[CONTRIBUTION NO. 171 FROM THE CENTRAL RESEARCH LABORATORIES OF THE MINNESOTA MINING AND MANUFACTURING CO.,[1] ST. PAUL 9, MINN.]

The Chemistry of Xylylenes. VII. Some Reactions of *p*-Xylylene that Occur *via* Cationic Intermediates[2]

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Although the reactivity of *p*-xylylene is comparable to that of a benzyl radical, its rate of reaction with protons and carbonium ions to afford *p*-substituted benzyl carbonium ions appears to be faster than its rate of coupling *via* the free radical mechanism. The nature of the final product is dependent upon the experimental conditions. Thus, a *p*-methyl benzyl ester was obtained when the benzyl carbonium ion was generated in the presence of a suitable acid, whereas aromatic substitution was favored when the benzyl carbonium ion was produced in an aromatic solvent such as phenol or toluene. A competing reaction was cationic polymerization of *p*-xylylene. This occurred especially when the reaction was carried out in an inert medium such as hexane. Interaction of *p*-xylylene with weak acids, such as acetic acid, did not occur unless a catalytic amount of strong mineral acid was present, and even these conditions afforded only high molecular weight telomers as the principal product. Low molecular weight esters and cyclo-di-*p*-xylylene were obtained, however, when a cold solution of *p*-xylylene was added dropwise to the hot organic acid.

Introduction

It was reported in previous publications[3-5] that *p*-xylylene is an extremely reactive diamagnetic compound that behaves chemically as if it were a diradical owing to its centers of high electron availability at the two terminal methylene groups. Coulson has reported that the calculated free valence at these sites[6] is comparable to that at the methylene group of a benzyl radical.[7] Accordingly, the reactivity of the methylene groups of *p*-xylylene should be in the order of magnitude expected of a benzyl radical.[8] Thus, α,α'-disubstituted derivatives of *p*-xylene are obtained when *p*-xylylene is added at −78° to solutions of monoradicals such as NO, NO_2, diphenylpicrylhydrazyl or to molecules that react *via* monoradical intermediates such as Cl_2, Br_2, I_2 and $(SCN)_2$.[4] Similarly, linear copolymers are obtained in the presence of diradicals such as oxygen.[9]

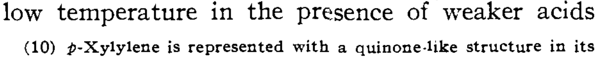
The reactivity of *p*-xylylene toward free radicals is so much greater than that of olefinic monomers such as styrene, acrylonitrile or butadiene that homopolymerization of the former goes to completion at −78° before interaction with the latter can occur even when the olefin is used as the solvent.[4] Similarly, polymerization of *p*-xylylene is not arrested by addition of "inhibitors," such as amines, nitro compounds, phenols, hydroquinones, quinones, mercaptans and terpene-B; *i.e.*, reaction of a free radical with *p*-xylylene is much faster at low temperature than with the "inhibitor." Insoluble high molecular weight poly-*p*-xylylene is always obtained at −78° despite the presence of these "inhibitors" even in threefold molar excess.

The half-life of a *p*-xylylene solution is about 22 hours at −78°, about 22 min. at −36° and less than a second at room temperature.[5] For the purpose of comparison it was shown that benzyl radicals can be preserved in solution at −78° for about 3 hours.[8] These results demonstrate clearly that from the standpoint of its chemical reactivity, *p*-xylylene[10] can be considered a pseudo-diradical.[11]

It was of interest to determine whether or not such a molecule could be made to react ionically, despite its inherent tendency to react *via* free radical mechanism, to afford high molecular weight insoluble poly-(*p*-xylylene). The possible nucleophilic character of the terminal methylene group might render this position more sensitive to attack by a proton than by a neutral radical. Addition of a proton at this site affords a *p*-substituted carbonium ion which should continue to react in several ways to produce a variety of low molecular weight compounds, depending upon the experimental conditions as indicated in Fig. 1. Hence, the extent to which the free radical mechanism has been superseded by the ionic mechanism can be determined by examination of the reaction products.

Results and Discussion

p-Methylbenzyl chloride was obtained in good yield when *p*-xylylene was added at −78° to an excess of HCl in ether. Under these conditions the *p*-xylyl carbonium ion reacted as fast as it was produced with excess HCl to afford *p*-methylbenzyl chloride. The alternative possibility, free radical polymerization, was suppressed completely. Similarly, *p*-methylbenzyl trifluoroacetate was obtained in good yield when the monomer was added to an excess of trifluoroacetic acid.



