Cyclic Acetylenes. IX. Synthesis of a Cyclic Octaacetylene Containing Anthracene Nuclei

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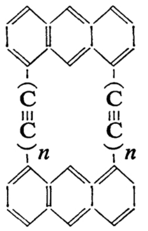
(Received July 10, 1962)

As reported in a previous paper1) of this series, we have synthesized a fully conjugated cyclic tetraacetylene containing anthracene nuclei. The extremely stable nature of the cyclic acetylene (I) urged the present authors to the synthesis of a higher homologue of I. The present paper deals with the synthesis of the same type cyclic octaacetylene (II).



I ($n=2$)
II ($n=4$)

1, 8-Dicarboxyanthracene which was derived from 1, 8-dichloroanthraquinone1) was converted to the corresponding dimethyl ester (III). The ester III was treated with hydrazine hydrate yielding the bishydrazide (IV). The decomposition of the benzenesulfonyl derivative of IV (V) in ethylene glycol in the presence

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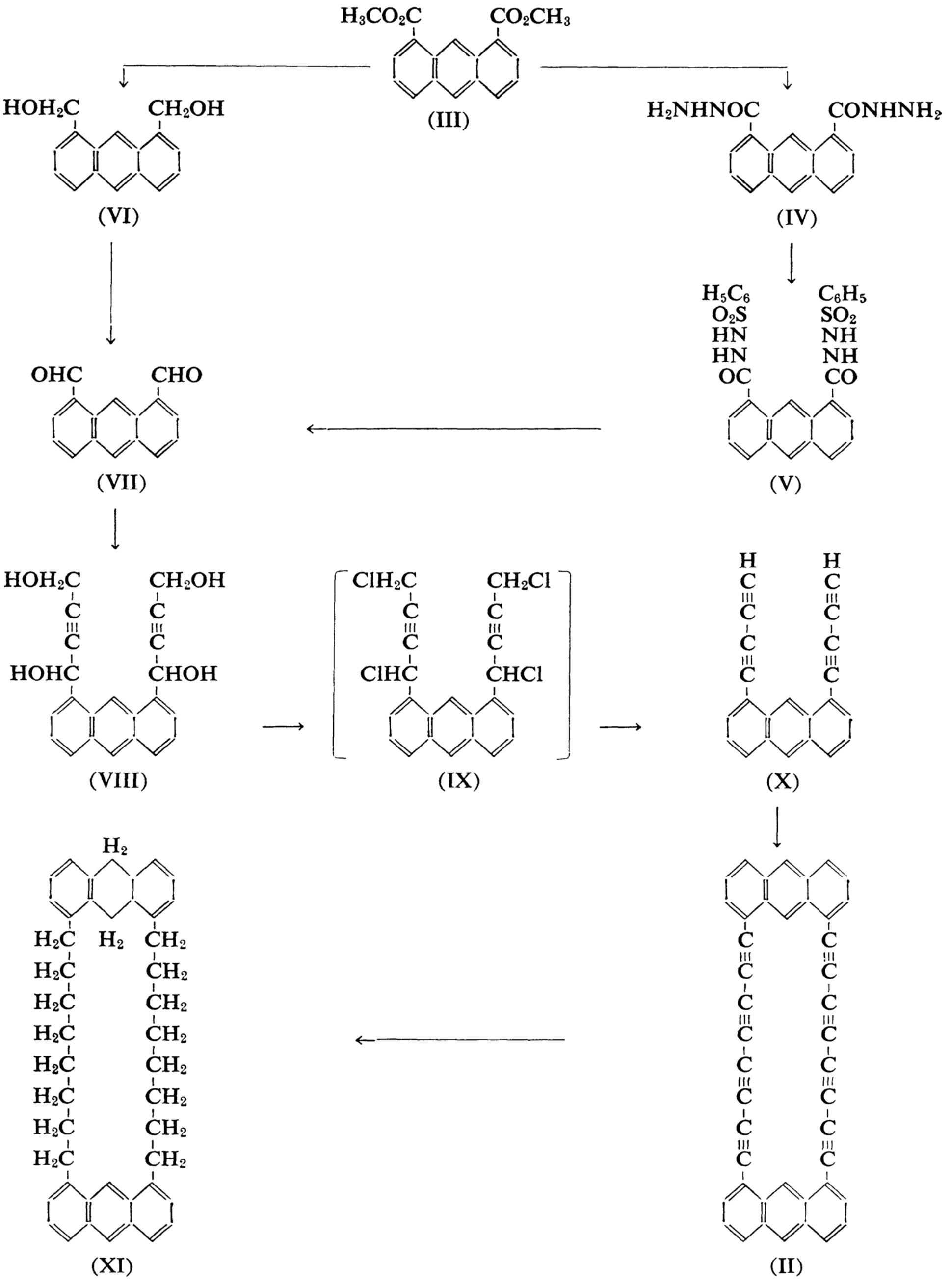
1) S. Akiyama, S. Misumi and M. Nakagawa, This Bulletin, 33, 1293 (1960).



