

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 phenyl-dichlorophosphine 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*-xylylene-phenylphosphine 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*-xylylene-phosphonic 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.

Acknowledgments.—The authors are indebted to Drs. H. L. Dinsmore and H. F. White, then of the M. W. Kellogg Co., to Dr. J. J. McBrady of Minnesota Mining and Manufacturing Co. for interpretation of the infrared data, and to the Analytical departments of the M. W. Kellogg Co. and Minnesota Mining and Mfg. Co. for elemental analyses.

(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

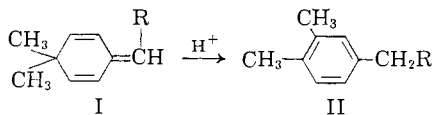
By L. A. ERREDE

RECEIVED OCTOBER 29, 1960

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

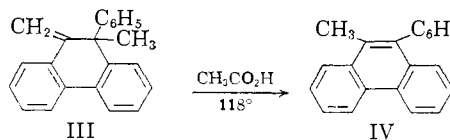
exo-Methylenecyclohexadienes^{1–6} are known to rearrange in acidic media to afford a variety of aromatic compounds. Thus, von Auwers and Ziegler reported¹ that 1-methylene-4,4-dimethylcyclohexadiene-2,5 and related compounds (I) rearrange ionically to give the corresponding 1,2-dimethyl-4-alkylbenzenes (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.*, **88**, 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.

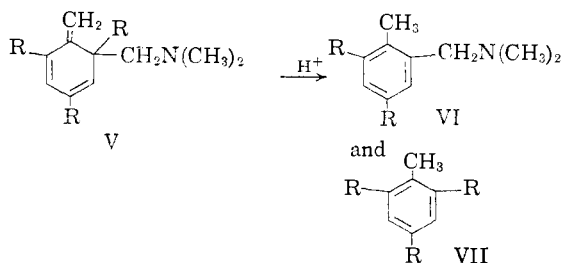
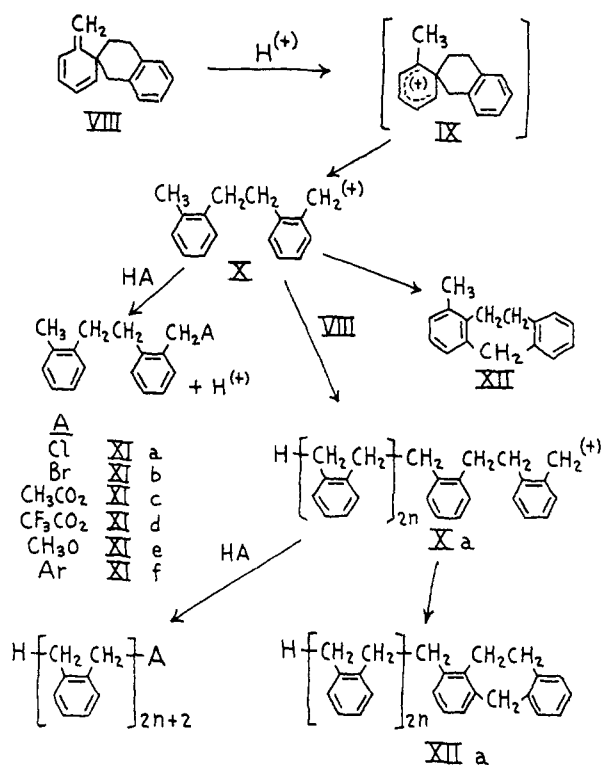


CHART I



The mechanism of aromatization undoubtedly involves the addition of a proton to the *exo*-methylene group of the parent compound followed by expulsion of one of the *gem* substituents as a carbonium ion.⁸ The rearrangement of the alkyl group, however, can occur intramolecularly or intermolecularly. Thus, the results obtained by von Auwers and Ziegler¹ are consistent with an intramolecular mechanism, whereas those of Shriner and Giepel² and those of Hauser and Van Eenam³⁻⁶ are consistent with an intermolecular mechanism.

Similar acid-catalyzed rearrangements occur with keto-cyclohexadienes and again some results can best be interpreted in terms of an intramolecular reaction^{8,9} whereas others are best interpreted in terms of an intermolecular reaction.¹⁰

The synthesis of *spiro-di-o-xylylene* (VIII) and some of its reactions *via* free radical intermediates have been reported in previous publications.^{11,12} The present paper is concerned with reactions of this compound that occur *via* cationic intermediates. The results demonstrate that either intramolecular or intermolecular ionic reactions occur quite selectively under the proper experimental conditions.