Unmodified poly-*p*-xylylene was obtained, however, when *p*-xylylene was made to polymerize at low temperature in the presence of weaker acids

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

(2) Presented before the Organic Chemistry Division of the American Chemical Society at its 137th Meeting, April, 1960.

(3) L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

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

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

(6) C. A. Coulson, P. P. Craig, A. MacColl and A. Pullman, *Disc. Faraday Soc.*, **2**, 36 (1947).

(7) C. A. Coulson, *ibid.*, **2**, 9 (1947).

(8) L. A. Errede and J. P. Cassidy, *J. Org. Chem.*, **24**, 1890 (1959).

(9) L. A. Errede and S. L. Hopwood, Jr., THIS JOURNAL, **79**, 6507 (1957).

(10) *p*-Xylylene is represented with a quinone-like structure in its singlet state and a benzene-like structure in its triplet state. Neither is a true representation of the molecule and the reader should refer to the calculations of Coulson[6] for a better representation.

(11) A pseudo-diradical is defined as a diamagnetic compound that behaves chemically as if it were a diradical.[3-6]

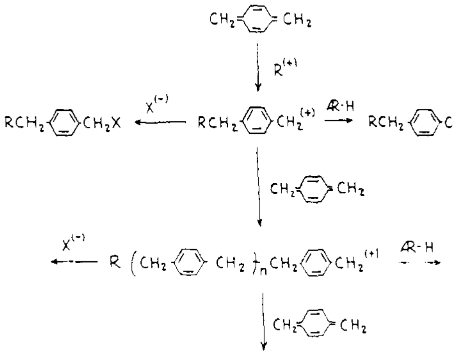
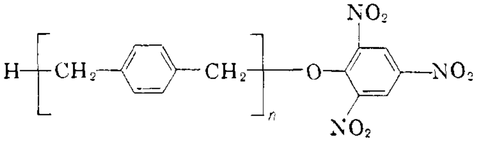


Fig. 1.

such as acetic acid, phenol or methanol. In each case the presence of terminating end-groups could not be detected by infrared analysis even when the polymerization was carried out in a solvent such as methanol or ether. Moreover, no appreciable interaction occurred when *p*-xylylene was polymerized at −78° in the presence of picric acid. This is a somewhat surprising result, since the compound is a strong acid. Apparently, addition of a proton did not occur under these conditions and consequently *p*-xylylene polymerized *via* the free radical mechanism.

Interaction of *p*-xylylene with these acids was realized, however, when the monomer solution at −78° was added dropwise to the acid or solution of the acid kept at 100°. In this way, the concentration of *p*-xylylene was kept low throughout the reaction; ionic dissociation of the acid was increased and the reactivity of the acid was enhanced thermally so that the experimental conditions favored ionic interaction. Thus, the addition of *p*-xylylene to a hot solution of picric acid afforded a mixture of linear polymeric product containing 6.67% N, which corresponds to an average degree of *p*-xylylene polymerization of *ca.* 4. The infrared spectrum of this material is consistent with the configuration



Similar results were obtained with acetic and benzoic acids, although the major product in these experiments was cyclo-di-*p*-xylylene. It was reported earlier that cyclo-di-*p*-xylylene was the major product when a cold solution of *p*-xylylene was added dropwise to hot toluene.[5]

High molecular weight telomers were obtained when *p*-xylylene was made to polymerize at low temperature in a solution of methanol and acetic acid containing a catalytic amount of strong mineral acid. The presence of mineral acid ensured the formation of *p*-methylbenzyl carbonium ion, but apparently homopolymerization *via* ionic mechanism was faster at −78° than interaction with the anion of acetic acid, despite the very high ratio of organic acid to *p*-xylylene. The infrared spectra of these telomers are similar to that of poly-*p*-xylylene but indicate the presence of ester end groups.