of sodium carbonate afforded 1, 8-diformylanthracene (VII)[2]. But the procedure was found to be scarcely feasible for the preparation of VII owing to its highly sensitive nature to reaction conditions which makes impossible to improve the low yield and the poor reproducibility. The reduction of the dimethyl ester III with lithium aluminum hydride yilded 1, 8-bis-hydroxymethylanthracene (VI). The attempts to convert VI into 1, 8-bis-bromomethyl derivative which is the potential starting material of the preparation of the dialdehyde VII according to the Sommelet[3] or the Kröhnke method[4], were prevented due to the poor solubility of VI in chloroform or carbon tetrachloride. Finally we have found

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[2] Cf., J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, **1936**, 584.

[3] Cf., M. Sommelet, *Compt. rend.*, **157**, 852 (1913); *Bull. soc. chim. France*, [4] **13**, 1083 (1913); S. J. Angyal, "Org. Reactions", Vol. VIII, J. Wiley & Sons, Inc., New York (1954), p. 197.

[4] F. Kröhnke and H. Schmeiss, *Ber.*, **72**, 440 (1939).

that the oxidation of VI by means of chromium trioxide in pyridine[5] results in the formation of VII in a reasonable yield.

The reaction of the lithium derivative of the tetrahydropyranyl ether of propargyl alcohol, 2-(prop-2′-yn-1′-yloxy)-tetrahydropyran with the dialdehyde VII was studied to obtain the tetraol VIII. The lithium derivative obtained by the action of lithium on the mercuric acetylide of the tetrahydropyranyl ether gave the tetraol VIII in a low yield. According to this result, the tetrahydropyranyl ether in tetrahydrofuran was treated with phenyllithium to attain a complete metalation. The reaction of the resulting lithium salt with the aldehyde VII at low temperature followed by the hydrolysis of the tetrahydropyranyl ether yielded the tetraol VIII in a reasonable yield. The tetrachloro-compound IX which was obtained by the treatment of VIII in tetrahydrofuran with thionyl chloride and pyridine was dehydrochlorinated without purification by the action of sodium amide in liquid ammonia yielding 1, 8-bis-butadiynylanthracene (X) as bright yellow fine needles in a reasonable yield. The terminal bis-diacetylene X was found to be fairly unstable substance. The crystals lose their bright surface lustre on exposure to air and form a brown material insoluble in common organic solvents. A dilute solution of X exhibits an intense, beautiful lilac fluorescence. The infrared spectrum of X showed absorptions at 2280 and 3200 cm^{-1} indicating the presence of ethynyl group and disubstituted carbon-carbon triple bond (Fig. 1). X forms red cuprous and orange-yellow silver acetylides.

In the course of the oxidative coupling of X to the cyclic octaacetylene II according to the method of Eglinton[6], we have encountered unexpected difficulty. A large amount of a decomposition product soluble in pyridine was formed when the oxidative coupling was carried out under ordinary conditions for several ten minutes at a slightly elevated temperature. In these cases, the isolation of the cyclic dimer II was practically impossible. Finally it was found that the oxidation had to be carried out at a temperature of ca. 20°C and be interrupted within 1 min. The cyclic octaacetylene II thus obtained was deep red fine needles which decomposed at ca. 160°C into brown solid keeping the shape of the crystals. The octaacetylene II was found to be a stable substance and could be kept without decomposition for a long time. No change of the electronic spectrum was observed after a benzene or a tetrahydrofuran solution of II was exposed to a direct sunlight or a mercury are lamp for some several hours. The analytical data and the infrared spectrum are consistent with the structure of II. The infrared spectrum of II exhibits strong absorptions at 2190, 2140 and 2110 cm^{-1} indicating the presence of polyacetylenic linkage and lacks the absorption arising from the C–H streching of ethynyl group (Fig. 1). Also a solution of II gave a negative test against alcoholic silver nitrate solution. The molecular weight of II could not be determined owing to its poor solubility in organic solvents. The Rast method also gave unsatisfactory result as a result of decomposition of II at the elevated temperature. The catalytic reduction of II in benzene over a large amount of palladium-on-charcoal afforded stable pale yellow crystals. The empirical formula of this substance was determined to be $(C_{22}H_{25})_n$. The molecular weight determination of this substance by Rast's method in camphor (found, 613) revealed that the molecular formula should be $(C_{22}H_{25})_2$, (calcd., 579). The dimeric nature of the coupling product II was unequivocally confirmed by this result.

