*Cyclic Acetylenes. I. Cyclic Derivatives of o,o'-Dihydroxydiphenyldiacetylene. An Example of a Strained Cyclic Diacetylene**

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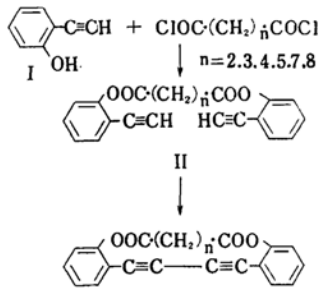
It is of interest to compare the physical and chemical properties of a strained acetylenic compound with that of a strainless analogue in relation to the reactive nature of benzyne intermediate[1]. Along with this line the authors have studied the synthesis of a cyclic diacetylene in which the structure of the molecule forces to bend the diacetylenic linkage. Recently a fairly large variety of cyclic polyacetylenes have been synthesized by several investigators[2], but most of these macrocycles seem to be strainless with regard to the triple bond.

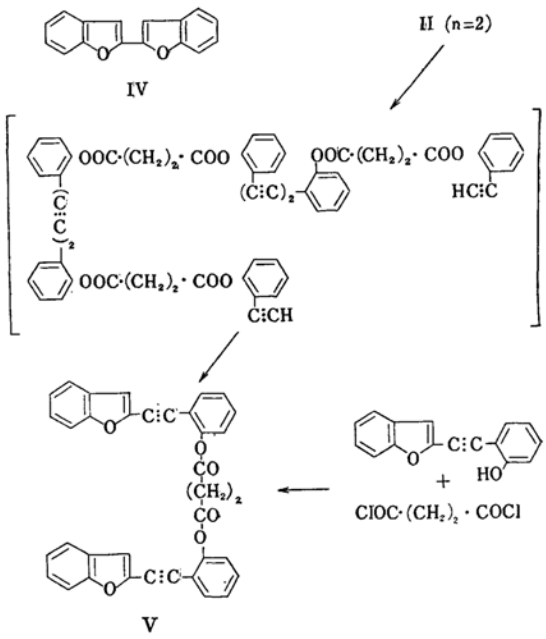
A series of cyclic derivatives of *o,o'*-dihydroxydiphenyldiacetylene have been synthesized according to the following scheme. *o*-Hydroxyphenylacetylene (I)[3] was converted into the polymethylene dicarboxylate (II) by the reaction with the corresponding diacid dichloride in alkaline media. By oxidative coupling of II ($n=2$, 3, 4, 5, 7 and 8) according to the procedure of Eglinton[2] the authors have obtained III_a, III_b, III_c, III_d and $III_{d'}$ in 20, 40, 21 and 7.5% ($III_d+III_{d'}$) yield, respectively. Two isomers were found in the case of $n=7$. The low-melting isomer (III_d, m. p. 111°C) completely changed to the high-melting isomer ($III_{d'}$, m. p. 125~127°C) on standing at room temperature for two weeks.



III_a ; n=3 , III_b ; n=4
III_c ; n=5 , III_d, $III_{d'}$; n=7

The structures of compounds III were inferred from analyses, molecular weight determinations, ultraviolet and infrared spectroscopy. The cyclic nature of III was also confirmed by the absence of free ethynyl absorption in infrared spectra (ca. 3300 cm^{-1}) and by titration against silver nitrate.

In the case of $n=3$, 2, 2'-dibenzofuranyl (IV)[4] was isolated in 25% yield together with III_a. IV was also obtained from the products of the coupling reaction of II ($n=2$) in 57% yield together with a small amount of compound V. The ultraviolet spectrum of V closely resembles that of 2-(2'-benzoyloxyphenylethynyl)-benzofurane[4] as illustrated in Fig. 1. The structure of V was confirmed by the



* For a preliminary announcement of a part of this work, see *Chem. & Ind.*, **1959**, 458.

1) G. Wittig, *Angew. Chem.*, **68**, 245 (1957); J. D. Roberts, "Chemical Society Symposia Bristol 1958", The Chemical Society, London (1958), p. 115.

2) G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 889; F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **79**, 4274 (1957) and preceding papers.

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

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

identity with a synthetic specimen which was obtained by the reaction of 2-(2'-hydroxyphenylethynyl)-benzofurane[4] and succinic acid dichloride in alkaline media.

