Further Studies on the Intramolecular Cyclization of o, o'-Dihydroxydiphenyldiacetylene

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(Received February 27, 1960)

In the previous paper, the present authors reported the formation of 2, 2'-dibenzofuranyl (III_c) from *o, o'*-dihydroxydiphenyldiacetylene (I) in alkaline madia¹⁾. The present paper deals with the same type of intramolecular cyclization of I and its silver salt IV in a neutral or an acidic medium.

Treatment of I in carbon tetrachloride with bromine yielded colorless needles in a 37% yield with evolution of hydrogen bromide. The structure of III_a was assigned to the substance from the analytical data, ultraviolet and infrared spectroscopic evidences (Figs. 1, 2 and Table I). The cyclization of I to III_a presumably involves the addition of bromine to the triple bands followed by the elimination of hydrogen bromide as indicated in the following scheme. The formation of diindole from *o, o'*-dinitrotolan which was reported by Ruggli and his associate seems to involve an essentially similar reaction²⁾. In the case of the reaction of iodine with I under the same

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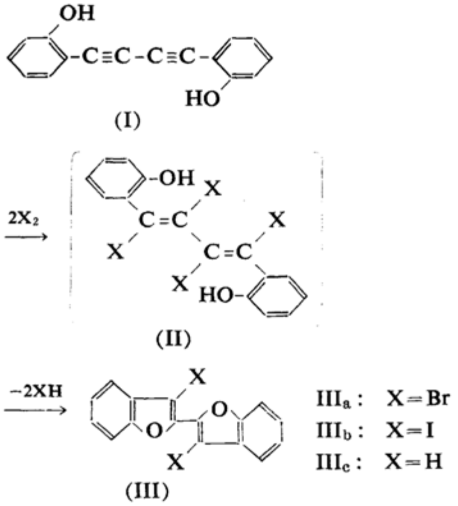
1) F. Toda and M. Nakagawa, This Bulletin, **32**, 514 (1959).

2) P. Ruggli, *Ber.*, **50**, 883 (1917); P. Ruggli and O. Schmid, *Helv. Chim. Acta*, **18**, 1215 (1935).

condition, compounds III_b and III_c were isolated in a 10% and a 29% yield respectively.



(I)

(II)

(III)

III_a : X=Br
III_b : X=I
III_c : X=H

When the reaction was carried out in the presence of finely powdered calcium carbonate in order to remove the evolved hydrogen iodide, the only product was found to be III_b. Treatment of III_b with hydroiodic acid resulted in the formation of III_c, therefore, the formation of III_c in the reaction of I with iodine is attributable to the reduction of III_b by hydrogen iodide. The infrared and ultraviolet spectrum of III_b are shown in Figs. 1, 2 and Table I together with its mother substance and analogues. As illustrated in Fig. 1, the infrared spectra of III_a and III_b lack absorption at 800 and 812 cm^{-1} which exsists in the spectra of III_c and related 2-substituted benzofurans. Therefore, the absorption at ca. 800 cm^{-1} may be ascribed to the out-of-plane deformation of the hydrogen atom at the 3-position of the benzofuran ring.

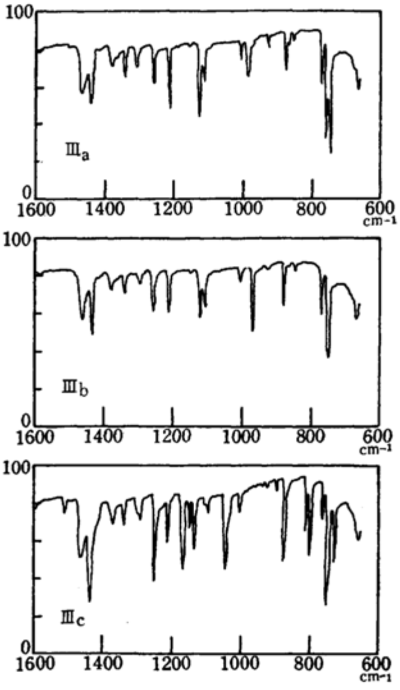


Fig. 1. The infrared spectra of 2,2′-dibenzofuranyl derivatives (Nujol mull)
III_a : 3,3′-Dibromo-2,2′-dibenzofuranyl
III_b : 3,3′-Diiodo-2,2′-dibenzofuranyl
III_c : 2,2′-Dibenzofuranyl

