# The Chemistry of Xylylenes. XII. Reactions of Spirodi-*o*-xylylene That Occur with Retention of the Spirostructure

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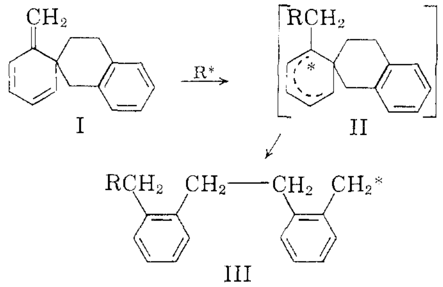
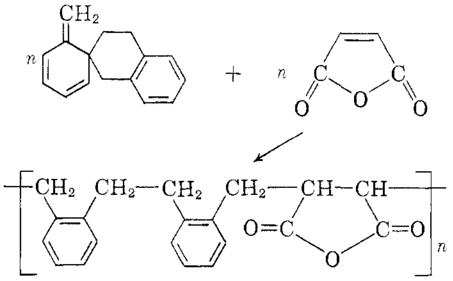
The synthesis of spirodi-*o*-xylylene (I) was reported in a previous publication.[1] The compound undergoes reaction by either free radical[1,2] or cationic mechanisms.[3] In both reaction sequences, however, addition of the attacking moiety occurs at the *exo*-methylene group to produce an unstable spiro intermediate (II) which undergoes aromatization affording a linear di-*o*-xylyl intermediate (III), the fate of which is determined by the choice of experimental conditions.



Thus, homopolymer or copolymers, and monofunctional or difunctional derivatives, of di-*o*-xylylene were prepared selectively by reaction with the appropriate reagents.[1-3] When reaction was carried out cationically, the di-*o*-xylyl cation intermediate (III) underwent intramolecular or intermolecular aromatic substitution by proper control of the reaction conditions.[3]

The structure of spirodi-*o*-xylylene suggests that it might be possible to effect Diels-Alder addition across the conjugated endo-diene system[4] despite the ease with which ring opening to di-*o*-xylylene occurs. In this respect, maleic anhydride appeared to be an interesting dienophile, as it is known that it is capable of undergoing Diels-Alder addition[4] as well as copolymerization[5] to give high molecular weight products.



When spirodi-*o*-xylylene was added at room temperature to maleic anhydride in benzene an exothermic reaction occurred and the product was isolated subsequently as the free acid in the form of a gummy mass that slowly solidified to a friable solid. Copolymer was not isolated and all of the reaction product appeared to be Diels-Alder adduct, IV, as shown in Fig. 1. The compound was identified by its elemental analysis, molecular weight, neutral equivalent, infrared spectrum, and NMR spectrum (Table I). Samples of the dicarboxylic acid (V) were reconverted to the anhydride (IV) by vacuum sublimation or by prolonged heating at 80°. The dicarboxylic acid and the corresponding anhydride were converted to the dimethyl ester by reaction at reflux temperature in methanol containing a trace amount of sulfuric acid. The assigned structures for these derivatives were verified by their respective infrared and NMR spectra (Table I). These results demonstrated that reaction occurred in every case with retention of the spiro configuration as shown in Fig. 1.

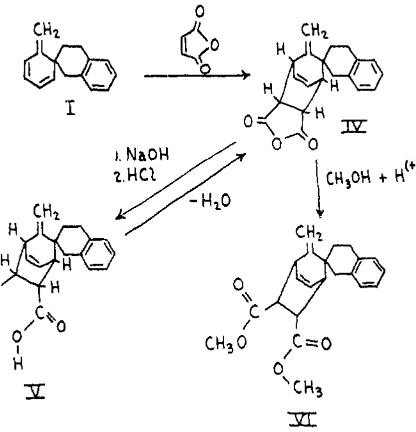


Figure 1

Spirodi-*o*-xylylene was allowed to react at room temperature with dimethyl acetylenedicarboxylate, and again the corresponding Diels-Alder adduct (VII) was obtained in good yield. The spiro configuration was retained when compound VII was reduced with hydrogen in the presence of Raney nickel. Only two of the three possible hydrogen equivalents were taken up as a result of the reduction. The infrared spectra and NMR data (Table I) indicate that the *exo*-$CH_2=$ was converted to $CH_3$ and that the residual double bond was conjugated with the ester carbonyl groups. Similarly, the spiro configuration was also retained intact when spirodi-*o*-xylylene (I) was hydrogenated in the presence of Raney Nickel to afford spiro[5.5]-2,3-benz-6-methylcyclane (IX).[1]

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(1) L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961).

