Cyclic Acetylenes. II. Attempted Synthesis of Cyclic Terephthalate of o, o′-Dihydroxydiphenyldiacetylene

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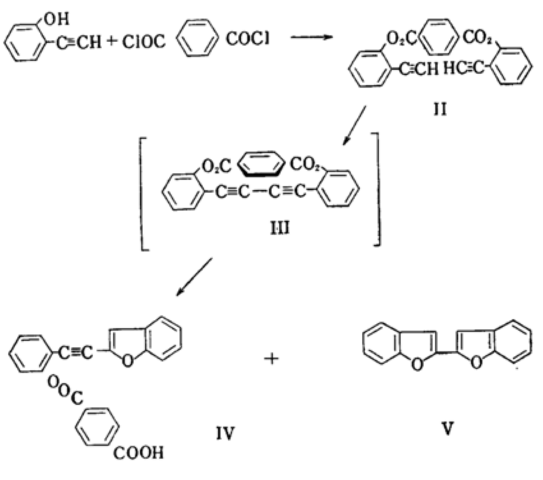
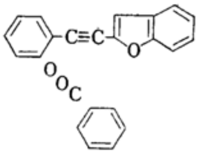
Cyclic terephthalate of *o, o′*-dihydroxydiphenyldiacetylene (III) may offer a suitable model substance for the investigation of transannular phenomena between the π-electron system of the benzene nucleus of terephthalic acid residue and that of diacetylenic linkage, because the scale model of this molecule indicates that the molecule is rigid, holding the terephthalate group closely in parallel with the diacetylenic linkage.

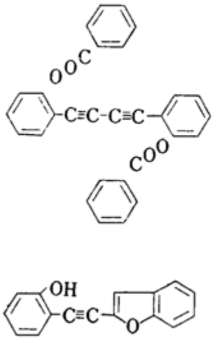
The synthesis of III has been attempted according to the following series of reactions. Di-2-ethynylphenyl terephthalate (II) was obtained in good yield by the reaction of *o*-hydroxyphenylacetylene (I)[1] with terephthaloyl chloride in aqueous acetone in the presence of sodium hydroxide.



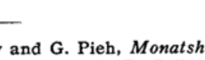
The oxidative coupling according to the Eglinton's procedure[2] at a reaction temperature of 55°C resulted in 2-(2′-benzofuranylethynyl)-phenyl hydrogen terephthlate (IV) in 5% yield. 2, 2′-Dibenzofuranyl (V)[3] and IV were isolated from the reaction products in 15 and 3% yield, respectively, when the reaction was carried out at a temperature of 60°C.



VI



VII



VIII

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[1] V. Prey and G. Pieh, *Monatsh. Chem.*, **80**, 790 (1949).

[2] G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737.

[3] F. Toda and M. Nakagawa, This Bulletin, **32**, 514 (1959).

The ultraviolet spectra of VIII³⁾ have three maxima in the long wavelength region (290～340 mμ), whereas the spectra of VI and di-2-(2′-benzofuranylethynyl-phenyl succinate⁴⁾ have only two peaks in the same region lacking the maximum at ca. 290 mμ indicating that the presence of the free hydroxyl group is responsible for the appearance of the maximum at ca. 290 mμ in the ultraviolet spectra of 2-phenylethynylbenzofurane type compounds. On the other hand, ester derivatives of *o, o*′-dihydroxydiphenyldiacetylene such as VII and *o, o*′-diacetoxydiphenyldiacetylene have always three λ_{max} in the long wavelength region. The ultraviolet spectrum of IV is closely related to that of VI lacking the absortion near 290 mμ (cf. Table I; Figs. 1 and 2). The infrared spectrum of IV indicates the presence of a carboxyl group (ν_{OH}, 2655, 2520 cm^{-1}; ν_{CO}, 1696 cm^{-1}) and ester group (ν_{CO}, 1735 cm^{-1}). From these findings the structure of hydrogen terephthalate of VIII was assigned to IV. Presumably internal strains resulting from steric or a dipolar replusion between the terephthalate group and the diacetylenic bond caused the cleavage of one or both of the ester linkage of III yielding IV or V. The same type of fission of ester linkage during the course of intramolecular oxidative coupling of a series of dialkynyl terephthalate was recently reported by Eglinton and Galbraith⁵⁾.

TABLE I

Compound	Absorption, mμ				
IV	242 (282)			311 (253)	332 (245)
VI	230 (308)			311 (364)	332 (371)
VII	230 (815)	**275** (229)	293 (265)	311 (346)	332 (299)
II	240 (1075)	**270** (146)			
VIII	250 (79)		298 (265)	318 (297)	340 (284)

All spectra were measured in 95% ethanol. The figures in parentheses are $\varepsilon_{max}\times 10^{-2}$. The bold figures indicate shoulder.