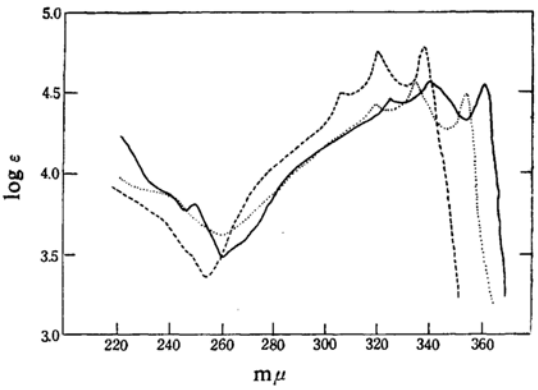


Fig. 2. The ultraviolet spectra of 2,2′-dibenzofuranyl derivatives.
…… : 3,3′-Dibromo-2,2′-dibenzofuranyl (III_a)
—— : 3,3′-Diiodo-2,2′-dibenzofuranyl (III_b)
---- : 2,2′-Dibenzofuranyl (III_c)

A quantitative formation of III_c was observed when the silver salt IV was exposed to light for a few days. The reaction of methyl iodide with IV which was kept in a brown desiccator for a day gave 2-(*o*-methoxyphenylethynyl)-benzofuran (VI) together with III_c. The structure of VI was inferred from the close resemblance of its ultraviolet and infrared spectrum with those of 2-(*o*-hydroxyphenylethynyl)-benzofuran (VII)[1] as shown in Fig. 3 and Table I.

It is the most interesting result that the silver salt IV was converted into III_c and

TABLE I. ULTRAVIOLET SPECTRA OF 3,3′-DISUBSTITUTED 2,2′-DIBENZOFURANYL AND RELATED COMPOUNDS

Compound	Absorption (λ_{max} in mμ in 95% ethanol)				
III_a			319 (253)	335 (352)	354 (299)
III_b	250 (63)		325 (276)	342 (395)	361 (338)
III_c		306 (316)	320 (589)	338 (601)	
VI	250 (75)	299 (251)	318 (305)	340 (294)	
VII	250 (79)	298 (265)	319 (297)	340 (284)	

The figures in parentheses are $\varepsilon_{max} \times 10^{-2}$.

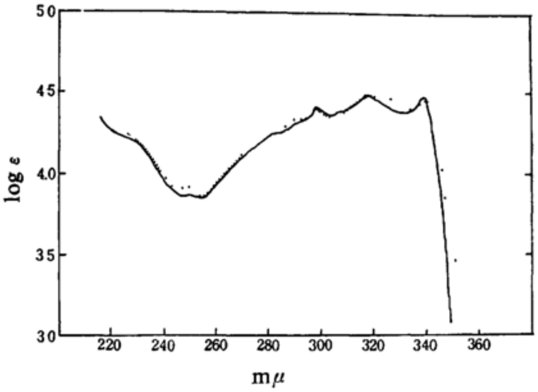


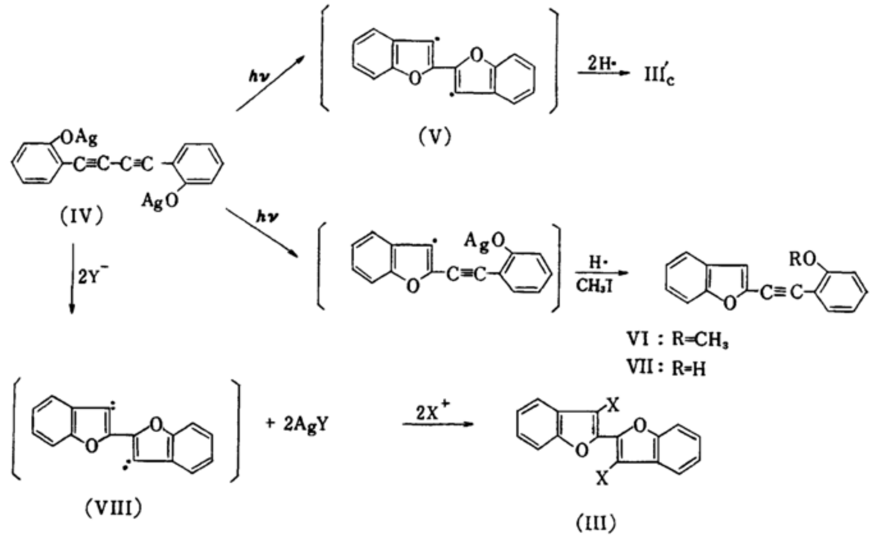
Fig. 3. The ultraviolet spectra of 2-substituted benzofurane derivatives.
——: 2-(*o*-Methoxyphenylethynyl)-benzofuran (VI).
……: 2-(*o*-Hydroxyphenylethynyl)-benzofuran (VII).

its derivatives in good yield by the reaction with various kind of reagents X-Y, such as hydrogen chloride, hydrogen iodide, acetic acid, potassium iodide, ammonium bromide, bromine, iodine and iodine chloride. The results are summarized in Table II.