Results and Discussion

Previous workers have demonstrated that addition of a proton to *exo*-methylenecyclohexadienes occurs at the *exo*-methylene group.¹⁻¹⁰ Similar

(8) R. T. Arnold, J. S. Buckley and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 3153 (1950).

(9) R. H. Burnel and W. I. Taylor, *J. Chem. Soc.*, 3486 (1954).

(10) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **79**, 4238 (1957); **79**, 756 (1957).

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

(12) L. A. Errede, *J. Polymer Sci.*, in press (1961).

addition to *spiro-di-o-xylylene* (VIII) may afford a *spiro*-carbonium ion intermediate IX which in turn should undergo aromatization to an *o*-(β -*o*-tolyl ethyl)-benzyl carbonium ion X (referred to hereafter as di-*o*-xylyl carbonium ion for the sake of convenience) that may continue to react in one of three ways: (1) intermolecularly with the solvent to form a linear telomeric product (XI), (2) intermolecularly with another *spiro-di-o-xylylene* molecule to form a polymeric carbonium ion (Xa), (3) intramolecularly *via* aromatic substitution to form a dibenzoheptadiene (XII). The reactions are outlined schematically in Chart I.

When the di-*o*-xylyl⁶ carbonium ion (X) was produced in the presence of excess acid, it reacted with the solvent medium to afford the corresponding di-*o*-xylyl derivative XI. Thus, di-*o*-xylyl chloride (XIa), di-*o*-xylyl bromide (XIb), di-*o*-xylyl acetate (XIc) and di-*o*-xylyl trifluoroacetate were obtained in good yield when *spiro-di-o-xylylene* was allowed to react with excess HCl, HBr, CH_3CO_2H and CF_3CO_2H , respectively. The derivatives, isolated in this study, were identified by means of their elemental analyses, infrared spectra and nuclear magnetic resonance spectra. The n.m.r. data are summarized in Table I.

TABLE I

N.M.R. DATA^a FOR LINEAR DERIVATIVES OF DI-*o*-XYLYLENE

| | A | B | a | b | c | d | e | f | Ref. |
|-----------------------|----------------------------------|---|------|------|------|------|------|-------------------|------|
| H | H | | 7.73 | 2.95 | 7.17 | 7.17 | 2.95 | 7.73 | 11 |
| I | I | | 5.61 | 2.85 | 6.95 | 6.95 | 2.85 | 5.61 | 11 |
| Br | Br | | 5.56 | 2.82 | 6.93 | 6.93 | 2.82 | 5.56 | .. |
| ArCH ₃ ... | CH ₂ Ar ^d | | 7.34 | 3.14 | 7.34 | 7.34 | 3.14 | 7.34 | 11 |
| ArCH ₃ ... | CH ₂ Ar ^e | | 6.97 | 3.10 | 6.97 | 6.97 | 3.10 | 6.97 | 11 |
| H | Cl | | 7.74 | 2.99 | 7.10 | 7.10 | 2.82 | 5.59 | .. |
| H | Br | | 7.70 | 2.95 | 7.04 | 7.04 | 2.83 | 5.66 ^b | .. |
| H | -O ₂ CCH ₃ | | 7.70 | 3.00 | 7.16 | 7.16 | 2.86 | 5.00 | .. |
| H | -O ₂ CCF ₃ | | 7.80 | 3.02 | 7.14 | 7.14 | 2.80 | 4.83 | .. |
| H | OCH ₃ | | 7.70 | 3.02 | 7.29 | 7.29 | 2.90 | 5.78 ^c | .. |

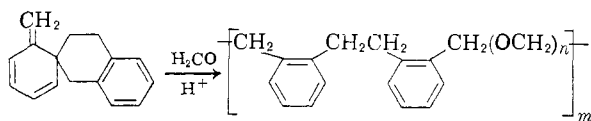
^a Data given in τ values as defined by G. V. D. Tiers (see ref. 14). ^b 8.00 for CH_3CO_2 . ^c 6.84 for CH_3O^- . ^d Poly-*o*-xylylene). ^e Cyclo-di-*o*-xylylene.

