Intramolecular Cyclization of o, o'-Dihydroxydiphenyldiacetylene

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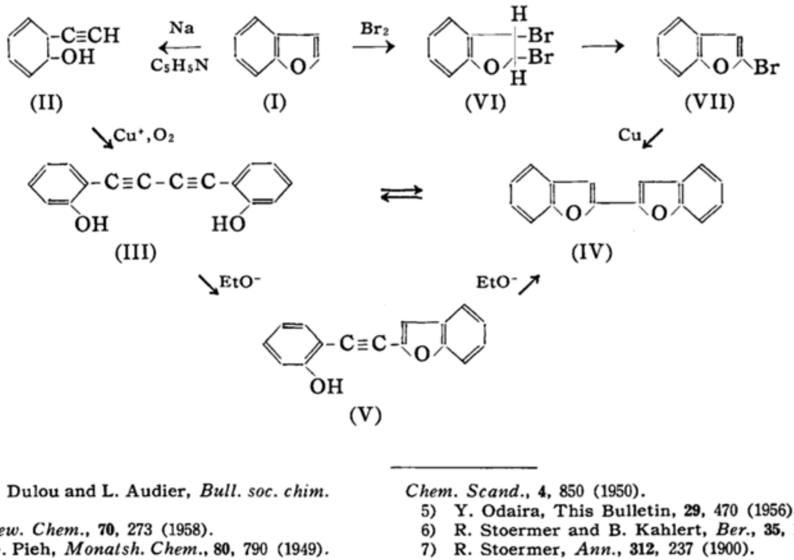
Recently the reactivity of acetylenic bond to the variety of nucleophilic reagents is well recognized, and the formation of furane ring by the intramolecular cyclization of acetylenic glycol[1] and acetylenic phenol[2] has been reported by several investigators. In the course of the studies concerning the synthesis of cyclic acetylenic compounds, the authors found that the nucleophilic addition of the hydroxyl groups in *o, o'*-dihydroxydiphenyldiacetylene (III) to the triple bonds in the same molecule yields benzofurane derivatives. The present paper reports the formation and the structure determination of the benzofurane derivatives thus obtained.

o-Hydroxyphenylacetylene (II) was prepared according to the method of Prey[3] cleaving the furane ring in coumarone I with sodium in pyridine. Oxidative coupling of II was carried out according to the procedure of Sörensen[4] yielding *o, o'*-dihydroxydiphenyldiacetylene (III) in good yield. The physical properties of III were identical with those of the previously reported values[5]. III was heated on a water bath for a few hours with diluted ethanolic sodium ethoxide solution or with aqueous sodium hydroxide solution forming a neutral material in quantitative yield. The U. V. and I. R. spectra of this substance indicate the absence of any acetylenic linkage and hydroxyl group. The presence of ether linkage was recognized from the characteristic absorption at 1250 cm^{-1}. The neutral material yielded III and an unidentified phenolic polymerized material on the treatment with sodium in pyridine at 160∼170°C. From these findings the structure of 2, 2'-dibenzofuranyl (IV) was assigned to the neutral material. This assignment was confirmed by the mixed melting point determination of the neutral material with a synthetic specimen which was obtained by the Ullmann reaction of 2-bromobenzofurane (VII). VII was prepared by the pyrolytic distillation of 2, 3-dibromocoumarane (VI)[6]. The attempt to prepare VII by the Hunsdiecker reaction of silver coumarilate VIII gave an unsatisfactory result. The products were found to be 5-bromocoumarilic acid (IX)[7] and so-called 2, 3, 7(?)-tribromocoumarone (X)[8].



