[Contribution from the Chemical Laboratories of the Polytechnic Institute of Brooklyn]

REACTIVITY OF TETRAPHENYL-*o*-XYLYLENE-α,α'-DIOL AS RELATED TO THAT OF TETRAPHENYLPHTHALIC ANHYDRIDE

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The refractory behavior of tetraphenylphthalic acid, its anhydride, and its esters with respect to esterification, saponification, and hydration has been tentatively attributed to the steric effect of the *o*-phenyl rings, although the ethyl ester trans-esterifies with ease (1). The purpose of this investigation was to prepare tetraphenyl-*o*-xylylene-α,α'-diol to determine whether the steric effect extended to reactions taking place one atom removed from the ring.

The most attractive procedure was the Diels-Alder reaction between tetracyclone and 2-butyne-1,4-diol patterned after similar known reactions (2–6, inc.). In refluxing *p*-cymene the reaction between tetracyclone and butyne-1,4-diol gives colorless crystals, m.p. 249.5–250°, in 59% yield. Carbon monoxide is evolved in the reaction. The product is soluble in organic solvents, but insoluble in water. It forms a 1:1 solvate with acetone, which is lost upon drying. Analysis for carbon and hydrogen was in accord with the expected values and the compound was assigned the structure III (Figure 1).

Proof of structure was attempted by oxidation to known tetraphenylphthalic acid with chromium (VI) oxide in acetic acid. However, only extensively degraded, unidentified products were isolated. Accordingly, reduction of tetraphenylphthalic anhydride (I) with one or three moles of lithium aluminum was attempted. In both cases, the product (II) melted at 249.5–250°; but a mixture melting point with the Diels-Alder product was depressed. Further differences were that it did not form a solvate with nor crystallize easily from acetone, that it was relatively insoluble in pyridine, and crystallized readily as plates from ethanol in contradistinction to III. III formed needles or rods from benzene while II formed cubes from this solvent. Analysis showed four fewer hydrogen atoms. Based on this evidence two possibilities were considered; namely, tetraphenyl-*o*-phthalaldehyde and tetraphenylphthalide (II).

Reaction of II with 2,4-dinitrophenylhydrazine gave only unreacted starting materials. II did not react with acetic anhydride in pyridine. Comparison of the infrared spectra (Figure 2) of the two compounds showed for II carbonyl absorption in a strained 5-membered ring and for III the hydroxyl group as the only oxygen function present. Therefore, II is most probably tetraphenylphthalide.

Although direct reduction of I to III was not possible under the conditions employed, II was easily reduced to III as shown by the melting point, 249.5–250°, and lack of depression in a mixture melting point with the Diels-Alder

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[1] Taken from the B. S. theses of E. F. B. (June 1953) and A. G. F. (June 1950).

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product. Likewise, both diols readily formed identical diacetates under the same conditions.