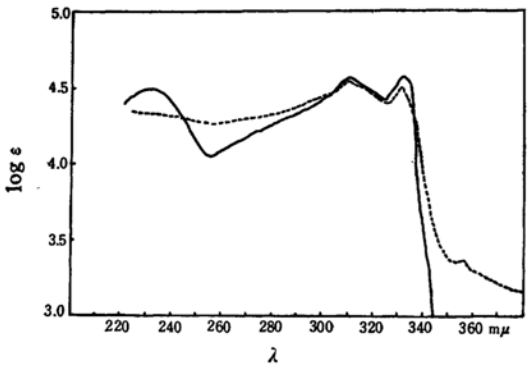
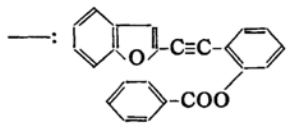


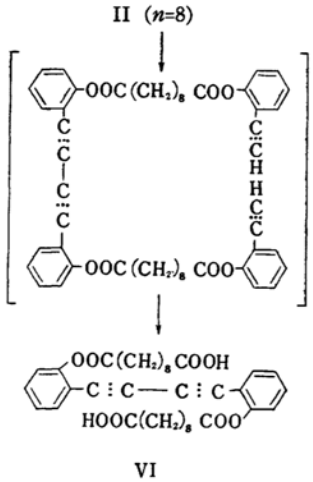
Fig. 1. The ultraviolet spectra of 2-(2'-benzoyloxyphenylethynyl)-benzofurane and V. The curve of V was drawn using the reduced ε values corresponding to the diyne-unit.

—: 

----: V

The mechanism of the formation of IV is not yet clear, but it may be formed from highly strained III cleaving the ester linkages simultaneously accompanying the benzofurane ring formation. It has been reported by the present authors that IV is formed in a quantitative yield from *o*, *o'*-dihydroxydiphenyldiacetylene on treatment with alkali[4]. IV and adipic acid are formed on the alkaline hydrolysis of III_b, but the formation of IV from *o*, *o'*-dihydroxydiphenyldiacetylene under the condition of Eglinton's oxidative coupling was not observed. Therefore, the simple interpretation such as the intramolecular cyclization to IV of *o*, *o'*-dihydroxydiphenyldiacetylene which is formed by the ring fission of the cyclic diyne is not acceptable as the mechanism of the formation of IV under the condition of the coupling reaction. Also the formation of V may be attributed to the fission of the ester linkages presumably in the course of cyclic trimerization of II ($n=2$).

The attempt to prepare III ($n=8$) have failed. In this case the only identified product was VI, and the formation of VI is also probably associated with the fission of the ester linkages during the course of cyclic dimerization of II ($n=8$).



VI

The most striking property of III_a is its high sensitivity to light in the solid state making a sharp contrast to the photostable nature of III_b, III_c, III_d and $III_{d'}$. The surface of the colorless crystals of III_a was rapidly coated with red colored, insoluble and high melting point material when the solid was exposed to a diffused light in the laboratory. But the solution of III_a was found to be fairly stable. These properties are closely related to those of some polyacetylene compounds[5].

Examination of the scale models of III indicates that III_b is a rigid and planar molecule with the two phenyl groups held in the same plane. On the other hand, the phenyl groups in III_c are not readily able to become coplanar on account of the bridging chain. The model of III_a clearly shows that the diacetylenic linkage is forced to bend owing to the short methylene chain holding its phenyl groups in a coplanar position. The anomalous photosensitivity of III_a may be attributed therefore to the bending of the diacetylenic bond. It has already been suggested by Bohlmann that the stabilization of a certain polyacetylenic compound bearing two bulky terminal groups is associated with the steric effect of the bulky groups retarding the formation of cross linkings[6]. The diacetylenic linkage in III_a seems to be more exposed to the outer environment of the molecule on account of its bending as compared with that linkage of the corresponding less strained cyclic diynes. Therefore the intermolecular approach to form cross linkings which is facilitated

5) Cf. J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones and M. C. Whiting, *J. Chem. Soc.*, **1952**, 1998.
6) F. Bohlmann and E. Inhoffen, *Chem. Ber.*, **89**, 1276 (1956).

by the presence of the distorted diacetylenic bond is, though it is not decisive, a possible cause of the unstable nature of III_a.