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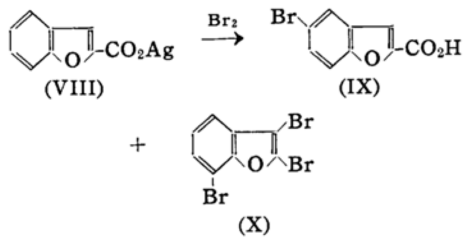
1) G. Dupont, R. Dulou and L. Audier, *Bull. soc. chim. France*, **1955**, 1078.
2) W. Ried, *Angew. Chem.*, **70**, 273 (1958).
3) V. Prey and G. Pieh, *Monatsh. Chem.*, **80**, 790 (1949).
4) T. Bruun, T. Morthei and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 850 (1950).
5) Y. Odaira, This Bulletin, **29**, 470 (1956).
6) R. Stoermer and B. Kahlert, *Ber.*, **35**, 1633 (1902).
7) R. Stoermer, *Ann.*, **312**, 237 (1900).
8) R. Stoermer and G. Calov, *Ber.*, **34**, 770 (1901).



A phenolic substance and IV was obtained when III in ethanol was refluxed for 1.5 hr. with a small amount of sodium ethoxide. The I. R. spectrum of the phenolic substance showed the characteristic absorption bands of acetylenic bond and hydroxyl group at 2207 cm^{-1} and 3380 cm^{-1} respectively. This substance was converted into IV quantitatively by the action of alkali. It is reasonable to conclude that the structure of the phenolic substance is 2-(*o*-hydroxyphenylethynyl)-benzofurane (V) formed by the half ring closure of III.

Experimental*

***o*, *o'*-Dihydroxydiphenyldiacetylene (III)**.—*o*-Hydroxyphenylacetylene3) (II, 23.6 g.) was mixed with cuprous chloride (14.5 g.), ammonium chloride (225 g.), concentrated aqueous ammonia 4.0 cc.) and water (572 cc.). The mixture was vigorously stirred at room temperature under an atomosphere of oxygen. The exothermic reaction was completed during the period of 6 hr. with the absorption of theoretical amount of oxygen. The reaction mixture was extracted with ether, washed with water and dried over anhydrous magnesium sulfate. The crude crystals obtained by the evaporation of the solvent were recrystallized from carbon tetrachloride yielding 23 g. (86%) of III, m. p. 142~143°C, colorless needles.

Anal. Found: C, 81.99; H, 4.30. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

U. V. max., 258, 276, 316 and 346 mμ ($\log \varepsilon =$ 4.13, 3.85, 4.55 and 4.39). I. R. max., 3300, 2180 and 1190 cm^{-1}.

Reaction of III with benzoyl chloride gave dibenzoyl derivative, m. p. 126~126.5°C (from ethanol), colorless needles.

Anal. Found: C, 81.58; H, 4.30. Calcd. for $C_{30}H_{18}O_4$: C, 81.43; H, 4.10%.

U. V. max., 230, 275, 311 and 332 mμ ($\log \varepsilon =$ 4.91, 4.36, 4.54 and 4.48). I. R. max., 2200, 1744, 1260 and 1240 cm^{-1}.

2, 2'-Dibenzofuranyl (IV) —III (1.0 g.) was dissolved in 30 cc. of 10~20% solution of sodium ethoxide in ethanol or of sodium hydroxide in water. No change was observed after keeping the solution overnight at room temperature. The solution was heated on a water bath for 1~2 hr. causing deposition of crystals. The cooled reaction mixture was filtered. Recrystallization from benzene or ethanol gave IV as colorless needles, m. p. 194.5~195.5°C in quantitative yield.

Anal. Found: C, 81.94; H, 4.47. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

U. V. max., 320 and 338 mμ ($\log \varepsilon = 4.77$ and 4.77). I. R. max., 1250 and 1170 cm^{-1}.

Synthesis of 2, 2'-Dibenzofuranyl (IV).—An intimate mixture of 2-bromocoumarone (VII, 1.0 g.) and activated copper bronze (2.5 g.) was heated to 225~240°C in an oil bath for 5 hr. The cooled reaction mixture was transferred to a sublimation apparatus, and was heated to 160~180°C at 20 mmHg. Colorless crystals were obtained as sublimate after removal of the unreacted VII. The crystals were recrystallized from ethanol giving 0.2 g. (40%) of colorless needles, m. p. 194.5~195.5°C. The mixed melting point determination with IV which was derived from III showed no depression.