TABLE II. REACTION OF THE SILVER SALT IV WITH X-Y

Reagent X	Reagent Y	Medium	Product
H	Cl	Water	2, 2′-Dibenzofuranyl (III_c)
H	I	〃	〃
H	CH_3CO_2	Acetic acid	〃
K	I	Water	〃
NH_4	Br	〃	〃
Br	Br	〃	3, 3′-Dibromo-2, 2′-dibenzofuranyl(III_a)
I	I	Carbon tetrachloride	3, 3′-Diiodo-2, 2′-dibenzofuranyl(III_b)
I	Cl	Water	〃

The photochemical transformation of IV into III_c proceeds probably through a radical mechanism. The photodecomposition of IV may produce a phenoxy radical, and the intramolecular addition of the oxygen radical to the triple bonds would yield an intermediate dibenzofuranyl radical (V) as illustrated in the following scheme. The radical may be stabilized by the substruction of hydrogen atoms from water or ethanol molecule yielding III_c*. Also the formation of VI is quite understandable assuming that the light induced half ring closure of IV is followed or is preceded by the ionic displacement of the silver atom by the methyl group. A same type of photochemical reaction of an acetylenic compound has been reported by Prey[3]. He found that the silver acetylide of *o*-hydroxyphenylacetylene yields benzofuran when irradiated with a quarz lamp. On the other hand, the above mentioned reactions of IV with various kinds of argentphilic reagents presumably proceed through an ionic mechanism. The substruction of silver cation from IV by the attack of the anionic moiety of the reagent Y^- should result in the formation of 2, 2′-dibenzofuranyl anion (VIII). The combination of the cationic moiety of the reagent X^+ or proton of the



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

* The silver salt was prepared as a pasty mass by the addition of an aqueous silver nitrate to a solution of I in ammoniacal ethanol.

solvent with VIII gives dibenzofuranyl (III_c) or its 3, 3′-disubstituted derivatives.

The bathochromic shifts of the spectrum of III_a, III_b and III_c are found to be in the expected sequence of $H < Br < I$ with respect to the substituents at the position of 3 and 3′. On the other hand, the hyperchromic effect of the substituents is in the sequence of $H < I < Br$. The low ε-values of the K-band of III_a and III_b as compared with that of III_c may be attributable to an increase of twist of the molecule around the 2, 2′-single bond caused by the presence of bulky halogen atoms at 3- and 3′-position. Similar phenomena have already been observed in several instances⁴⁾, and were explained in terms of the diminished probability of excitation of the molecule to a coplanar excitation state.

Experimental*

Formation of 3, 3′-Dibromo-2,2′-dibenzofuranyl (III_a) from *o,o′*-Dihydroxydiphenyldiacetylene (I).—Bromine (3.2 g.) was added to a suspension of finely powdered I (2.4 g.) in dry carbon tetrachloride (40 cc.). An evolution of hydrogen bromide under an exothermic reaction was observed. The mixture was shaken for one hour with occasional cooling with water. The crystals separated were filtered, and the solvent was evaporated. The remaining solid was combined with the crystals, washed with hot ethanol. Recrystallization from benzene yielded III_a as colorless needles, 1.5 g. (37%), m. p. 225°C.

Found: C, 48.58; H, 2.03; Br, 41.02. Calcd. for $C_{16}H_8O_2Br_2$: C, 49.02; H, 2.05; Br, 40.77%.

I. R. max., 1255 (=C–O–), 875 (furan ring) cm^{-1}.

Formation of 3, 3′-Diiodo-2, 2′-dibenzofuranyl (III_b) and 2, 2′-Dibenzofuranyl (III_c) from *o, o′*-Dihydroxydiphenyldiacetylene (I).—A mixture of I (1.2 g.), dry carbon tetrachloride (25 cc.) and iodine (2.6 g.) was allowed to stand for 3 days at room temperature. The solvent was removed by distillation, and the careful fractional recrystallization of the residual solid from ethanol resulted in the separation of two substances. The less soluble substance was found to be III_b, 0.25 g. (10%), m. p. 212°C.

Found: C, 39.59; H, 1.59; I, 52.58. Calcd. for $C_{16}H_8O_2I_2$: C, 39.54; H, 1.64; I, 52.22%.

I. R. max., 1252 (=C–O–), 875 (furan ring) cm^{-1}.

The more soluble substance, 0.35 g. (29%), m. p. 193∼194.5°C was identified as III_c by a mixed melting point determination with an authentic specimen.

A mixture of I (0.95 g.), dry carbon tetrachloride (30 cc.), iodine (2.06 g.) and finely powdered calcium carbonate (1.6 g.) was kept at room temperature for 2 days. The inorganic salt was removed by filtration and extracted with hot benzene. The extract was combined with the filtrate and the solvent was removed under reduced pressure. The residue thus obtained was digested with hot benzene. The crude crystals obtained by the evaporation of the solvent in vacuo was recrystallized from ethanol yielding 0.32 g,. (16%) of III_b, m. p. 212°C as colorless needles.