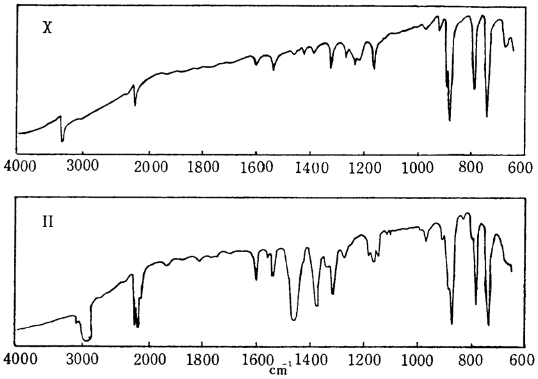

Fig. 1. The infrared spectra of 1, 8-bis-butadiynylanthracene (X) (KBr-disk) and cyclic-octaacetylene (II) (Nujol mull).

The infrared spectroscopy of the hydrogenated product revealed the presence of 1, 2, 4, 5-tetrasubstituted benzene nucleus. Also the presence of anthracene nucleus was inferred from the characteristic ultraviolet absorption. The structure of XI was tentatively assigned to the reduction product on the bases of the above-mentioned evidences.

As stated above, the oxidative coupling of X gave II in a poor yield under the restricted conditions. This fact makes a sharp contrast with fact that the oxidative coupling of 1, 8-diethynylanthracene[1] yields the cyclic tetraacetylene I in a quantitative yield. This difference seems to be rather surprising in view of their similar molecular geometry which

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[5] Cf., G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

[6] G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, **1956**, 737; *J. Chem. Soc.*, **1959**, 886.

is most favorable to the cyclic dimerization. It was confirmed that II was stable in the reagent of Eglinton's oxidative coupling. A solution of II in the reagent was diluted with a large amount of water and extracted with benzene. After treatment according to the usual manner, the benzene solution was subjected to a spectroscopic examination. An identical electronic spectrum was obtained. On the other hand, the cuprous salt of X readily decomposed in pyridine forming a decomposition product. This behavior makes a contrast with the stable nature of the cuprous salt of 1,8-diethynylanthracene in the same solvent. The details of the oxidative coupling of X is not clear, but it seemed to be related with the enhanced flexibility of the diacetylenic groups in X as compared with the rigid ethynyl groups in 1, 8-diethynylanthracene.

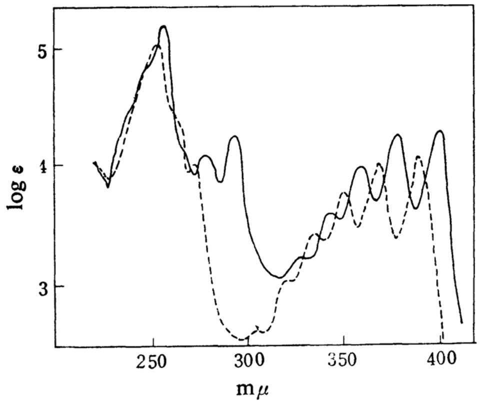

Fig. 2. The electronic spectra of 1-ethynylanthracene (------) and 1-butadiynylanthracene (XI, ——).

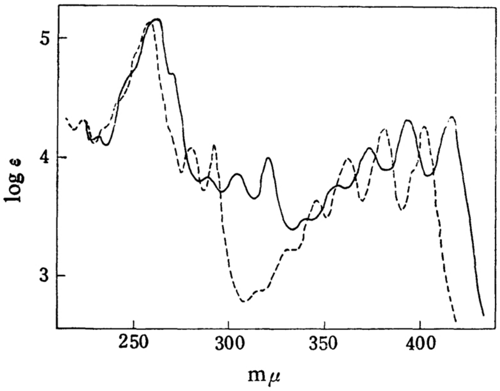

Fig. 3. The electronic spectra of 1, 8-diethynylanthracene (------) and 1, 8-bis-butadiynylanthracene (X, ——).