The catalytic reduction of 2,2′-diacetoxydiphenyldiacetylene (VII), III_a and III_b were carried out using a palladium on charcoal catalyst. It was hoped that III_a might exhibit some abnormalities in the course of hydrogenation resulting from the ring strain, but the experimental results indicated no marked difference in the rates of hydrogenation as illustrated in Fig. 2. The fact that the hydrogenation of III_a stopped after absorption of ca. 90% of theoretical amount of hydrogen is probably ascribed to the formation of minor amount of the above mentioned photopolymer during the course of reduction.

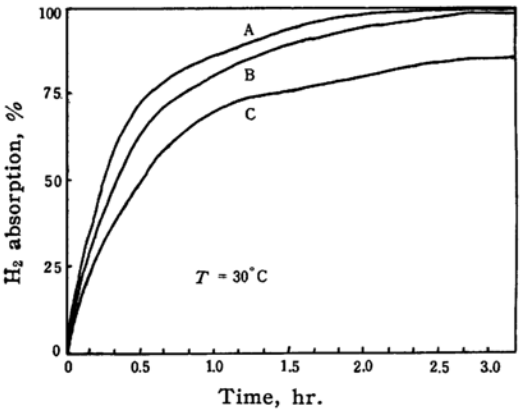


Fig. 2. The rates of hydrogenation of VII, III_a and III_b.
A: VII B: III_b C: III_a

These situations seem to be reflected in the ultraviolet spectra of III_a, III_b, III_c and III_d. VII was used as a comparison for an open chain analogue of III. As indicated in Table I and Fig. 3, the ultraviolet spectra of these diacetylene are closely related and are different only in the absorption intensities without any significant wavelength displacements. The extinction coefficients ε of λ_{max} of the long wavelength region (290~340 mμ) of III_b are larger than that of VII, but the ε values of III_a, III_c, III_d and $III_{d'}$ in the same region are smaller than that of VII.

TABLE I

Compound	Absorption								
VII			250 (479)	260 (483)	275 (240)	291 (337)	310 (445)	331 (398)	
III_a	229.5 (304)	**235** (260)			**275** (88)	292 (198)	310 (322)	331 (292)	
III_b					275 (113)	291 (290)	310 (535)	332 (541)	
III_c			248.5 (267)		**275** (122)	293 (171)	310 (216)	331 (174)	
III_d			248 (301)	260 (304)	275 (152)	290 (227)	309 (337)	331 (304)	
$III_{d'}$			249 (325)	260 (322)		292 (197)	310 (241)	331 (200)	
V							310 (343)*	331 (315)*	
VI			250 (361)	260 (364)	**275** (155)	292 (204)	310 (248)	331 (216)	
$VIII_a$			250 (305)	260 (316)	275 (153)	290 (219)	309 (288)	331 (255)	
$VIII_b$			250 (277)	260 (284)	275 (124)	291.5 (205)	309.5 (284)	331 (244)	
IX_a				260 (294)	275 (112)	**310** (207)	326 (316)	349 (267)	
IX_b				260 (272)	275 (95)	**310** (190)	327 (293)	349 (251)	
X_a			**240** (204)	260 (213)	**275** (85)	305 (168)	323 (270)	345 (236)	
X_b			**240** (204)	260 (216)	**275** (97)	**305** (166)	323 (252)	345 (218)	

The figures indicate the λ_{max} in mμ.
The figures in parentheses are $\varepsilon_{max} \times 10^{-2}$.
Asterisk indicates the ε value of per dyne unit.
The bold figures indicate shoulders.
All spectra were measured in 95% ethanol.