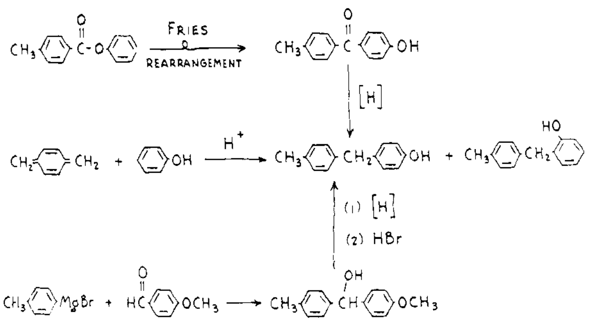
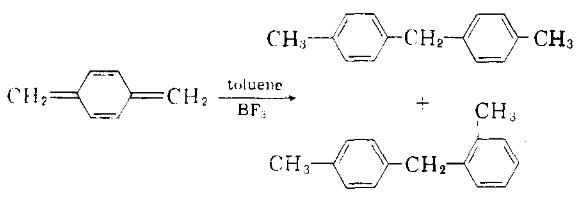


Fig. 2.

Aromatic substitution occurred when the *p*-methylbenzyl carbonium ion was produced in solvents such as phenol and toluene. Thus, a mixture of the *o*- and *p*-isomers of *p*-methylbenzylphenol was obtained exclusively when a solution of *p*-xylylene kept at −78° was added dropwise to hot phenol containing a catalytic amount of H_2SO_4. The structure of the major product, 4-methyl-4′-hydroxydiphenylmethane, was verified by independent syntheses as outlined in Fig. 2. Thus, 4-methyl-4′-hydroxybenzophenone was prepared by the Fries rearrangement of phenyl-*p*-methylbenzoate and the ketone was then reduced to 4-methyl-4′-hydroxydiphenylmethane. In an alternate synthetic route, 4-methoxy-4′-methylbenzhydrol was prepared by the addition of *p*-tolylmagnesium bromide to anisaldehyde. The benzhydrol was then reduced to the corresponding aromatic ether which in turn was demethylated to give 4-hydroxy-4′-methyldiphenylmethane. The melting points and infrared spectra of the products, prepared as described above, were identical with that of the *p*-isomer obtained *via* ionic reaction of *p*-xylylene with phenol. The structure of the *o*-isomer, 4-methyl-2′-hydroxydiphenylmethane, was inferred from its infrared spectrum.

In another experiment, a mixture of *o*- and *p*-ditolylmethanes was obtained when BF_3 was added at −78° to a solution of *p*-xylylene in toluene, whereas poly-(*p*-xylylene) was obtained in the absence of the Lewis acid.



Polymerization of *p*-xylylene *via* cationic mechanism was made to occur at −78° in an inert solvent such as hexane by addition of a catalytic amount of Lewis acids, such as BF_3, $SbCl_5$, $AlCl_3$, $TiCl_4$, H_2SO_4 and CCl_3CO_2H. Reaction was completed in a matter of minutes after addition of the catalyst, whereas the half-life of the control solution was about 22 hours. Apparently the intermediate carbonium ion, produced by interaction of the acid with *p*-xylylene, propagates rapidly by successive addition of monomer units as shown in Fig. 1. The molecular weight of the polymer produced ionically is probably low, since it was observed that this material could be pressed at temperatures as low as 300° into translucent buttons that were extremely brittle. A lower degree of polymerization would be anticipated on the basis of the ionic mechanism outlined in Fig. 1. Telomerization by aromatic substitution in a hexane solvent is still important owing to the presence of unreacted *p*-xylene unavoidably accumulated during the preparation of the *p*-xylylene solution.[12]

No appreciable interaction of *p*-xylylene with styrene, vinylpyridine and acrylonitrile occurred when *p*-xylylene was made to polymerize at −78° *via* a cationic mechanism. Mixtures of poly-(*p*-xylylene) and small amounts of vinyl polymer were obtained instead. Apparently, addition of the carbonium ion intermediate to *p*-xylylene is so much faster than the alternative possibility for addition to vinyl monomer that unmodified poly-(*p*-xylylene) is obtained despite the presence of the vinyl monomer in much higher concentration.

Interaction of *p*-xylylene with nucleophilic reagents did not occur appreciably. In order for this reaction to occur, the approaching anion must be strong enough to polarize the *p*-xylylene molecule and then react with it to form the corresponding benzyl anion. Obviously, the activation energy for this reaction is higher than coupling of a radical with a radical-like species and, consequently, reaction of *p*-xylylene with an anion cannot compete with inherent tendency of *p*-xylylene to polymerize *via* the radical mechanism. Thus, negative results were obtained when *p*-xylylene was made to polymerize at −78° in the presence of ethyl- or butyllithium. In each case, the reaction mixture was quenched with CO_2 and then warmed to room temperature. Poly-(*p*-xylylene) and propionic acid or valeric acid were the only products isolated in significant amounts.

