of the polymer in benzene was 0.33. It softened at 80° and could be pressed into transparent flexible films that embrittled with age.

Only a thin film of polymeric material had condensed along the gooseneck connector kept at room temperature. Most of the products of reaction were trapped in the low temperature flask. An excess of aqueous HCl was added to the frozen mixture and the flask was then warmed to room temperature to afford a two-phase liquid system that was separated by extraction with ether. The ether solution was evaporated under nitrogen leaving an amber oil as residue which represented about 80% of the reaction products. The infrared spectrum of this oil indicated that it was a complex mixture of hydrocarbons, olefins, alcohols and ethers. The mixture reacted readily with I_2, $KMnO_4$ in acetone and slowly with diphenylpicrylhydrazyl.

The oil was stored at −20° for about a week during which time it became a semi-solid mass of needle-like crystals. These needles (about 25% of the reaction products) were removed by filtration at −20° and then purified further by recrystallization from heptane to afford large colorless crystals of cyclo-di-*o*-xylylene (V) (m.p. 112.0–112.5°, lit.[14b] m.p. 109–111°). The compound was identified further by its infrared spectrum (strong bands at 13.3 μ, indicating *o*-substituents, plus the usual aromatic and methylene bands from 3.3 to 7.0 μ) and its nuclear magnetic resonance spectrum (τ values: 3.10 for aromatic H and 6.97 for CH_2).

In one experiment a 55-g. sample of the oil from which cyclo-di-*o*-xylylene was separated as described above was dissolved in 1 liter of heptane. A small amount of poly-*o*-xylylene remained and this was removed by filtration. The clear solution was passed through a chromatography column 3 ft. long, 0.75 in. i.d., filled with 0.5 lb. of neutral Al_2O_3. Successive 250-cc. fractions were taken. The non-volatile residue obtained from the first seven fractions was an amber oil (42 g., $n^{26.5}D$ 1.5998, m.p. −5° to 0°) b.p. 130–135° (3 mm.) (virtually all of the sample underwent polymerization before distillation started to occur). The oil was reactive toward iodine, bromine and $KMnO_4$ in acetone, and diphenylpicrylhydrazyl. It polymerized slowly at room temperature and rapidly at 100° to afford poly-(*o*-xylylene). Infrared spectrum of the oil indicated the presence of *o*-substituted xylene (see Fig. 2A; strong band at 13.4 μ and an unusual band at 11.36 μ probably indicative of an *exo*-methylene double bond). Its ultraviolet absorption spectrum (λ_{max} 3040 Ål, ϵ 2558; Fig. 1A) indicated the presence of conjugate double bonds. Its elemental analysis and molecular weight indicated that the product was a dimer of *o*-xylylene. The nuclear magnetic resonance data (see Fig. 3A) were consistent with the structure of spiro-(5,5)-2,3-benz-6-methyleneundeca-7,9-diene(III) (spiro-di-*o*-xylylene).

Anal. Calcd. for $C_{16}H_{16}$: C, 92.29; H, 7.74; mol. wt., 208. Found: C, 91.9; H, 7.9; mol. wt., 220.

An ether (3.7 g.) was obtained as a semi-solid residue from the next six (250 cc.) fractions eluted by hexane from the chromatography column. The residue was purified by recrystallization from ethyl acetate and then from heptane. The product was obtained in the form of white crystals (m.p. 51–52°) and the compound was identified as bis-(*o*-methylbenzyl) ether by its infrared spectrum in KBr (strong bands at 3.3–3.5, 6.88, 13.70 μ for *o*-methylbenzyl and 8.86, 9.30 μ for the ether group, slight difference noted when sample was run as a Nujol mull), its nuclear magnetic resonance spectrum (τ values: 2.85 for aromatic C–H, 5.52 for aromatic CH_2O and 7.72 for CH_3) and its elemental analysis.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02; mol. wt., 226.3. Found: C, 85.0; H, 8.1; mol. wt., 232.

A sample of the ether was converted to *o*-toluic acid (m.p. 104–105°) *via* oxidation using $K_2Cr_2O_7$ in acetic acid.

The chromatography column was developed further using benzene instead of heptane and a mixture of esters was collected as residues (2.4 g. total) from the next ten 250-cc. portions. Their infrared spectra indicated that they were aromatic esters similar to benzyl benzoates. The products, however, were not characterized further.

Diethyl ether was then used as the eluting solvent in place of benzene and an alcohol was obtained as an oily residue (1.4 g.) from the next four 250-cc. fractions. The oil was identified as *o*-methylbenzyl alcohol (m.p. 36–37°)[26] by its infrared spectrum[26] (strong bands at 3.0, 3.3–3.5, 6.88, 9.68, 9.98, 13.52 μ) and its nuclear magnetic resonance spectrum (τ value: 2.96 for aromatic H, 5.63 for Ar–CH_2O, 6.22 for OH and 7.91 for CH_3). A sample of the alcohol was also converted to its phenylurethan derivative (m.p. 78–80°)[27] *via* reaction with phenyl isocyanate according to the procedure of Shriner and Fuson.[28]

Finally an additional 0.9 g. of oil was recovered from the chromatography column by adding a large amount of methanol. This oil was characterized as a mixture of unsaturated alcohols by its infrared spectrum.

From these data it was calculated approximately that in this decomposition at least 90% of the *o*-methylbenzyltrimethylammonium hydroxide was converted to *o*-xylylene which in turn reacted further to afford spiro-di-*o*-xylylene (50%), poly-(*o*-xylylene) (20%), cyclo-di-*o*-xylylene (20%) and bis-(*o*-methylbenzyl) ether (5%).

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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^{27}_{D} 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)-dibenzyl 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.

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The Chemistry of Xylylenes. IX. The Copolymerization of *p*-Xylylene with Phosphorus Trichloride and Related Compounds[2a]

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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. Thus, reaction of *p*-xylylene at −78° with monoradicals 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*-xylene 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

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[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.

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