When a catalytic amount of Lewis acid was used to initiate reaction in methanol solution, di-*o*-xylyl methyl ether (XIe) was obtained as the major product, whereas in the absence of the catalyst poly-*o*-xylylene was the major product. Presumably, polymerization occurred at room temperature *via* a free radical mechanism as described in an other publication.¹² A mixture of *o*- and *p*-di-*o*-xylyltoluenes was produced when the ionic reaction was carried out in toluene. Similarly a mixture of telomeric di-*o*-xylylphenols and di-*o*-xylylphenyl ethers was obtained when *spiro-di-o-xylylene* was caused to react in phenol. These results resemble those obtained with *p*-xylylene.¹³ Although aromatic substitution occurred exclusively with *p*-xylylene, some ether formation was also noted with *spiro-di-o-xylylene*.

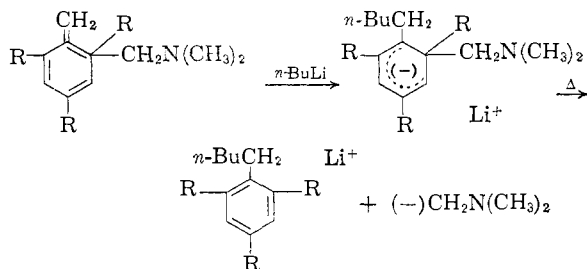
(13) L. A. Errede, J. M. Hoyt and R. S. Gregorian, *J. Am. Chem. Soc.*, **82**, 5224 (1960).

When a catalytic amount of acid was added to *spiro*-di-*o*-xylylene dissolved in a large volume of hexane, the resulting carbonium ion intermediate underwent intramolecular aromatic substitution to give 1-methyl-dibenzo(a,d)cyclohepta-1,4-diene (XII) in good yield. When the concentration of *spiro*-di-*o*-xylylene was increased, polymerization was favored and the yield of XII was decreased accordingly. Intramolecular cyclization was also suppressed in favor of intramolecular reactions by increasing considerably the concentration of acid catalyst, thereby affording compounds of type XI. Nevertheless, some cycloheptadiene (XII) was formed even in the presence of an appreciable concentration of acid catalyst such as $\text{CF}_3\text{CO}_2\text{H}$.

Copolymers of di-*o*-xylylene and formaldehyde were formed when *spiro*-di-*o*-xylylene was caused to react ionically in the presence of excess trioxanes, or in the presence of formaldehyde freshly prepared by thermal decomposition of paraformaldehyde.



Hauser and Van Eenam have reported³⁻⁶ that butyllithium adds *exo*-methylenecyclohexadieneamines *via* an anionic mechanism to afford yellow organometallic adducts which in turn can be converted to the corresponding amylbenzene by decomposition in refluxing xylene.



The corresponding organometallic adduct was not obtained, however, when *spiro*-di-*o*-xylylene was allowed to react at room temperature with *n*-butyllithium or *n*-butylmagnesium bromide. Low molecular weight poly-(*o*-xylylene) was obtained instead, as indicated by its infrared spectrum and the relatively low inherent viscosities of its solutions in benzene (0.10 to 0.15 as compared to 0.60 to 0.70 when polymerization was allowed to occur at room temperature in hexane¹² *via* free radical mechanism). The formation of a yellow precipitate as a transient intermediate was not observed, and only valeric acid was isolated in another experiment when the reaction mixture of *spiro*-di-*o*-xylylene and *n*-butyllithium was quenched with CO_2 . Apparently, the formation of a stable organometallic adduct is not a general reaction for *exo*-methylenecyclohexadienes, but rather may be limited to *exo*-methylenecyclohexadieneamines exemplified by V.

Experimental

Starting Material.—The preparation of *spiro*-di-*o*-xylylene is described in a previous publication.¹¹ The *spiro*-

di-*o*-xylylene used in these experiments was contaminated with some cyclo-di-*o*-xylylene and bis-(2-methylbenzyl) ether.¹¹ Although the impurities can be removed by chromatography, the procedure is laborious and considerable *spiro* compound is lost by reaction with atmospheric oxygen or by polymerization. The impurities, however, do not interfere with the reactions investigated, but merely complicate the separation and identification of the reaction products. Consequently, impure *spiro*-di-*o*-xylylene was used for this qualitative study.