These results demonstrate that a pseudo-diradical such as *p*-xylylene reacts very rapidly at −78° with a proton or carbonium ion but not with an anion. This observation leads one to wonder whether or not the same is true for a monoradical such as benzyl radical. Such a reaction would lead to the formation of a charged molecule, but if the "resonance stabilization energy" of this species is about the same as the radical, the reaction would be reversible and the benzyl radical would be consumed by coupling in the normal way.

$$C_6H_5CH_2\cdot + H^{(+)} \rightleftarrows C_6H_5CH_3{}^{(+)}$$

$$2C_6H_5CH_2\cdot \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

Experimental Results[13]

***p*-Methylbenzyl Chloride (*p*-Xylyl Chloride).**—*p*-Xylylene (0.1 mole) in hexane (1 liter) was added at −78° to 0.5 liter of ether saturated with anhydrous HCl. The resulting solution was warmed to room temperature. Only a trace amount of polymer was formed and this was removed by filtration. The excess solvent was removed by distillation at atmospheric pressure and the residual oil was separated by vacuum distillation. *p*-Xylyl chloride (b.p. 45–47° (1.3 mm.)) was isolated in 57% yield.

Anal. Calcd. for C_8H_9Cl: 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 was converted to *p*-tolylacetonitrile by treatment with NaCN in aqueous methanol. The cyano compound was hydrolyzed in aqueous NaOH to the sodium salt of the acid. Acidification and subsequent recrystallization of the isolated product from hexane yielded white needles of *p*-tolylacetic acid (m.p. 86–88°, lit.[14] 88–89°).

***p*-Methylbenzyl Trifluoroacetate.**—*p*-Xylylene (0.1 mole) in 1.5 liters of hexane was added at −78° to 35 g. of trifluoroacetic acid dissolved in 250 cc. of methylene chloride. The resulting solution was warmed to room temperature and a trace of polymeric material was removed by filtration. The excess solvent was removed from the mother liquor by distillation at atmospheric pressure. The residual oil was separated by vacuum distillation to yield 19 g. of *p*-methylbenzyl trifluoroacetate (b.p. 109–110° (32 mm.)) $n^{22}D$ 1.4454, density at 23° 1.1837, m.p. 3–6°.

Anal. Calcd. for $C_{10}H_9O_2F_3$: C, 55.09; H, 4.16; F, 26.1; mol. wt., 218. Found: C, 55.2; H, 4.32; F, 26.3; mol. wt., 206.

A sample of the ester was saponified by treatment with aqueous NaOH at about 40°. The alcohol produced was insoluble in the reaction mixture and was removed by filtration. The compound was recrystallized from hexane to yield white needles of *p*-tolyl carbinol (m.p. 55–57°, lit.[14] m.p. 60°). A portion of the alcohol was converted to the corresponding phenylurethan (m.p. 76.0–77.5°) by reaction with phenyl isocyanate.

The other product of saponification, the sodium salt of trifluoroacetic acid, was identified by conversion to the *p*-bromophenacyl ester (m.p. 96.5–97.5°; no depression observed with an authentic sample prepared from CF_3CO_2H by reaction with *p*-bromophenacyl bromide).

Telomerization of *p*-Xylylene with Picric Acid.—*p*-Xylylene (0.1 mole) in 1.5 liters of toluene kept at −78° was added over a period of 2 hours to 25 g. of picric acid dissolved in 250 cc. of toluene kept at 110°. The excess solvent was removed by distillation at atmospheric pressure under nitrogen. The residue was leached with dilute NaOH, hot ethanol and then with hot toluene. The insoluble tan residue, 12 g., contained 6.67% nitrogen, corresponding to a ratio of *p*-xylene to picric acid of 3.8 to 1. The telomeric mixture did not melt below 300°.

Similar results were obtained when *p*-xylylene was added to hot acetic acid and to hot benzoic acid. A mixture of low molecular weight esters (about 20%) and cyclo-di-*p*-xylylene (about 80%) were the principal products in each case. The esters were identified by their infrared spectra (strong absorption at 5.75μ for ester and 12.45 molar *p*-substituted xylene) and by saponification to afford a mixture of *p*-substituted benzyl alcohols and the corresponding acid salt.