As illustrated in Figs. 2 and 3, the electronic spectra of 1-ethynyl-⁽⁷⁾, 1-butadiynyl-⁽⁸⁾, 1, 8-diethynyl-⁽¹⁾ and 1, 8-bis-butadiynylanthracene exhibit absorption curves characteristic to anthracene nucleus excepting the wavelength region of 270~320 mμ. The characteristic feature of the electronic spectra of these acetylenic compounds appears in this wavelength. 1-Ethynylanthracene has an absorption peak in this region. 1-Butadiynyl- and 1, 8-diethynylanthracene exhibit two absorption peaks. Whereas three absorption maxima appeared in the case of 1, 8-bis-butadiynylanthracene (X). The spectra of 1, 1′-dianthryldiacetylene⁽⁶⁾, 1, 1′-dianthryltetraacetylene⁽⁷⁾, the cyclic tetraacetylene I⁽¹⁾ and the cyclic octaacetylene II were summarized in Fig. 4. The fine structures in the spectra of 1, 1′-dianthryltetraacetylene and II are much more indistinct as compared with those of 1, 1′-dianthryldiacetylene and the cyclic tetraacetylene I. It is of interest to note that the fine structure in the spectra of α, ω-diphenyl- or α, ω-dialkylpolyynes become more and more distinct with the increasing number

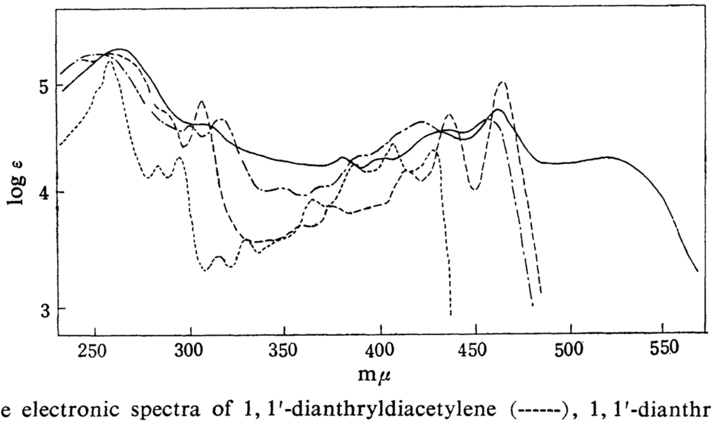

Fig. 4. The electronic spectra of 1, 1′-dianthryldiacetylene (------), 1, 1′-dianthryltetraacetylene (—·—·—·) cyclictetraacetylene (I, ------) and cyclicoctaacetylene (II, ——).

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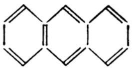
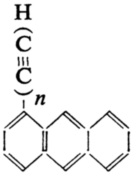
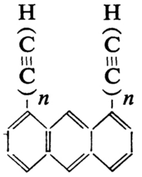
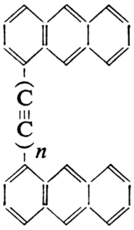
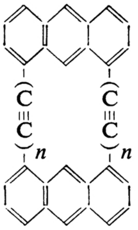
7) S. Akiyama and M. Nakagawa, This Bulletin, 33, 1293 (1960).

8) S. Akiyama, S. Misumi and M. Nakagawa, This Bulletin, 35, 1826 (1962).

TABLE I. THE BATHOCHROMIC SHIFTS OF THE ELECTRONIC SPECTRA OF THE ACETYLENES

	Compound		λ_{max} (mμ)	ε	Shifts in mμ from								Solvent
					1	2	3	4	5	6	7	8	
1			374	7400	—	—	—	—	—	—	—	—	C
2		$n=1$	391	11500	17	—	—	—	—	—	—	—	C
3		$n=2$	402	17800	28	11	—	—	—	—	—	—	H
4		$n=1$	402	17400	28	11	0	—	—	—	—	—	C
5		$n=2$	416	19950	42	25	14	14	—	—	—	—	E
6		$n=2$	428	24600	54	37	26	26	12	—	—	—	C
7		$n=4$	457	40700	83	66	55	55	41	29	—	—	B
8		$n=2$	465	91200	91	74	63	63	49	37	8	—	B
9		$n=4$	520	20420	146	129	118	118	104	92	63	55	T

Solvent: C=cyclohexane; H=n-hexane; E=ethanol; B=benzene; T=tetrahydrofuran

of the acetylenic linkage making a contrast with the case of the acetylenic derivatives of anthracene[9].