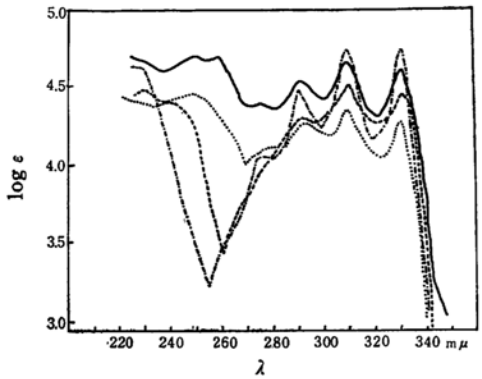
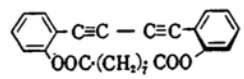


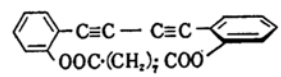
Fig. 3. The ultraviolet spectra of VII and the cyclic diacetylenes (III_a, III_b and III_c).
——: VII ----: III_a
-·-·-: III_b ·····: III_c

The decrease of the ε values are in the sequence of $III_b > VII > III_a > III_c$ indicating the important role of the uniplanar phenyl groups in affecting the intensity of absorption. This fact suggests that the spectra associate with transitions between non-planar ground states and near planar excited states[7]. The largest ε values of III_b in this region may be due to the rigid and planar structure of the molecule having maximum conjugation between the two phenyl groups and the acetylenic bonds. On the other hand, the smaller ε values of III_a as compared with VII may be attributed to the diminished probability of excitation of the molecule to an excitation state in which the diacetylenic linkage should take a linear configuration. The low intensity of absorption of III_c, III_d and $III_{d'}$ may also be regarded as the twisted position of the phenyl groups in these molecules affecting to reduce the probability to a uniplanar state of excitation.

The ultraviolet spectra of III_d and $III_{d'}$ are different as shown in Table I and Fig. 4. The absorption intensity in the long wavelength region of $III_{d'}$ is much lower than that of III_d indicating the presence of a larger degree of twist of the phenyl groups in $III_{d'}$ as illustrated in the following formulae. Examination of the scale models of III_d and $III_{d'}$ indicates that the methylene chain in III_d is much more crowded than in $III_{d'}$. Therefore, the relief of compression energy of methylene chain seems to be responsible to the



III_d



$III_{d'}$

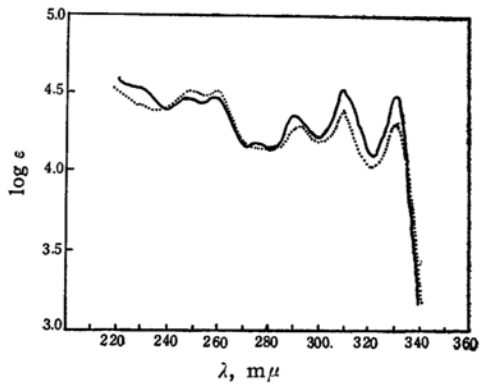
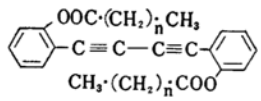


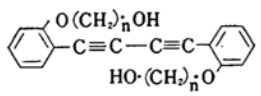
Fig. 4. The ultraviolet spectra of the isomeric cyclic diacetylene (III_d and $III_{d'}$).
——: III_d ·····: $III_{d'}$

stabilization of III_d to $III_{d'}$. The isolation of III_d and $III_{d'}$ may be regarded as the first example of the presence of a new type of conformational isomers in which the diacetylenic linkage behaves as pivot bond.

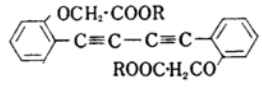
The low absorption intensity in the ultraviolet spectrum of VI is also explained by the hypochromic effect of non-coplanar



VII : n=0
$VIII_a$: n=1
$VIII_b$: n=2



IX_a : n=2
IX_b : n=3



X_a : R=CH_3
X_b : R=C_2H_5

7) E. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954); Also cf. E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

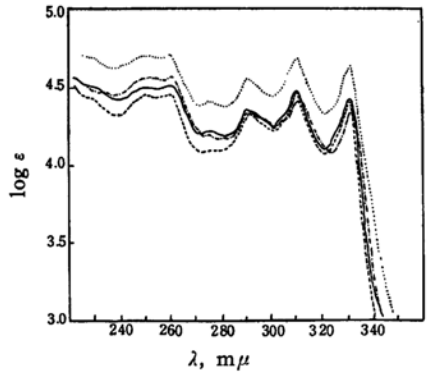


Fig. 5. The ultraviolet spectra of 2,2'-diacyloxydiphenyldiacetylenes.
·····: VII ——: $VIII_a$
----: $VIII_b$ -·-·: VI

phenyl groups. Further examples of the effect are obtained in the series of VIII, IX and X. As illustrated in Fig. 5 and Table I, the increase in the number of methylene group in VIII resulted in the decrease of the intensity of absorption. The steric effect of the acyl group affecting the hypochromic shift of the ultraviolet spectra of VIII seems to show a tendency approaching to a definite value when the steric requirement of the group reaches a certain degree, namely, the differences of ε values between VII and $VIII_a$, $VIII_b$ and the differences between VII and VI are quite large, while the difference between $VIII_a$ and $VIII_b$ and that of VI and $VIII_a$, $VIII_b$ are relatively small.