Acid-catalyzed Alkylation of Phenol.—*p*-Xylylene (24 g.) in 3 liters of toluene kept at −78° was added over a period of 2 hours to a solution of 3 cc. of H_2SO_4 in 500 g. of phenol kept at 125–130°. The toluene was flash-distilled out of the reaction mixture about as fast as it was introduced. The solution was cooled to room temperature and washed with water. The excess phenol was removed by vacuum distillation. The residue was dissolved in 400 cc. of benzene and the phenolic material was removed by extraction with aqueous base. The aqueous solution was acidified with 5 *N* H_2SO_4 and the phenolic oil was dissolved in benzene. The organic solution was washed thoroughly with water, and then evaporated on a steam-bath to yield 33.2 g. of brown viscous oil. The oil was separated by vacuum distillation at 0.1 mm. pressure into three main fractions: (1) 8.67 g., b.p. 128–130°, $n^{21}D$ 1.5892; (2) 12.20 g., b.p. 136–142°, mol. wt. 199; (3) 3.59 g., b.p. 210°, mol. wt. 314; and (4) 1.62 g. of residue.

Molecular weight determinations and infrared spectra indicated that fraction 1 was mostly 4-methyl-2′-hydroxydiphenylmethane, fraction 2 was mostly 4-methyl-4′-hydroxydiphenylmethane and fraction 3 was a telomeric mixture of similar alkylation products whose average degree of polymerization was about 2. Fraction 2 was crystallized from hexane to yield very fine, white needles of the diphenylmethane (m.p. 81.5–82.0°).

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[12] Solutions of *p*-xylylene are prepared by condensation of pyrolyzed *p*-xylene in a solvent kept at low temperature.[3] The pyrolysis is usually only about 10% complete. Hence a solution 0.1 molar with respect to *p*-xylylene is about 1 molar with respect to *p*-xylene.

[13] Melting points and boiling points are uncorrected.

[14] J. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12; mol. wt., 198. Found: C, 84.9, 84.6; H, 6.75, 6.88; mol. wt., 199.

4-Methyl-4′-hydroxydiphenylmethane.—Phenyl-*p*-toluate (m.p. 77.0–77.5°) was made to undergo the Fries rearrangement according to the general directions of Rossenmunde and Schnurr.[15] The product was recrystallized from benzene, and 4-methyl-4′-hydroxybenzophenone was obtained in 36% yield in the form of flat needles (m.p. 173–174°).

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.4; H, 6.02.

The ketone was reduced to the diphenylmethane according to the directions of Clemmensen[16] in 50% yield. The product was recrystallized from hexane as a white solid (m.p. 77–78°). Final purification was effected by sublimation and the white solid obtained thereby melted sharply at 81.5–82.0°. The infrared spectrum of this product was identical with that of the *p*-compound obtained *via* interaction of *p*-xylylene with phenol.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.80; H, 7.12. Found: C, 84.6; H, 7.01.

4-Methyl-4′-hydroxydiphenylmethane was also synthesized *via* an alternative route as follows: 4-Methoxy-4′-methylbenzhydrol (m.p. 63–64°) was prepared in 33% yield from 0.30 mole of anisaldehyde, 0.35 mole of magnesium and 0.34 mole *p*-bromotoluene according to the directions of Balfe, *et al.*[17] The corresponding diphenylmethane was then obtained in 30% yield as a colorless liquid (b.p. 139–141° (2 mm.), n^{25}_{D} 1.5615) by reduction of the benzhydrol with sodium in absolute ethanol according to the procedure indicated by Klages.[18] The liquid slowly crystallized in the form of colorless platelets (m.p. 30–31°). The aromatic ether was then converted to 4-hydroxy-4′-methyldiphenylmethane in 30% yield *via* the Ziesel method for demethylation as described by Shriner and Fuson.[19] Final purification was effected by recrystallization from hexane. The compound was obtained in the form of fine white needles (m.p. 80–81°) which showed no depression in melting point when mixed with the 4-hydroxy-4′-methyldiphenylmethane obtained from the reaction of *p*-xylylene with phenol or *via* the above alternative synthesis. A diphenylurethan derivative (m.p. 140–141°) was prepared by causing the aromatic phenol to react with phenyl isocyanate in pyridine.