Di-*o*-xylyl Chloride (XIa) and Di-*o*-xylyl Bromide (XIb).—*spiro*-Di-*o*-xylylene (7 g.) dissolved in anhydrous ether (100 cc.) was added dropwise to anhydrous ether (400 cc.) saturated with anhydrous HCl. The solution was kept at room temperature for 4 days and then the excess solvent was removed by evaporation. Di-*o*-xylyl chloride (5.8 g.) was obtained as an oil (b.p. 122–126° at 0.25 mm. pressure). The compound was crystallized from hexane in the form of white crystals, m.p. 65–66°. The assigned structure was verified by the infrared spectrum (bands at 6.25, 6.34 and 6.72 μ for aromatic group; 6.83 and 6.89 for CH_2 ; 7.27 μ for CH_3 ; 13.15 μ for *o*-substituents on aromatic ring; and 15.05 μ for C–Cl) and by the nuclear magnetic resonance spectrum (Table I),¹⁴ of the compound.

Anal. Calcd. for $\text{C}_{16}\text{H}_{17}\text{Cl}$: Cl, 14.49; mol. wt., 244.8. Found: Cl, 14.9; mol. wt., 245.

The experiment was repeated using HBr and di-*o*-xylyl bromide (b.p. 152–160° at 1 mm., m.p. 70.5–72.0°) was obtained in about 70% yield. The assigned structure was verified by its infrared spectrum (bands at 6.25, 6.34 and 6.73 μ for aromatic structure; 6.84 and 6.90 μ for CH_2 ; 7.28 μ for CH_3 ; 13.27 μ for *o*-substituted aromatic ring) which is very similar to that of di-*o*-xylyl chloride, and by its nuclear magnetic resonance spectrum (Table I).

Di-*o*-xylyl Acetate (XIc).—*spiro*-Di-*o*-xylylene (5 g.) dissolved in acetic acid (50 cc.) was allowed to react at room temperature for about a week. The mixture was separated by distillation. An oil (2.5 g., b.p. 134–135° at 0.3 mm.) was obtained and was crystallized from hexane to afford di-*o*-xylyl acetate in the form of cubic crystals, m.p. 70–71°. The structure of di-*o*-xylyl acetate (XIc) was assigned on the basis of its infrared spectrum (bands at 5.74 μ for C=O; 6.23, 6.31 and 6.69 μ for aromatic structure; 6.87 μ for CH_2 ; 7.26 and 7.36 μ for the two CH_3 groups; 8.17 μ for C–O of acetate; 13.32 μ for *o*-substituted aromatic ring) and its nuclear magnetic resonance spectrum (Table I).

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.56; H, 7.51; mol. wt., 268.3. Found: C, 80.7; H, 7.7; mol. wt., 276.

1-Methyldibenzo[a,d]cyclohepta-1,4-diene (XII) and Di-*o*-xylyl Trifluoroacetate (XIId).—Impure *spiro*-di-*o*-xylylene (5 g.) dissolved in hexane (50 cc.) was added slowly at 0° to a solution of $\text{CF}_3\text{CO}_2\text{H}$ (25 cc.) in hexane (250 cc.). The reaction mixture was warmed to room temperature and the hexane was removed by evaporation. The residue was distilled at 0.23 mm. to afford four fractions: (1) 2.5 g., b.p. 116–121°; (2) 1.5 g., b.p. 121°; (3) 0.5 g., b.p. 121–122°; and (4) 1.2 g. residue. Fraction 4 was poly-(*o*-xylylene) as indicated by its infrared spectrum.¹² Fraction 3 was recrystallized from heptane to yield bis-(*o*-methylbenzyl) ether in the form of white crystals, m.p. 51–52°.¹² The ether was identified by its melting point and its infrared spectrum.¹¹

Fractions 1 and 2 were recrystallized from methanol at –15° to give in each case a hydrocarbon compound in the form of white needles; 2.5 g., m.p. 67.5–68.5°. Its infrared spectrum indicated that the product was an aromatic compound having CH_3 and CH_2 substituents (bands at 7.36 and 6.90 μ , respectively) in *o*- and *m*-positions (bands at 13.20 and 13.43 μ for *ortho* and at 12.92 and 14.14 μ for *meta*). The nuclear magnetic resonance data (τ -values, 2.99, 3.12 for phenyl; H, 5.96 for CH_2 ; 6.93 for CH_2CH_2 ; and 7.80 for CH_3) were in agreement with the assigned configuration of 1-methyldibenzo[a,d]cyclohepta-(1,4)-diene¹⁴ (XII).