Anal. Found: C, 82.25; H, 4.33. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%. I. R. max., 1250 and 1170 cm^{-1}. The I. R. spectra of these two specimens were found as superimposable over the entire region of wave length.

2-(*o*-Hydroxyphenylethynyl)-benzofurane (V).—Heating of III (1.2 g.) in 60 cc. of very diluted ethanolic sodium ethoxide for 1.5 hr. on a boiling water bath resulted in crystallization. Recrystallization from benzene yielded 0.4 g. (33%) of IV, m. p. 194.5~195.5°C. The mother liquor of the recrystallization was concentrated to form crude crystals, which were recrystallized from light petroleum (b. p. 55~75°C) employing active charcoal to give 0.5 g. (41%) of V as colorless needles, m. p. 102.5°C.

Anal. Found: C, 82.24; H, 4.33. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

U. V. max., 250, 298, 318 and 340 mμ ($\log \varepsilon =$ 3.83, 4.38, 4.44 and 4.45). I. R. max., 3380, 2207 and 1269 cm^{-1}.

V is slightly soluble in aqueous sodium hydroxide. Reaction of V with benzoyl chloride gave monobenzoate, colorless needles, m. p. 117°C.

Anal. Found: C, 81.62; H, 4.27. Calcd. for $C_{23}H_{14}O_3$: C, 81.64; H, 4.17%.

The solution of V (0.1 g.) in ethanolic sodium ethoxide was refluxed for 3 hr., forming colorless crystals in quantitative yield. This was identified as IV by mixed melting point determination with previously obtained IV.

Ring Cleavage of 2, 2'-Dibenzofuranyl (IV).—A mixture of IV (0.4 g.), pyridine (4.0 g.) and sodium (0.3 g.) was refluxed for 3.5 hr. under nitrogen atomosphere. Water was added cautiously to the reaction mixture to decompose the unreacted sodium, and the mixture was extracted with ether. The aqueous layer was acidified with 2 N hydrochloric acid, and extracted with ether. The ethereal extract was washed with 2 N hydrochloric acid and water successively. The dried ether solution was evaporated, and the residue was repeatedly recrystallized from carbon tetrachloride affording a small amount of

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* Melting points were not corrected. All U. V. and I. R. spectra were measured employing ethanolic solution and nujol mull respectively.

crystals, m. p. 140～141°C. The mixed melting point of this substance with III showed no depression.

Hunsdiecker Reaction of Silver Coumarilate (VIII). — Bromine (7.5 g.) in dry carbon tetrachloride (20 cc.) was added in one portion on well dried VIII (10.0 g.) at room temperature. Vigorous evolution of gas was observed, and the color of bromine disappeared during the period of 2 hr. The mixture was kept for 3 hr. to complete the reaction. The reaction mixture was extracted with ether, and the extract was washed with aqueous solution of sodium hydrogen carbonate to remove acidic materials. The alkaline solution was neutralized with 2 N hydrochloric acid, and extracted with ether. The ether solution was washed with water and dried. The solvent was removed by distillation and the recrystallization of the residue from aqueous ethanol gave 5 g. (56%) of 5-bromocoumarilic acid (IX), m. p. 256°C as colorless needles. (lit. value m. p. 253°C)[7].

Anal. Found: Br, 33.40. Calcd. for $C_9H_5O_3Br$: Br, 33.19%.

The ether layer which was washed with sodium hydrogen carbonate solution was washed with water and dried. The crude neutral crystals obtained by the evaporation of the solvent were recrystallized from aqueous ethanol yielding 2.0 g. (15%) of colorless needles, m. p. 81～83.5°C.

Anal. Found: Br, 67.07. Calcd. for $C_8H_3OBr_3$: Br, 67.60%.

This would be identical with so-called 2,3,7(?)-tribromocoumarone (X, m. p. 84～85°C) prepared by Stoermer[7,8].

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