BF_3-catalyzed Alkylation of Toluene.—A clear solution of *p*-xylylene (0.04 mole) in 0.5 liter of toluene was saturated with gaseous BF_3, and the reaction mixture was kept at −78° for 1.5 hours. Methanol (100 cc.) was then added and the resulting solution was warmed to room temperature. A small amount of insoluble polymeric material (0.20 g.) was removed by filtration. The excess solvent of the mother liquor was removed by distillation at atmospheric pressure, leaving 9.5 g. of non-volatile oil as residue. The presence of a mixture of diphenylmethanes in the non-volatile oil was indicated by its infrared spectrum.[20]

A second 500-cc. aliquot of the original solution, to which no BF_3 was added, was carried through in parallel as a control experiment. In contrast to the above weight distribution, 2.49 g. of insoluble poly-*p*-xylylene and 3.6 g. of an almost crystalline residue was obtained. The latter was the usual mixture of pyrolysis and subsequent polymerization products.[20]

Acknowledgments.—The authors are indebted to Drs. H. Dinsmore and H. White, then of the M. W. Kellogg Co., and Dr. J. J. McBrady of the Minnesota Mining and Manufacturing Co. for the interpretation of the infrared spectra.

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[15] W. K. Rossenmunde and W. Schnurr, *Ann.*, **460**, 56 (1928).

[16] E. Clemmensen, *Ber.*, **47**, 681 (1914).

[17] M. P. Balfe, E. A. W. Downer, A. A. Evans, J. Kenyon, R. Poplett, C. E. Searle and A. L. Tarnoky, *J. Chem. Soc.*, 797 (1946).

[18] A. Klages, *Ber.*, **39**, 2589 (1906); E. F. Pratt, R. K. Preston and J. D. Draper, THIS JOURNAL, **72**, 1367 (1950).

[19] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 103.

[20] L. A. Errede and J. P. Cassidy, THIS JOURNAL, **82**, 3653 (1960).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND, COLLEGE PARK, MD.]

The Synthesis of Some Linear Polyphenyls

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The synthesis of several aryl-substituted cyclohexenones, linear polyphenyls and halopolyphenyls is reported.

The syntheses of some quater- and quinquephenyls has been reported earlier from this Laboratory.[1] These methods have now been utilized to obtain more complex cyclohexenones, larger polyphenyls and bromopolyphenyls.

4-Bromo-*m*-terphenyl has now been prepared by the two formula sequences (A) and (B).

The products II and IV are indistinguishable, although on the basis of the above reactions they should be isomeric. Aromatization of II and IV was readily accomplished by bromination and dehydrobromination without isolation of the brominated intermediate. In sequence (B) some *p*-phenylenedimagnesium bromide from *p*-dibromobenzene was present since a reasonable amount of the tetrahydro compound V was isolated; V was subsequently aromatized with palladium–charcoal to VIII (R = C_6H_5).

Compound III, 4-bromo-*m*-terphenyl, was found to undergo the interchange reaction with *n*-butyllithium[2] and subsequent reaction of the aryllithium with the enol ether of dihydroresorcinol provided VI which was then utilized to obtain several new polyphenyls (VIII).

In these reactions R–M was either a Grignard reagent or an aryllithium. Thus, a new quinquephenyl, three sexiphenyls and a septiphenyl, IX, were obtained.

An attempt to prepare the Grignard reagent in tetrahydrofuran from the bromodihydro compound II led to the coupled product X, a tetrahydro compound, which was aromatized to the sexiphenyl XI.

It follows that more complex aryl bromides or ketones will provide intermediates for larger and more complex polyphenyls. Further, since there is no procedure available to prove the structure of the different polyphenyls, alternate methods of

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[1] (a) G. F. Woods and I. W. Tucker, THIS JOURNAL, **70**, 2174, 3340 (1948); (b) G. F. Woods and F. T. Reed, *ibid.*, **71**, 1348 (1949); (c) G. F. Woods, A. L. Van Artsdale and F. T. Reed, *ibid.*, **72**, 3221 (1950); (d) G. F. Woods, F. T. Reed, T. E. Arthur and H. Ezekiel, *ibid.*, **73**, 3854 (1951).

[2] R. G. Jones, in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.