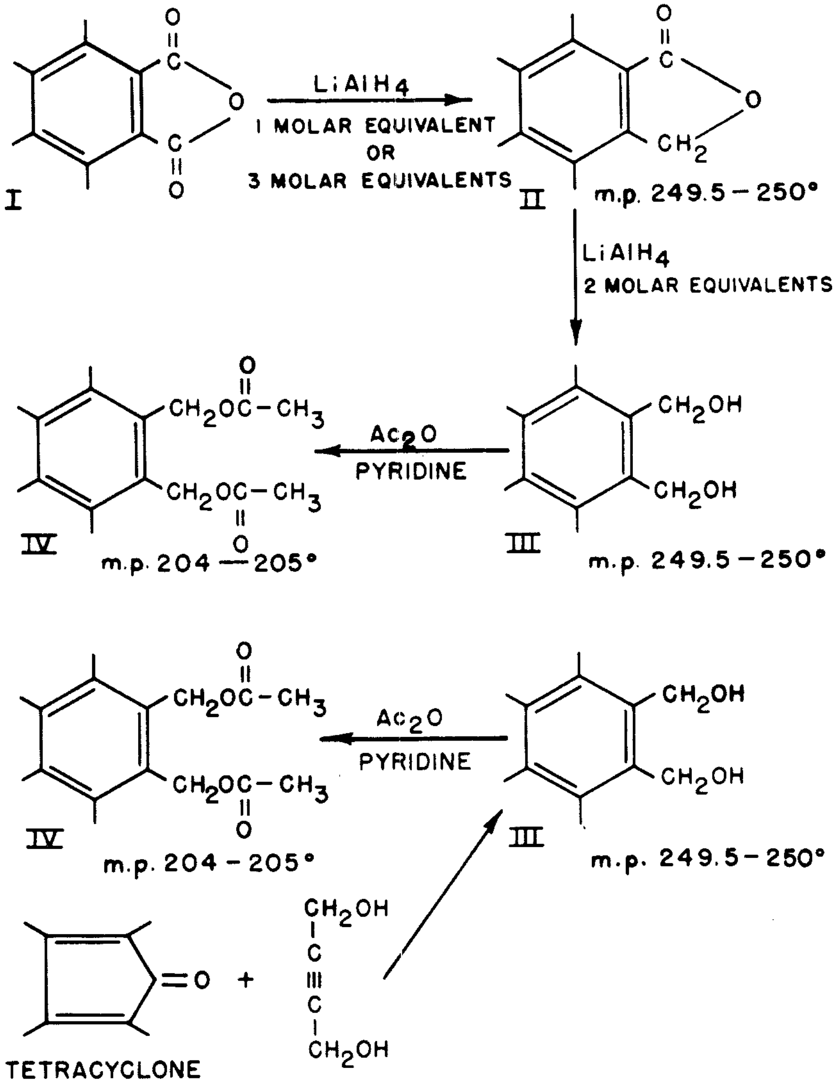

FIG. I. REACTION SEQUENCE. (EACH LINE SHOWN ON THE CENTRAL RING REPRESENTS A PHENYL RING)

Since III readily forms a diacetate, the steric factors (or others) do not operate at an atom once removed from the central ring.

It is interesting to compare the reduction of tetraphenylphthalic anhydride and tetraphenylphthalide with similar experiments reported in the literature (7–19). The direct reduction of an anhydride to a dialcohol is well known. An excess