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}$: C, 92.29; H, 7.74; mol. wt., 208. Found: C, 92.1; H, 7.8; mol. wt., 220.

The mother liquor was evaporated to dryness and the residue (1 g.) was identified by its infrared spectrum as a mix-

(14) The nuclear magnetic resonance data refer to τ -values as described by G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

ture of di-*o*-xylyl trifluoroacetate (XI_d) and the dibenzocycloheptadiene XII in the ratio of about 1- to -1.

In another experiment *spiro*-di-*o*-xylylene (6 g.) dissolved in heptane (20 cc.) was added slowly to a solution of CF₃-CO₂H (50 cc.) and heptane (20 cc.). The two-phase mixture was agitated vigorously at room temperature until a homogeneous slightly green fluorescent solution was obtained. The solution was allowed to remain at room temperature for 2 days. The excess solvent was removed by evaporation and the residue was separated by distillation at 0.45 mm. pressure. The main fraction (4.9 g., b.p. 130-136°) was a mixture of di-*o*-xylyl trifluoroacetate and bis-(*o*-methylbenzyl) ether as indicated by its infrared spectrum (bands at 5.60 μ for C=O; 6.23, 7.32, 6.70 μ for aromatic grouping; 8.1 to 8.9 μ for C—F and C—O of acetate; 13.30 μ for *o*-substituents. Small bands at 9.28 and 9.55 μ indicate some ether impurity). This was confirmed by its nuclear magnetic resonance spectrum (Table I; τ -values: 7.80 for CH₃, 3.02 for phenyl, 7.14 for ethylene, 2.80 for phenyl, 4.85 for methylene of the ester and 7.70 for CH₃, 2.85 for phenyl, 5.52 for methylene of ether). Elemental analysis (13.3% F) and average molecular weight (293) indicated that the ester to ether ratio in the mixture was about 2.3- to -1. The non-volatile residue (1.5 g.) was poly-(*o*-xylylene) as indicated by its infrared spectrum. The infrared spectrum of the forerun (0.5 g., b.p. < 130°) indicated the presence of some dibenzocycloheptadiene.

Di-*o*-xylyl Methyl Ether (XI_e).—Three drops of H₂SO₄ was added to *spiro*-di-*o*-xylylene (7 g.) dissolved in methanol (200 cc.). The mixture was allowed to react at room temperature for 4 days. The excess solvent was removed by evaporation and the residue (6.5 g.) was separated by distillation at 0.15 mm. to afford two main fractions: (1) 5.0 g., b.p. 120-126°; and (2) 0.9 g. residue. The infrared spectrum (bands at 6.29, 6.34, 6.72 μ for aromatic structure; 6.88 μ for CH₂; 7.27 and 7.38 for the two CH₃ groups; 9.20 μ for C—O—C and 13.32 μ for *o*-substituted aromatic ring) and nuclear magnetic resonance spectrum (Table I) indicates that fraction 1 is di-*o*-xylyl methyl ether. The molecular weight, as determined by the method of Neumeier,¹⁶ was 235 (theor. for C₁₆H₂₀O, 240).

In a control experiment, *spiro*-di-*o*-xylylene (5.2 g.) dissolved in methanol (75 cc.) was kept at room temperature for 2 weeks. No ether was obtained and only poly-(*o*-xylylene),^{11,12} as indicated by its infrared analysis, was isolated instead (1.6 g. as solid polymer, m.p. 110-130°, inherent viscosity 0.676; and 4.0 g. as low molecular weight telomeric oil).

Reaction of *spiro*-Di-*o*-xylylene with Phenol.—*spiro*-Di-*o*-xylylene (10 g.) and phenol (25 g.) dissolved in heptane

(15) J. J. Neumeier, *Anal. Chim. Acta*, **20**, 523 (1959).