The same trend is also observed in the case of IX_a, IX_b, X_a and X_b as indicated in Figs. 6 and 7 and in Table I.

The characteristic feature in the ultraviolet spectra of III_a and III_b are the presence of a sharp and intense λ_{min} at ca. 260 mμ, the ε values are only one-

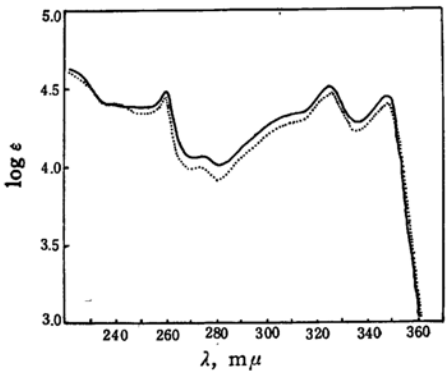


Fig. 6. The ultraviolet spectra of 2,2'-di-ω-hydroxyalkyloxydiphenyldiacetylenes.
——: IX_a ·····: IX_b

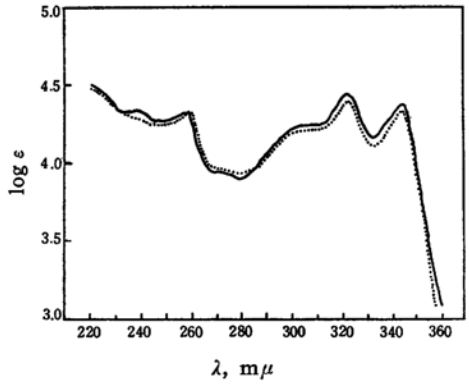


Fig. 7. The ultraviolet spectra of 2,2'-di-(alkyloxycarbonylmethoxy-diphenyl-diacetylenes.
——: X_a ·····: X_b

tenth of the corresponding ε of III_c and III_d. The proximity effect of *o,o'*-bridging chain which is held closely parallel with the diacetylenic linkage may be a possible explanation of this fact, but it is premature to deduce a conclusion from these few examples.

Further studies in the same direction are now in progress.

Experimental**

General Procedure of the Preparation of Di-*o*-ethynyl-phenyl Polymethylene Dioate (II, n=2, 3, 4, 5, 7 and 8).—Polymethylene dioic acid chloride (2 mol.) was added to the solution of *o*-hydroxyphenylacetylene[4] (I, 1 mol.) in 10% aqueous solution of potassium hydroxide (7 equiv.). The mixture was shaken under ice cooling. The oily material separated was extracted with ether, washed with aqueous potassium hydroxide and water successively. The colorless viscous oil obtained on evaporating the solvent was used without further purification. For example, in the case of n=7, azelaic acid chloride (9.0 g., 0.04 mol.) was added in one portion to the solution of I (2.4 g., 0.02 mol.) in 10% aqueous solution of potassium hydroxide (7.8 g., 0.14 mol.), and the mixture was shaken for 1 hr. The reaction mixture was extracted with ether, washed with aqueous potassium hydroxide and water. The ether extract was dried over anhydrous magnesium sulfate. A colorless oil was obtained by the evaporation of the solvent (3.3 g., 85%). The crude II [n=7, I.R. max., 3260 (-C≡CH), 2860, 2920 (-CH_2-), 1762 cm^{-1} (ester)] gave yellow cuprous acetylide by Ilosvay's reagent, and gave white silver salt by an alcoholic silver nitrate solution.