The position of absorption maxima, their ε-values and the relative shifts of the maxima of the above-mentioned acetylenic derivatives as compared with anthracene are tabulated in Table I. The comparison of the spectra of 1, 1'-dianthryltetraacetylene and the cyclic tetraacetylene I indicates that the red-shift of the maximum at the longest wavelength of I from the acyclic analogue is only 8 mμ, but the ε-value of I is over twice as large as that of the acyclic tetraacetylene. The large difference in the ε-values is remarkable, because these two compounds have the same structural units. The five absorption peaks at the longer wavelength region in the spectrum of II correspond well with those of the spectrum of the cyclic tetraacetylene I*, but the magnitude of red-shifts of the corresponding absorption peaks increases with the increasing wavelength of the maxima (4, 11, 17, 25 and 55 mμ). The characteristic of the spectrum of the cyclic octaacetylene II is the relatively low absorption intensity at the maximum of the longest wavelength, but the absorption intensities of other peaks are found to be higher than those of the corresponding peaks of I. Another remarkable feature of the spectrum of II is its high absorption intensity over a wide range of wavelength. It was found that the log ε-value was over 4.0 from 230 to 550 mμ.

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[9] Cf., M. Nakagawa, *Proc. Japan Acad.*, **26** (10), 38, 43 (1950); H. H. Schlubach, *Ann.*, **537**, 110 (1951); F. Bohlmann, *Chem. Ber.*, **84**, 545, 785 (1951).

* The absorption peaks of I are as follows: λ_{max} 258 mμ (log ε, 5.22) (in *n*-hexane), 307 (4.82), 340 (3.66), 358 (3.79), 376 (3.93), 392 (3.90, shoulder), 413 (4.22), 437 (4.67), 465 (4.96) (in benzene).

Experimental*

1, 8-Dimethoxycarbonylanthracene (III). — A stirred mixture of 1, 8-dicarboxyanthracene¹⁾ (50 g., 0.188 mol.), (methanol 1000 ml.) and concentrated sulfuric acid (20 g.) was refluxed for 8 hr. The reaction mixture was chilled with ice precipitating crystalline solid. The solid was washed with a small amount of methanol and water, successively, yielding yellow needles, m. p. 104~105°C (34 g.). The filtrate was concentrated under reduced pressure. The residue was poured into water (100 ml.) and extracted with benzene (60 ml.). Further crop of yellow needles, m. p. 104~105°C (10.5 g.) was obtained from the benzene extract. The combined yield was found to be 81%. Crystallization from methanol gave pure III, long yellow needles, m. p. 104~105°C.

Found: C, 73.41; H, 4.68. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80%.

Anthracene-1, 8-bis-carbohydrazide (IV.). — A solution of the methyl ester (III, 85 g., 0.28 mol.) in 99% ethanol (430 ml.) containing 80% hydrazine hydrate (170 ml.) was refluxed for 4 hr. Deposition of crystals was observed after 30 min. The reaction mixture was cooled in an ice-bath, and the crystals deposited were filtered, washed with ethanol (100 ml.) and water (300 ml.), successively, yielding crude IV, yellow needles, m. p. 279~288°C (decomp.), 75 g., (92%). The crude material was recrystallized twice from ethanol to give pure IV, yellow needles, m. p. 292~293°C (decomp.).

Found: C, 64.86; H, 4.87; N, 18.97. Calcd. for $C_{16}H_{14}O_2N_4$: C, 65.29; H, 4.80; N, 19.04%.

Bis-benzenesulfonyl Derivative of IV (V).— The hydrazide (IV, 73 g., 0.25 mol.) and benzenesulfonyl chloride (146 g.) were dissolved in dry pyridine (365 ml.) and the mixture was stirred at 0°C. Gradual deposition of light yellow crystals was observed. After 3 hr., the reaction mixture was allowed to warm up to room temperature and the stirring was continued for further 5 hr. The solid deposited was filtered, washed successively with a small amount of pyridine, diluted hydrochloric acid and water yielding light yellow crystalline powder, m. p. 260~264°C (decomp.), 133 g. (92%). This substance was recrystallized 3 times from pyridine yielding pure V, light yellow fine crystals, m. p. 263~264°C (decomp.).