Reduction of III_b with Hydrogen Iodide.—Hydroiodic acid (57% aqueous solution, 4 g.) was added to a solution of III_b (50 mg.) in carbon tetrachloride (30 cc.), and the mixture was shaken for 2 days at room temperature. Treatment of the reaction mixture afforded crystalline solid. Fractional recrystallization of the crude solid gave recovered III_a, 30 mg., m. p., 211∼212°C and a small amount of III, m. p. 190∼194°C.

Preparation of the Silver Salt of *o, o′*-Dihydroxydiphenyldiacetylene (IV). — Silver nitrate (2.8 g.) in water (5.0 cc.) was added to the solution of I (1.8 g.) in a mixture of concentrated ammonia (1.2 cc.) and ethanol (15 cc.). The light yellow precipitate formed was collected by filtration and washed with ethanol, yielding 2.8 g. (ca. 80%) of the silver salt (IV). The attempt to determine the melting point of the saltfailed. A gradual decomposition was observed, when the salt (IV) was heated in a capillary tube, and the substance in the tube fused at 194.5∼195.5C showing the melting point of III_c.

Photodecomposition of the Silver Salt (IV).—Finely powdered IV was exposed to a diffused light in the laboratory for a few days. The resulted greyish powder was digested with benzene. The solvent was removed by distillation, and the residue was recrystallized from benzene or ethanol yielding colorless needles, m. p. 194.5∼195.5°C in an almost quantitative yield. This substance was identified as III_c by a mixed melting point determination with an authentic specimen.

Formation of 2, 2′-Dibenzofuranyl (III_c) from the Silver Salt IV.—A mixture of freshly prepared IV and aqueous hydroiodic acid (57%) was shaken for 5 min. The precipitate formed was collected and washed with water and ethanol, successively. The residue was digested with hot benzene. Concentration of the benzene solution afforded crude crystals. Recrystallization of the crude product from ethanol resulted in colorless needles, m. p. 194.5∼195.5°C in good yield. The mixed melting point of this substance with authentic III_c showed no depression. Similar treatment of IV with concentrated hydrochloric acid, acetic acid, aqueous solution of potassium iodide (30%) and aqueous solution of ammonium bromide (30%) also yielded III_c in good yield.

Formation of 3, 3′-Dibromo-2, 2′-dibenzofuranyl (III_a) from the Silver Salt IV.—To a suspension of a freshly prepared IV in water, bromine was added drop by drop with shaking until the color of bromine persists. The insoluble material was collected by filtration, and washed with water and ethanol successively. The residue was digested with hot benzene and the solvent was evaporated. The crude crystals thus obtained were recrystallized from ethanol yielding colorless needles, m. p. 220∼223°C, which showed no depression of the melting point on admixture with previously obtained III_a.

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4) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, 173, 117 (1954); F. Toda and M. Nakagawa, This Bulletin, 33, 223 (1960).

* No melting points are corrected.

Formation of 3, 3′-Diiodo-2, 2′-dibenzofuranyl (III_b) from the Silver Salt IV. — A mixture of freshly prepared IV, iodine and dry carbon tetrachloride was shaken for 5 min. Silver iodide formed was removed by filtration. The crude crystals obtained by the evaporation of the solvent were recrystallized from ethanol resulting in colorless needles, m. p. 211∼212°C. This substance showed no depression of the melting point on admixture with authentic III_b.

The reaction of iodine chloride with IV under the same condition also gave III_b in good yield.

Formation of 2-(*o*-Methoxyphenylethynyl)-benzofuran (VI) from the Silver Salt IV.—The silver (IV, 2.8 g.) which was kept in a brown desiccator for a day was mixed with methyl iodide (1.5 g.) and dry benzene (5.0 cc.). The mixture was refluxed for 1.5 hr. The precipitate formed was collected by filtration, and extracted with hot benzene (30 cc.). The crude crystals obtained by the evaporation of the solvent was digested with cold ethanol (15 cc.). The insoluble material was recrystallized from benzene resulting in colorless needles, 1.08 g. (78%), m. p. 194.5∼195.5°C. The mixed melting point of this substance with 2, 2′-dibenzofuranyl (III_c) showed no depression. The alcoholic solution was diluted with water, and the crude crystals formed were recrystallized from a diluted ethanol resulting in VI, colorless needles, 100 mg. (6%), m. p. 72°C.

Found: C, 82.33; H, 4.94. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87%.

I. R. max., 1246, 1265, 1040 (=C-O-), 2200 ($-C\equiv C-$), 884 (furan ring), 807, 792 (δ CH of 3-position of furan ring) cm^{-1}.

The present authors wish to thank the Ministry of Education for a grant-in-aid. The authors are also grateful to Dr. T. Shiba, Mr. M. Okumiya and Miss K. Koike for the microanalyses.

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