Oxidative Coupling of Di-*o*-ethynylphenyl Adipate (n=4). — The mixture of II (n=4, 1.5 g.), cupric

** Not all melting points are corrected. Infrared spectra were measured using liquid film or nujol mull method.

acetate monohydrate (15 g.) and pyridine (150 g.) was stirred for 4 hr. at 55°C. The stirring was continued for additional 1 hr. at room temperature. Most of the pyridine was removed from the reaction mixture under reduced pressure. Water (1000 ml.) was added to the residue and extracted with ether (1000 ml.). The ether extract was washed with aqueous cupric acetate and water, successively. The ethereal solution was dried over anhydrous magnesium sulfate. The solvent was removed and the residual solid was recrystallized from ethanol giving III_b (0.6 g., 40%) as colorless needles, m. p. 123.5°C.

Anal. Found: C, 76.83; H, 4.54; mol. wt. (Rast), 325. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68%; mol. wt., 344.

I. R. max., 1758 cm^{-1} (ester).

III_b gave no precipitation with alcohlic silver nitrate solution.

Hydrolysis of III_b. — III_b (0.1 g.) was dissolved in an aqueous alcoholic solution of potassium hydroxide (ethanol 15 ml., water 2 ml. and potassium hydroxide 0.3 g.). The solution was refluxed for 3 hr. on a boiling water bath. The crystals were recrystallized from ethanol yielding colorless needles, m. p. 194.5~195.5°C which showed no depression of the mixed melting point with an authentic sample of 2,2'-dibenzofuranyl (IV)[4]. The filtrate was washed with ether and the aqueous layer was acidified with 2 N hydrochloric acid, extracted with ether. Treatment of the ether extract gave adipic acid, m. p. 148~150°C. The mixed melting point with pure adipic acid showed no depression.

Oxidative Coupling of Di-*o*-ethynylphenyl Glutarate (II, n=3). — II (n=3, 2.5 g.) was mixed with cupric acetate monohydrate (20 g.) and pyridine (200 g.). The mixture was agitated for 4 hr. at 55°C. The insoluble precipitate was removed from the reaction mixture by filtration and was washed with ether. The filtrate was distilled under reduced pressure to remove pyridine. The residue was extracted with ether (600 ml.). The ether extract and the ethereal washing was combined and washed with a saturated aqueous solution of cupric acetate and water. The ether solution was dried over anhydrous magnesium sulfate and concentrated to 100 ml. The crystals deposited at this stage were filtered (m. p. 194.5~195.5°C, 0.2 g.). The crystals were identified as 2,2'-dibenzofuranyl (IV) by the mixed melting point determination. The solvent was removed from the filtrate and the residue was recrystallized from ethanol employing active charcoal, giving colorless needles mixed with hexagonal plates. Further recrystallization of the mixed crystals from ethanol (50 ml.) gave 0.2 g. of IV. The total yield of IV was found as 0.4 g. (25%). Slightly impure III_a was obtained as hexagonal plates (m. p. 133~134°C, 0.5 g., 20%) on standing the alcoholic filtrate. Recrystallization of this material gave pure III_a, m. p. 135~136°C.

Anal. Found: C, 76.33; H, 4.08; mol. wt. (Rast), 350. Calcd. for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27%; mol. wt., 330.

I. R. max., 1755 cm^{-1}.

The surface of the crystals of III_a changed to red on exposure to a diffused light in the laboratory. An amorphous, high melting material remained when the colored crystals were dissolved in ethanol.

Oxidative Coupling of Di-*o*-ethynylphenyl Pimelate (II, n=5). — II (n=5, 1.4 g.) was oxidized with cupric acetate monohydrate (1.5 g.) in pyridine (150 g.) at 55°C. After 3 hr., the reaction mixture was treated similarly as described above yielding a viscous oil (1.3 g.). The mixture of the oil with methanol (2 ml.) gradually solidified on standing. Repeated recrystallization from methanol using active charcoal gave III_c as colorless needles, m. p. 120.5~121.5°C, 0.3 g (21%).

Anal. Found: C, 76.94; H, 5.06; mol. wt. (Rast), 364. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%; mol. wt., 358.

I. R. max., 1760 cm^{-1}.

III_c gave no precipitation with alcoholic silver nitrate.

***o,o'*-Diacetoxydiphenyldiacetylene (VII).** — Acetic anhydride (2.0 g.) was introduced in one portion to the solution of *o,o'*-dihydroxydiphenyldiacetylene (0.4 g.) in aqueous potassium hydroxide (water 40 ml., potassium hydroxide 1.4 g.). The mixture was shaken under ice cooling. The solid deposited was collected by filtration and recrystallized from ethanol yielding VII as colorless needles, m. p. 134°C.