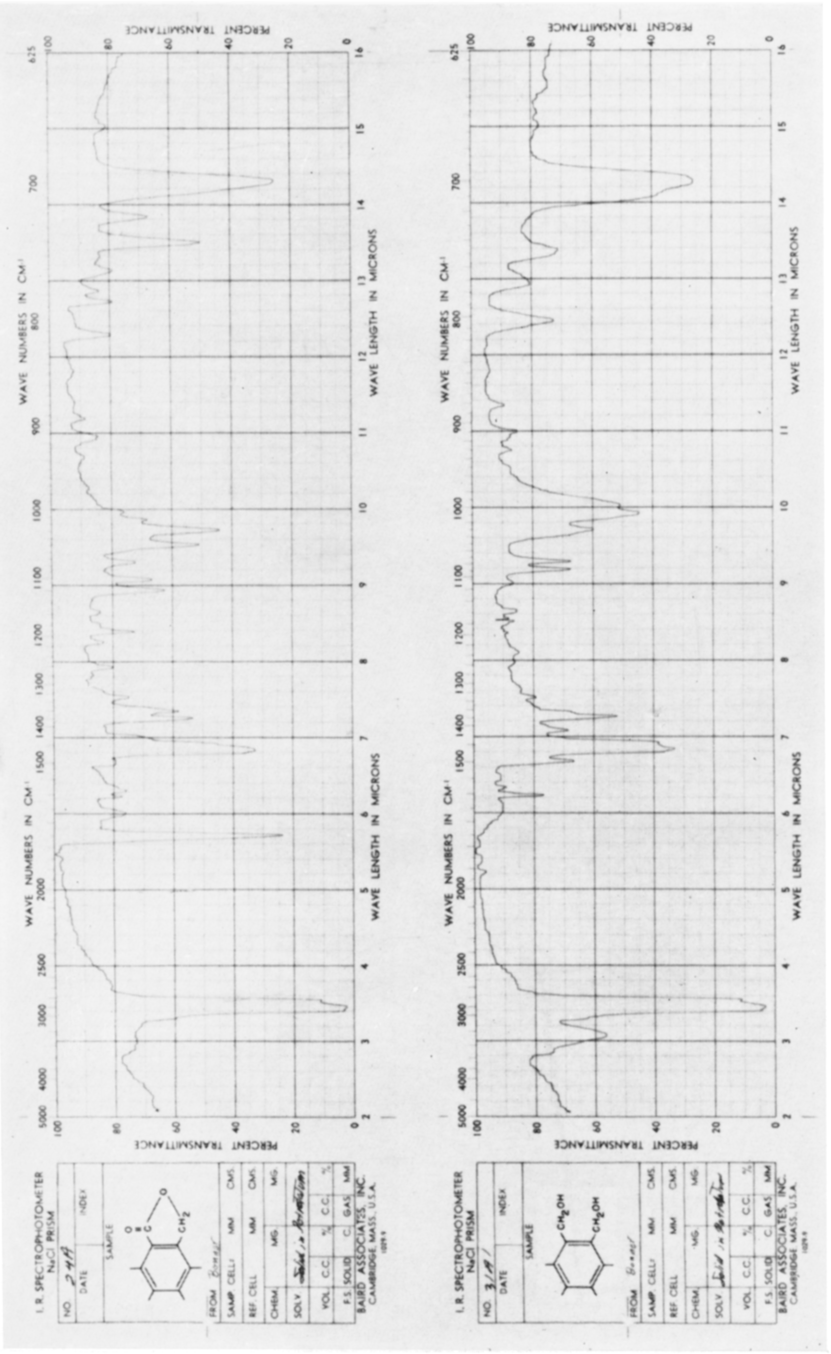

FIG. 2. INFRARED SPECTRA OF TETRAPHENYLPHTHALIDE AND TETRAPHENYL-o-XYLYLENE-α,α'-DIOL.

or an equivalent quantity of lithium aluminum hydride has been reported to give only a mixture of phthalyl alcohol and unreacted phthalic anhydride (16), whereas the inverse addition has given phthalide (19). A dependence upon temperatures has also been noted; namely, that naphthalene-1,2-dicarboxylic acid anhydride gives only the lactone of 2-hydroxymethyl-1-naphthoic acid in ethyl ether (14). The lactone is not reduced upon further treatment under these conditions. In boiling *n*-butyl ether, the anhydride does give the corresponding diol directly.

The unusual feature of the reduction of tetraphenylphthalic anhydride is the inability to obtain the diol directly although the intermediate is reduced in good yield under the same conditions to the diol. An explanation is not readily forthcoming although steric factors may play a part (15, 16). This work is being continued.

EXPERIMENTAL

Starting materials. 2-Butyne-1,4-diol, generously supplied by the General Aniline and Film Corporation, melted at 57–58° (ethyl acetate). *p*-Cymene was washed repeatedly with cold, concentrated sulfuric acid until no color formed on shaking, and then successively with water, 10% sodium carbonate, finally with water, dried over calcium chloride and distilled, b.p. 176–177°. Tetraphenylphthalic anhydride, m.p. 286–287°, was prepared according to M. E. Synerholm (21). Sublimation gave a product, m.p. 288°.

Tetraphenyl-o-xylylene-α,α'-diol (III) from the Diels-Alder reaction. A solution of 7.69 g. (0.020 mole) of tetracyclone (20) and 1.72 g. (0.020 mole) of 2-butyne-1,4-diol in 30 ml. of *p*-cymene was refluxed for five hours. Additional 2-butyne-1,4-diol (0.86 g.) was then added and the solution was refluxed six hours longer (total 11 hours). At this time the characteristic purple-red color of tetracyclone had disappeared and carbon monoxide was no longer evolved. The solution was washed into a flask with 70 ml. of benzene, 200 ml. of water was added and the mixture was distilled with steam to remove solvents. Cooling gave 8.6 g. of a yellow solid. Crystallization of 5 g. of this crude product from acetone (Nuchar) gave 3.4 g. (58% based on tetracyclone taken) of large yellow crystals.

Anal. Calc'd for $C_{32}H_{26}O_2 \cdot CH_3COCH_3$: acetone, 11.6. Found (by loss in weight on drying at 100° at 25 mm.): 12.0.

For analysis the product was recrystallized from acetone and dried, m.p. 249.5–250° (colorless crystals).

Anal.[3] Calc'd for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92.
Found: C, 86.51; 86.57; H, 5.87, 5.84.

Starting with 3.84 g. (0.010 mole) of tetracyclone and 6.88 g. (0.080 mole) of 2-butyne-1,4-diol, only 0.83 g. of product (1.88 mmole, 19%) was isolated.

Tetraphenyl-o-xylylene-α,α'-diol diacetate. Acetic anhydride (8 g., 0.101 mole) was added to a solution of 2.00 g. (4.52 mmole) of tetraphenyl-*o*-xylylene-α,α'-diol in 20 ml. of pyridine (dried over potassium hydroxide, b.p. 115–116°). After refluxing for 5 minutes, the reaction mixture was poured into 75 g. of ice and water, filtered, and dried at 100° to give 2.12 g. (4.03 mmole, 89%) of crude diacetate, m.p. 204–205°. Recrystallization from ethanol gave colorless crystals, m.p. 204–205°.

Anal.[3] Calc'd for $C_{36}H_{30}O_4$: C, 82.10; H, 5.74.
Found: C, 81.88; H, 5.82.