(500 cc.) were allowed to react at room temperature for 3 days. The excess heptane was removed by distillation at atmospheric pressure. The residue was distilled at 1 mm. pressure to afford four fractions: (1) 14 g. of phenol, b.p. 47°; (2) 4.7 g., b.p. 130-138°, mol. wt. 328; (3) 4.5 g., b.p. 195-196°; (4) 3 g. residue. Fraction 2 was leached with dilute aqueous NaOH leaving 2.0 g. as residue. This residue was identified by infrared analysis as 1-methyldi-benzo(a,d)cyclohepta-(1,4)-diene (XII) and was obtained in the form of white crystals (m.p. 68.5-69.5°) after one recrystallization from methanol.

The aqueous NaOH extract was acidified with dilute HCl to afford a phenolic oil. Its infrared spectrum (bands at 2.99 μ for OH; 6.22, 6.28, 6.63, 6.73 μ for aromatic; 6.90 μ for CH₂; 7.30 μ for CH₃; 8.15 μ for aromatic C—O; 12.20, 12.83, 13.34 and 13.54 μ for complex aromatic substitution) and its molecular weight indicated that this was a telomeric mixture of *o*- and *p*-isomers of di-*o*-xylyl phenol (XI_f). Fractions 3 and 4 were mixtures of telomeric phenols and phenyl ethers as indicated by their respective infrared spectra.

The experiment was repeated in the absence of a mutual solvent and a mixture of telomeric ethers and phenols was again obtained, but no evidence for the formation of the dibenzocycloheptadiene was detected.

Copolymerization of *spiro*-Di-*o*-xylylene and Formaldehyde.—A mixture of trioxane (5 g.), *spiro*-di-*o*-xylylene (2.5 g.), ether (50 cc.) and a catalytic amount of H₂SO₄ (3 drops) was allowed to react at room temperature for 3 days. The excess solvent was removed by evaporation. The residue was dissolved in a minimum amount of benzene and the solution was added dropwise to a 20-fold by volume excess of methanol to afford 2 g. of insoluble polymer which was separated by filtration. Its infrared spectrum (bands at 2.99 μ for OH end-groups; 5.82 μ C=O end-group; 6.24, 7.33 and 6.71 μ for aromatic; 6.90 for CH₂; broad band 9.0 to 10.5 μ for C—OC; 13.35 μ for *o*-substituted aromatic ring) molecular weight (1600) and elemental analysis (77.0% C; C; 6.6% H) indicated that the product was a polyether of formaldehyde and di-*o*-xylylene units having carbonyl or hydroxyl end groups.

Similar results were obtained when formaldehyde vapor, generated by thermal decomposition of paraformaldehyde, was condensed into a solution of *spiro*-di-*o*-xylylene in hexane containing a trace amount of formic acid. Formaldehyde was liberated when the copolymer was subjected to thermal degradation.

Acknowledgments.—The author is indebted to Dr. J. J. McBrady for interpretation of the infrared and nuclear magnetic resonance data.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, STANFORD, CALIF.]

Relative Inversion and C1 Acetoxy Exchange Rates During Anomerization of Acetylated 2-Deoxy-D-glucose. The Ionic Mechanism¹

BY WILLIAM A. BONNER

RECEIVED AUGUST 29, 1960

Previous studies of the acid-catalyzed anomerization of acetylated aldopyranoses by both polarimetric and radiochemical techniques have led to an ambiguity, in that the data are amenable to interpretation in terms of either an S_N1 or S_N2 mechanism. The origin of this ambiguity lies in the participation of the C2 acetoxy group in the anomerization process for all 1,2-*trans* anomers previously studied. A distinction between these two mechanisms should be possible by employing the anomers of tetra-*O*-acetyl-2-deoxy-D-glucopyranose, where such C2 acetoxy participation is precluded. These anomers, labeled in the C1 acetoxy group with carbon-14, have been prepared and subjected to anomerization and C1 acetoxy exchange rate studies under several conditions. In all cases the C1 acetoxy exchange rate exceeded the inversion rate by a factor of 1.8-3.7, an observation which accords with the predictions of an ionic S_N1 mechanism and precludes the intervention of an S_N2 mechanism.

The action of a Lewis acid catalyst in acetic anhydride and acetic acid on pure anomers of acetylated aldopyranoses induces equilibration of

the latter to a mixture in which the α -anomer usually predominates.² This anomerization reaction, which is of considerable preparative utility, has been studied mechanistically in recent years by

(1) The author is indebted to the National Science Foundation for its generous support of a portion of this investigation.

(2) W. A. Bonner, *J. Am. Chem. Soc.*, **81**, 1448 (1959).