Anal. Found: C, 75.33; H, 4.31. Calcd. for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43%.

I. R. max., 1755 cm^{-1} (ester).

Oxidative Coupling of Di-*o*-ethynylphenyl Succinate (II, n=2). — The mixture of II (n=2, 2.5 g.) was stirred for 3 hr. at 55°C and the stirring was continued further 30 min. at room temperature. The most of pyridine was removed under reduced pressure. Water was added to the residue and the mixture was extracted with ether (1000 ml.). The extract was washed with saturated solution of cupric acetate and water, successively. The dried ether extract was reduced to 100 ml. and the needle-like crystals deposited (0.4 g., m. p. 194.5~195.5°C) were collected by filtration. This was identified as IV by mixed melting point determination. The solvent was removed from the filtrate resulting in a mixture of viscous oil and crystals. The crystals separated by filtration were washed with hot ethanol, giving IV (0.7 g.). The recrystallization of the combined IV from benzene using charcoal, yielded 1.0 g. (57%) of IV. The oily filtrate gradually solidified on standing. The solid was treated with ethanol and charcoal to result in V, colorless needles, m. p. 157.5~158.5°C, 20 mg. (ca. 1%).

Anal. Found: C, 78.23; H, 4.09; mol. wt. (Rast), 517. Calcd. for $C_{36}H_{22}O_6$: C, 78.54; H, 4.03%; mol. wt., 550.

I. R. max., 1755 cm^{-1} (ester).

V gave a negative test against alcoholic silver nitrate.

Synthesis of Di-2-(2'-benzofuranylethynyl)-phenyl Succinate (V). — 2-(2'-Hydroxyphenylethynyl)-benzofurane[4] (50 mg.) was dissolved in the solution of potassium hydroxide (0.35 g.) in water (10 ml.). Succinoyl chloride (0.31 g.) was added in one portion to the alkaline solution and was shaken to result in a crystalline solid. The solid was collected by filtration, washed with water and alcohol. Recrystallization from ethanol gave colorless needles, m. p. 157.5~158.5°C, 30 mg. (51%). The mixed melting point with V, the product of the oxidative coupling of II (n=2), showed no depression. The infrared spectra of these two substances were found as identical over the entire region of wavelength.

Oxidative Coupling of Di-*o*-ethynylphenyl Nonanedioate (II, n=7). — The mixture of II (n=7, 2.0 g.), cupric acetate monohydrate (15 g.) and pyridine (150 g.) was stirred for 3.5 hr. at 55°C. Pyridine was removed under reduced pressure. Water (1000 ml.) was added to the residue and the mixture was extracted with ether (1000 ml.). The ethereal layer was washed with saturated solution of cupric acetate and water, successively, and dried over anhydrous magnesium sulfate. A viscous oil (0.5 g.) obtained by removing the solvent was mixed with ethanol (2.0 ml.). The mixture was kept to result crystallization. The crystals were collected by filtration (filtrate A). The crystals were recrystallized from ethanol and separated by filtration (filtrate B). Further recrystallization from ethanol gave $III_{d'}$ as colorless needles, m. p. 125~127°C, 50 mg. (2.5%).

Anal. Found: C, 77.20; H, 5.73. Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5 74%.

The crude crystals obtained by the concentration of the combined filtrates A and B were treated with ethanol and charcoal and recrystallized from ethanol, resulting in III_d as colorless needles, m. p. 111°C, 100 mg. (5%).

Anal. Found: C, 77.56; H, 5.68; mol. wt. (Rast), 399. Calcd. for $C_{25}H_{22}O_4$: C, 77.70; H, 5.74% mol. wt., 386.

After being kept for two weeks at room temperature the melting point of III_d raised to 125~127°C and the mixed melting point of the material with $III_{d'}$ showed no depression. The ultraviolet spectra of III_d and $III_{d'}$ measured after 4 days from the isolation are listed in Table I.

Oxidative Coupling of Di-*o*-ethynylphenyl Decanedioate (II, n=8). — II (n=8, 2.5 g.) was treated with cupric acetate monohydrate (15 g.) in pyridine (200 g.) at 55°C for 4 hr. The same treatment of the reaction mixture as stated in the case of II (n=7) resulted a crystalline solid. Recrystallization of the solid from ethanol employing charcoal yielded VI as amorphous powder, m. p. 149~151.5°C, 0.3 g. (16%).