Attempted oxidation of tetraphenyl-o-xylylene-α,α'-diol. One gram of the diol in a solution of 2 g. of chromium (VI) oxide in 35 ml. of acetic acid was allowed to stand one hour during which time the red color became green. Dilution with water, treatment with hot

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[3] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

5% sulfuric acid, and then 5% potassium hydroxide left a brown-colored product which had not melted at 325°. Recrystallization from glacial acetic acid gave a tan product, m.p. 257–259°, which depressed the m.p. of tetraphenylphthalic anhydride. An attempt to chromatograph the brown product gave a quantity of yellow-brown powder, m.p. 244.5–256°, and some melting at 260–261°. These products depressed the melting point of tetraphenylphthalic anhydride and were not examined further.

Reduction of tetraphenylphthalic anhydride with one mole of lithium aluminum hydride. The technique of using a Soxhlet extractor to add the anhydride to the ether solution of lithium aluminum anhydride was used (12). From 6.78 g. (0.015 mole) of tetraphenylphthalic anhydride in the thimble, 0.6 g. (0.016 mole) of crushed lithium aluminum hydride in 500 ml. of ethyl ether and seven hours of reflux, a slightly yellow and turbid solution formed. Water (5 ml.) was cautiously added through the condenser. After the vigorous reaction had subsided, the mixture was poured into 200 g. of ice and 100 ml. of 10% sulfuric acid. Separation and distillation of the solvent left a white powder which, after two recrystallizations from 95% ethanol, yielded 5.59 g. (0.013 mole, 86%) of small white plates, m.p. 249.5–250°.

Anal.[4] Calc'd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06.
Found: C, 87.08, 87.48; H, 5.22, 5.29.

A mixture melting point of this product with tetraphenyl-*o*-xylylene-α,α'-diol was depressed, m.p. 240–242°. An attempt to form the 2,4-dinitrophenylhydrazone (22) with the product obtained in this paragraph was unsuccessful.

A separate experiment using the same procedure and starting with 1.15 g. (2.6 mmole) of tetraphenylphthalic anhydride and 0.3 g. (8.0 mmole) of lithium aluminum hydride gave 0.69 g. of the same product, m.p. 249.5–250°, which again depressed the melting point of tetraphenyl-*o*-xylylene-α,α'-diol, m.p. 241–245°.

Anal.[4] Calc'd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06.
Found: C, 87.50; H, 5.18.

Reduction of tetraphenylphthalide. The reduction was performed as before starting with 1.0 g. (2.4 mmole) of tetraphenylphthalide and 0.2 g. (4.8 mmole) of lithium aluminum hydride, 500 ml. of ethyl ether, and refluxing for 1.5 hours. After adding 5 ml. of water portionwise through the condenser, the mixture was added to 200 g. of ice and 100 ml. of 10% sulfuric acid. Separation and distillation of the solvent gave a white powder. Purification was effected in a liquid chromatogram on alumina (F-20, Aluminum Company of America) using benzene as the solvent and 10% ethanol in benzene as the eluant. After distillation of the solvent, the remaining solid was recrystallized from acetone, giving 0.56 g. (1.3 mmole, 53%) of colorless cubes, m.p. 249.5–250° (rods from benzene). A mixture melting point of this product with tetraphenyl-*o*-xylylene-α,α'-diol was not depressed, m.m.p. 249.2–249.5°. It did depress the melting point of the starting material, m.m.p. 240–242°.

Anal.[4] Calc'd for $C_{32}H_{26}O_2$: C, 86.85; H, 5.92.
Found: C, 86.57; H, 5.49.

Tetraphenyl-o-xylylene-α,α'-diol diacetate from reduction product of tetraphenylphthalide. Prepared as before starting with 0.20 g. of diol, the diacetate was obtained in 87% yield, m.p. 204–205°. A mixture melting point with the diacetate obtained from the Diels-Alder reaction product was not depressed, m.p. 204–205°.

Anal.[4] Calc'd for $C_{36}H_{20}O_4$: C, 82.10; H, 5.74.
Found: C, 82.07; H, 5.81.

SUMMARY

The Diels-Alder reaction between tetracyclone and 2-butyne-1,4-diol gives tetraphenyl-*o*-xylylene-α,α'-diol. Proof of structure was obtained by reduction

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[4] Analysis by Dr. K. Ritter, Basel, Switzerland.

with lithium aluminum hydride of tetraphenylphthalic anhydride to tetraphenylphthalide and thence to tetraphenyl-*o*-xylylene-α,α'-diol. The diacetate was readily formed in good yield showing that the phenyl groups did not interfere greatly with this reaction. Certain peculiarities of the reduction of tetraphenylphthalic anhydride have been brought out.

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