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

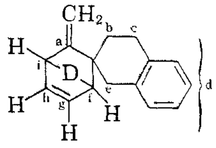
(3) L. A. Errede, *J. Am. Chem. Soc.*, **83**, 959 (1961).

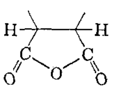
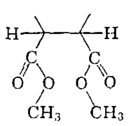
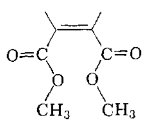
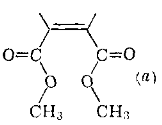
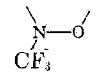
(4) M. C. Kloetzel, *Org. Reactions*, **4**, 1 (1948); H. L. Holmes, *Org. Reactions*, **4**, 60 (1948); L. W. Butz, *Org. Reactions*, **5**, 253 (1950).

(5) M. C. deWilde and G. Smets, *J. Polymer Sci.*, **5**, 253 (1950).

TABLE I

NUCLEAR MAGNETIC RESONANCE DATA[13] FOR SPIRODI-*o*-XYLYLENE AND SOME OF ITS DIELS-ALDER ADDUCTS



| Compound | D | a | b | c | d | e | f | g | h | i | H Atoms on D |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | None | 5.07 | 8.1 | 7.2 | 3.0 | 7.2 | 4.2 | 4.2 | 4.2 | 4.2 | |
| IV |  | 4.97<br>5.27 | 8.3 | 7.2 | 2.97 | 6.47 | 7.2 | 3.68 | 3.68 | 6.77<br>7.02 | 7.20 for<br>H<br>\|<br>C—C=O |
| VI |  | 5.07<br>5.38 | 8.3 | 7.2 | 3.00 | 7.2 | 7.2 | 3.8 | 3.8 | 7.2 | 6.34 + 6.60 for $CH_3O$; 7.2 for<br>H<br>\|<br>C—C=O |
| VII |  | 4.93<br>5.32 | 8.3 | 7.3 | 2.98 | 7.3 | 5.6 | 3.5 | 3.5 | 5.6 | 6.28 + 6.44 for $CH_3O$ |
| VIII |  | 9.17[a] | 8.3 | 7.2 | 3.06 | 7.2 | 7.2 | 8.3[a] | 8.3[a] | 7.2 | 6.25 + 6.41 for $CH_3O$ |
| X<br>or<br>XI |  | 4.90<br>5.16 | 8.2 | 7.3 | 2.96 | 7.3 | 6.1 | 3.5 | 3.49 | 6.1 | |

[a] *Exo*-double bond at "a" and double bond at h-g converted to the corresponding saturated bonds by hydrogenation.

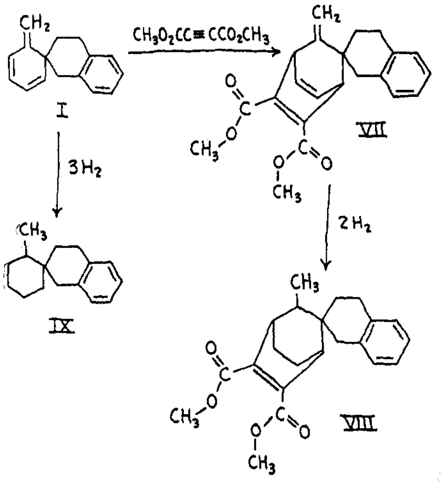
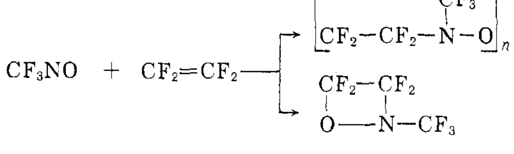


Figure 2

It is known that nitrosobenzene can undergo Diels-Alder addition[6-9] or copolymerization[10] depending upon the experimental conditions and the choice of comonomer. Thus, nitrosobenzene reacts with butadienes[6-9] to afford the corresponding Diels-Alder adduct, but it copolymerizes with *p*-xylylene to afford high molecular weight polymer.[10] Similarly, it was reported that nitrosotrifluoromethane reacts readily with tetrafluoroethylene to give selectively either high molecular weight copolymer[11] or perfluoromethyloxazetidine[12]:



$$CF_3NO + CF_2{=}CF_2 \longrightarrow \begin{cases} \left[CF_2{-}CF_2{-}\overset{CF_3}{\overset{|}{N}}{-}O\right]_n \\ \begin{array}{l} CF_2{-}CF_2 \\ \,|\qquad\quad | \\ O{-}{-}N{-}CF_3 \end{array} \end{cases}$$

Neither a copolymer nor an oxazetidine was obtained, however, when spirodi-*o*-xylylene was caused to react at room temperature with nitroso-

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(6) O. Wichterle and M. Kolinsky, *Chem. Listy*, **47**, 1787 (1953); *Chem. Abstr.*, **47**, 4342 (1953).