Anal. Found: C, 72.29; H, 6.83. Calcd. for $C_{36}H_{42}O_8$: C, 71.74; H, 7.02%.

I. R. max. (measured in hexachlorobutadiene), 2920, 2850 (-CH_2-), 2650 (carboxyl OH), 1755 (ester) and 1703 cm^{-1} (carboxyl CO).

VI is readily soluble in aqueous sodium hydrogen carbonate and sodium hydroxide solution and gave a negative test against an ethanolic silver nitrate.

2,2'-Dipropionyloxydiphenyldiacetylene ($VIII_a$). — Propionic anhydride (2.6 g.) was added in one portion to the solution of 2,2'-dihydroxydiphenyldiacetylene[4] (0.47 g.) in water (20 ml.) and potassium hydroxide (1.6 g.). The mixture was shaken with occasional cooling with ice water. The solid separated was recrystallized from ethanol to result in $VIII_a$, m. p. 56°C, 0.5 g. (70%).

Anal. Found: C, 76.06; H, 5.29. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24%.

I. R. max., 1770 cm^{-1} (ester).

2,2'-Dibutylyloxydiphenyldiacetylene ($VIII_b$). — 2,2'-Dihydroxydiphenyldiacetylene (1.2 g.) was reacted with butyric anhydride (8.0 g.) according to the same procedure described above for the preparation of $VIII_a$. The reaction mixture was extracted with ether and the extract was washed with aqueous alkali and water. The solvent was evaporated from the dried extract yielding crude crystals. Recrystallization of the crude material from aqueous ethanol resulted in $VIII_b$, m. p. 51°C, 1.4 g. (75%).

Anal. Found: C, 76.61; H, 5.93. Calcd. for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92%.

I. R. max., 1755 cm^{-1} (ester).

2,2'-Di-(β-hydroxyethoxy)-diphenyldiacetylene (IX_a). — The reaction of *o,o'*-dihydroxydiphenyldiacetylene with ethylenechlorohydrine in the presence of sodium ethoxide gave IX_a. IX_a thus obtained was separated into two forms, labile form (m. p. 75~76°C) and stable form (m. p. 90~91°C). The labile crystals readily changed to the stable form on standing at room temperature.

Anal. Found: C, 74.64; H, 5.57. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

I. R. max., 3350 (-OH), 2145 (-C≡C-) and 1244 cm^{-1} (=C-O-).

2,2'-Di-(γ-hydroxypropoxy)-diphenyldiacetylene (IX_b). — *o*-(γ-Hydroxypropoxy)-phenylacetylene (b. p. 142~143°C/7 mmHg) which was obtained in 88% yield by the reaction of *o*-hydroxyphenylacetylene[1] and 3-bromo-1-propanol in the presence of sodium ethoxide was oxidatively coupled according to the method of Sörensen[8]. Treatment of the reaction mixture resulted in IX_b as colorless needles in 57% yield, m. p. 103°C.

Anal. Found: C, 75.54; H, 6.01. Calcd. for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33%.

I. R. max., 3320 (-OH), 2145 (-C≡C-), 1252 cm^{-1} (=C-O-).

2,2'-Di-(alkyloxycarbonylmethoxy)-diphenyldiacetylene (X_a and X_b). — The reaction of *o,o'*-dihydroxydiphenyldiacetylene with methyl bromoacetate in the presence of sodium ethoxide resulted in X_a as colorless needles in 75% yield, m. p. 143°C.

Anal. Found: C, 70.04; H, 4.90. Calcd. for $C_{22}H_{18}O_6$: C, 69.83; H, 4.80%.

I. R. max., 1745 cm^{-1} (ester).

X_b was prepared in the same manner employing

8) T. Bruun, T. Morthei and N. A. Sörensen, *Acta Chem. Scand.*, 4, 850 (1950).

ethyl bromoacetate, m. p. 98.5～99°C, colorless needles.

Anal. Found: C, 70.57; H, 5.36. Calcd. for $C_{24}H_{26}O_6$: C, 70.92; H, 5.46%.

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