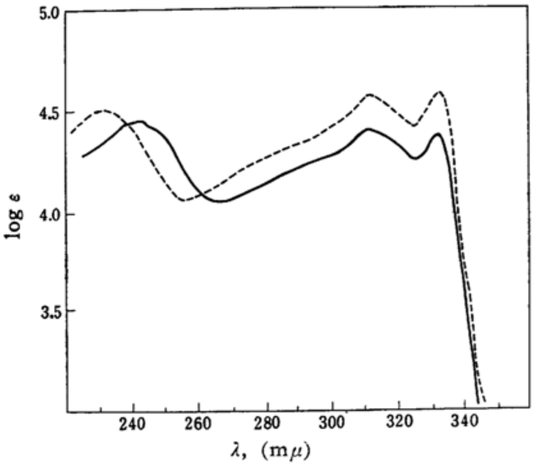

Fig. 1. The ultraviolet spectra of 2-[2′-(*p*-carboxybenzoyloxy)-phenylethynyl]-benzofurane (IV) and 2-(2′-benzoyloxyphenylethynyl)-benzofurane (VI).
——: IV ------: VI

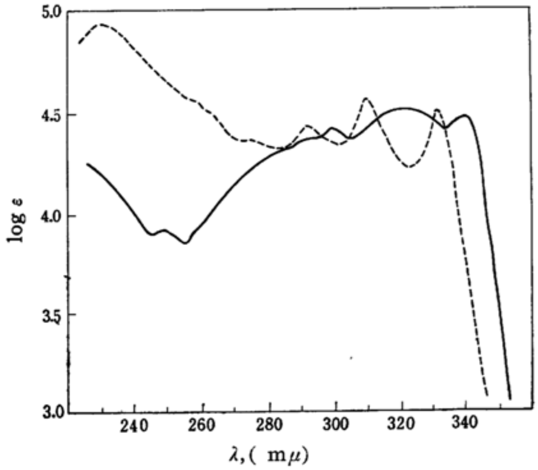

Fig. 2. The ultraviolet spectra of 2,2′-dibenzoyloxydiphenyldiacetylene (VII) and 2-(2′-hydroxyphenylethynyl)-benzofurane (VIII).
------: VII ——: VIII

It is interesting to note that the infrared spectrum of VIII shows the absorption of disubstituted acetylenic bond at 2207 cm^{-1}, but the corresponding absorption disappears in the spectra of IV, VI and VII. The low intensity of absorption in ultraviolet region of IV, as compared with that of VI, is attributable to the hypochromic influence of the more bulky terephthalic acid group as discussed in the previous paper of the series⁴⁾.

Further studies on the synthesis of cyclic derivatives of *o, o*′-dihydroxydiphenyldiacetylene containing a para-disubstituted benzene as the *o, o*′-bridging chain are now in progress.

Experimental*

2-Ethynylphenyl Terephthalate (II).—*o*-Hydroxyphenylacetylene (I, 0.6 g) was dissolved in a mixture of sodium hydroxide (0.2 g.), acetone (10 ml.)

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4) F. Toda and M. Nakagawa, This Bulletin, **33**, 223 (1960).

5) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 889.

* Not all melting points are corrected.

and water (1.0 ml.). Terephthaloyl chloride (0.5 g.) in acetone (10 ml.) was added to the solution at a time. The mixture was shaken with occasional cooling with ice. The solid deposited was filtered to yield somewhat crude II, m.p. 177°C (decomp.), 0.9 g. (97%), which was recrystallized from ethanol to give pure II, colorless leaflets, m.p. 177.5°C (decomp.).

Anal. Found: C, 78.25 ; H, 3.70. Calcd. for $C_{24}H_{14}O_4$: C, 78.68; H, 3.85%.

I.R. max., 3265 cm^{-1} ($-C\equiv CH$), 1741 cm^{-1} (ester), 1248, 1264 cm^{-1} ($=C-O-$).

II gives yellow cuprous acetylide with Ilosvay's reagent and white silver salt with ethanolic silver nitrate solution.

Oxidative Coupring of II at 55°C.—II (2.0 g.) in pyridine (50 g.) was added to the solution of cupric acetate monohydrate (15 g.) in pyridine (100 g.). The mixture was kept at 55°C for 5 hr. The precipitate was removed and most of the solvent was removed under reduced pressure. The residue was mixed with water (1000 ml.) and extracted with ether (1000 ml.). The extract was washed with a saturated solution of cupric acetate and water, successively. The dried ethereal solution was concentrated to 100 ml., and the greenish yellow precipitate formed was removed. Concentration of the filtrate yielded crude crystals. After treatment with acetone and charcoal, the crude material was repeatedly recrystallized from xylene to give pure IV, colorless needles, m.p. 222.5~223°C (decomp.), 0.1 g. (5%).

Anal. Found: C, 75.38; H, 3.86; mol. wt. (Rast), 343. Calcd. for $C_{24}H_{14}O_5$: C, 75.39; H, 3.69%; mol. wt., 382.

Oxidative Coupling of II at 60°C.—II (3.0 g.) in pyridine (150 g.) was added through a Hershberg type dropping funnel to the vigorously stirred solution of cupric acetate monohydrate (15 g.) in pyridine (150 g.) at 60°C over a period of 4 hr., and stirring was continued for additional 1.5 hr. at the same temperature. The precipitate formed was removed by filtration. After removal of pyridine in vacuo, the residue was diluted with water and extracted with benzene (400 ml.). The benzene layer was treated according to the usual manner. Evaporation of the solvent gave a greenish black solid. The solid was digested with ether, and the solvent was removed to give crystals, which were refluxed with ethanol (20 ml.) and the insoluble material was removed by filtration. The filtrate was cooled to yield crystals, which were repeatedly recrystallized from xylene to yield IV, m.p. 222.5~223°C (decomp.), 100 mg. (3%). On concentration of the mother liquor, V, colorless needles, m.p. 190~194°C, 0.3 g. (15%) was obtained, which undepressed the melting point of an authentic sample[3].

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