(7) S. Kojima, *J. Chem. Soc. Japan* (*Ind. Chem. Section*), **57**, 371 and 819 (1954); *Chem. Abstr.*, **49**, 10966f (1955); *Chem. Abstr.* **50**, 4903a (1956).

(8) Y. A. Arbuzov and T. A. Pisha, *Doklady Akad. Nauk.*, **116**, 71 (1957); *Chem. Abstr.*, **52**, 6357d (1958).

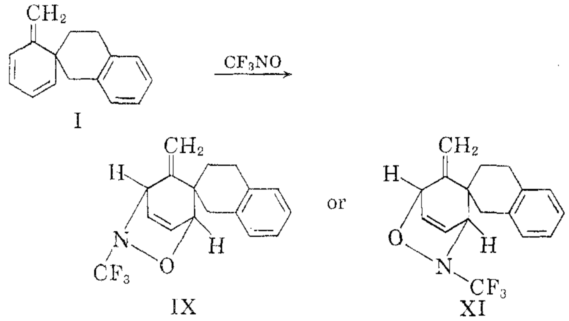
(9) Y. A. Arbuzov and T. A. Pisha, *Proc. Acad. Sci. U.S.S.R.*, **116**, 817 (1958).

(10) L. A. Errede and J. M. Hoyt, *J. Am. Chem. Soc.*, **82**, 436 (1960).

(11) G. H. Crawford, D. E. Rice, and J. C. Montermoso, Abstract of Papers presented at 137th Meeting, American Chemical Society, p. 7L (1960).

(12) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.* 1881 (1955).

trifluoromethane. Instead, the corresponding Diels-Alder adduct was obtained in good yield. This adduct is a white crystalline compound that melts at 142.5–143.0°. Its infrared and NMR spectra verified that Diels-Alder addition had occurred across the endo-diene system but it was not possible to differentiate between X or XI as the correct structure for the reaction product.



I

IX or XI

Furthermore, addition of a dienophile to the conjugate endo-diene system of spirodi-*o*-xylylene can occur either *endo* or *exo* to the methylene bridge. The NMR data and the sharpness of the melting point of the reaction products suggest that predominantly one form may have been produced. These problems of stereoisomerism have not as yet been resolved.

## EXPERIMENTAL

*Maleic anhydride adduct* (IV) *and its dimethyl ester* (VI). Spirodi-*o*-xylylene (8 g. crude) was added to room temperature to maleic anhydride (8 g.) dissolved in benzene (about 20 cc.). The reaction was slightly exothermic and the temperature increased from room temperature to about 40°. The solution was cooled to room temperature and then extracted with dilute aqueous sodium hydroxide. The aqueous alkaline extract was acidified with dilute hydrochloric acid and a white tacky product precipitated from solution. This was redissolved in dilute base and again a tacky product was obtained on acidification. The material slowly solidified to a friable solid (5.6 g., m.p. 70–85°). Its infrared spectrum indicated the presence of *o*-xylene (bands at 6.31, 5.58, and 13.43 μ), *exo*-methylene (band at 11.22 μ) and carboxylic acid groups (broad band at 3–4 μ, band at 5.83, broad at 10.5–11 μ). Its neutral equivalent was 166 (Calcd. for $C_{20}H_{20}O_4$ : 162). A small sample was dehydrated by vacuum sublimation thereby converting the free acid groups to the anhydride (bands at 5.39, 5.65 μ) as indicated by its infrared spectrum. The product now melted at 95–97°.

*Anal.* Calcd. for $C_{20}H_{18}O_3$: C, 78.41; H, 5.89; mol. wt. 306.36. Found: C, 77.7; H, 6.1; mol. wt. 307.

The NMR data[13] for the anhydride (Table I) support structure IV.

A sample (1 g.) of the product melting at 70–85° was dissolved in 50 cc. methanol to which 4 drops of sulfuric acid was added. The mixture was kept at reflux temperature for 2 days. The excess solvent was removed by evaporation at room temperature. The residue was dissolved in carbon tetrachloride, washed with water, dried, and again evaporated to dryness leaving an amber oil as residue.

*Anal.* Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.87; mol. wt. 352.4. Found: C, 74.5; H, 7.1; mol. wt. 387.

Its infrared spectrum (no broad absorption at 3–4 μ for acid OH, sharp bands around 3.42 μ for CH; 5.75 μ for ester C=O; 6.33, 6.66, 13.88 μ for *o*-xylene structure, 6.08 μ for C=C; 11.28 μ for *exo*-methylene) is consistent with compound VI. The NMR data (Table I) are consistent with the anticipated dimethyl ester derivative of the Diels-Alder adduct of maleic anhydride and spirodi-*o*-xylylene (VI).

*Dimethyl acetylene dicarboxylate adduct* (VII). Crude spirodi-*o*-xylylene (6 g.) dissolved in dimethyl acetylenedicarboxylate (10 g.) was allowed to react at room temperature for 2 days and then separated by distillation at 0.17 mm. into four fractions: (1) 5.0 g., b.p. 40–43°, (2) 1.5 g., b.p. 110–115°, (3) 4.5 g., b.p. 182–195°, (4) 1.5 g. residue, b.p. 185°. Fraction (1) was identified as starting material by its infrared spectrum. Fraction (2) was a mixture of cyclodi-*o*-xylylene (m.p. 112.0–112.5°) and bis(*o*-methylbenzyl)-ether (m.p. 45–50) also identified by infrared analyses. Fraction (3) was crystallized from methanol and then from heptane to afford the Diels-Alder adduct (VII) in the form of fine white needles (m.p. 123–124°).

*Anal.* Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33; mol. wt. 350.4. Found: C, 75.1; H, 6.2; mol. wt. 365.

Its infrared spectrum (bands at 5.78, 5.87 μ for ester C=O; 6.12 μ for C=C; 11.23 μ for *exo*-methylene and 6.62, 6.70, 13.37 μ for *o*-xylene group) is consistent with compound VII. Its NMR spectrum data (Table I) also verified that the compound was the anticipated Diels-Alder adduct (VII).

*Hydrogenation of compound* VII. The Diels-Alder adduct (VII, m.p. 123–124°) obtained *via* reaction of dimethyl acetylenecarboxylate with spirodi-*o*-xylylene was dissolved in benzene and then hydrogenated in an Aminco Bomb at room temperature using molecular hydrogen at 67 atm. and Raney Nickel catalyst. About 2 molar equivalents of hydrogen were consumed as indicated by the drop in pressure. The product was purified by distillation at 0.14 mm. pressure (b.p. 150–160°).

*Anal.* Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39; mol. wt. 354. Found: C, 74.7; H, 7.4; mol. wt. 360.

Its infrared spectrum verified the formation of a $CH_3$ group, as indicated by the appearance of a band at 7.36 μ and the corresponding large decrease of the *exo*-methylene band at 11.23 μ. Absorption bands associated with the disubstituted dimethyl maleate group (5.82, 6.10 μ) were still present. The NMR data (τ values: 3.06, 6.25, 6.41, 7.2, 8.32, 9.17) and the infrared spectrum are consistent with structure VIII.

*$CF_3NO$ Diels-Alder adduct* X *or* XI. Spirodi-*o*-xylylene (5 g.) and nitrosotrifluoromethane (1.7 g.) were sealed at −78° in a 25-cc. evacuated ampoule. The mixture was allowed to react heterogeneously at room temperature with continuous rocking for 3 days. During this time the characteristic blue color associated with nitrosotrifluoromethane disappeared completely from the gas phase. The reaction mixture was dissolved in heptane and then chilled to −78°. A white solid precipitated from solution. The precipitate (1.3 g., m.p. 130–140°) was purified by recrystallization from a methanol water solution to afford the adduct in the form of white needles (m.p. 142.5–143.0°).

*Anal.* Calcd. for $C_{17}H_{16}ONF_3$: C, 66.46; N, 4.56; F, 18.55; mol. wt. 307. Found: C, 66.7; N, 4.38; F, 18.4; mol. wt. 311.

Its infrared spectrum (bands at 11.13 μ for *exo*-methylene; bands 6.25, 6.33, 6.69 μ and in the region 13.1–13.35 μ for *o*-xylene group; strong absorption 8.0–8.8 μ for nitrosotrifluoromethane) and its NMR data (Table I) are consistent with structures X or XI.

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(13) The NMR data refer to τ values as described by G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).