Found: N, 9.71. Calcd. for $C_{28}H_{22}N_4O_6S_2$: N, 9.75%.

1, 8 - Bis - hydroxymethylanthracene (VI).—The methyl este (III, 29.4 g., 0.10 mol.) was placed in a Soxhlet type extractor and extracted with ether (1.4 l.) containing lithium aluminum hydride (3.8 g., 0.10 mol.). The ester III was completely extracted during 4 hr. The reflux was continued for further 3 hr. to complete the reduction. Ethyl acetate (9 ml.) was added to the ice-cooled reduction mixture and the solvent was distilled out. 6 N-Hydrochloric acid (250 ml.) was added to the residue and the insoluble substance was collected, washed successively with diluted hydrochloric acid and water yielding crude VI, light yellow fine needles, m. p. 215~217°C, 23.0 g. (97%). Crystallization from ethanol gave pure VI, light yellow cubes, m. p. 217~218°C.

Found: C, 80.31; H, 5.93. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92%.

IR: 3260 (-OH), 1010 cm^{-1} (C-O), (KBr-disk).

1, 8-Diformylanthracene (VII).—*a*) *By the Alkaline Decomposition of V.*—A solution of the bis-benzenesulfonyl derivative (V, 11.5 g., 0.02 mol.) in anhydrous ethylene glycol (240 ml.) was heated to 165°C. Finely powdered anhydrous sodium carbonate (25 g.) was added in one portion to the solution accompanying vigorous frothing. After 10 sec., the solution was poured into water (600 ml.) and the precipitate formed was filtered, washed with water yielding yellowish brown solid (1.8 g.). The solid was digested with hot benzene. Concentration of the benzene solution resulted in the crude dialdehyde (VII), yellow needles, m. p. 181~185°C, 0.7 g. (15%). Recrystallization from benzene gave pure VII, m. p. 189~191°C.

Found: C, 81.83; H, 4.29. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

b) *By the Oxidation of the Bis-hydroxymethyl Derivative VI.*—A solution of VI (4.8 g., 0.02 mol.) in dry pyridine (120 ml.) was added in one portion to an ice-cooled solution of chromium trioxide (16 g., 0.16 mol.) in dry pyridine (160 ml.) and the mixture was shaken. The cooling-bath was removed after 20 min. The mixture was shaken for 2 hr. at room temperature and poured into water. The precipitate formed was filtered, washed with water affording a brown powder (4.4 g.). The powder thus obtained was extracted with benzene (100 ml.) employing Soxhlet type extractor. Evaporation of the solvent gave yellow leaflets, m. p. 187~190°C, 3.5 g. (75%). Recrystallization from benzene yielded pure VII, yellow cubes, m. p. 189~191°C.

Found: C, 82.06; H, 4.29. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

IR: 2710 (-CHO), 1675 cm^{-1} (-C=O), (KBr-disk).

UV $\lambda_{max}^{Tetrahydrofuran}$ mμ (log ε): 235.5 (4.45), 259.5 (4.87), 330 (3.73), 352 (3.62), 371 (3.77), 397 (3.87), 418 (3.79).

1, 8-Bis (1′, 4′-dihydroxybut-2′-ynyl)-anthracene (VIII).—*a*) *Via 2-(Prop-2′-yn-1′-yloxy)-tetrahydropyran Mercuric Salt.*—The mercuric acetylide of tetrahydropyranyl ether of propargyl alcohol (11.5 g., 0.024 mol.) was prepared according to the method of Johnson¹⁰⁾ was refluxed for 1.5 hr. with an excess of lithium in dry dioxane (120 ml.) in an atmosphere of nitrogen. The solution of the lithium acetylide thus prepared was transferred into another reaction vessel, and was mixed with a solution of the dialdehyde (VII, 0.94 g., 0.004 mol.) in dioxane (50 ml.) and tetrahydrofuran (120 ml.). The mixture was stirred for 4 hr. at 10°C and then 4 N sulfuric acid (100 ml.) was added under ice-cooling. After stirring for 1 hr., the mixture was extracted with benzene (200 ml.), washed successively with saturated solutions of sodium chloride, sodium hydrogen carbonate and sodium chloride, and dried (sodium sulfate). Removal of the solvent under reduced pressure resulted in a dark red oil. Light brown

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* All melting points are not corrected.

10) J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

amorphous solid, m. p. ca. 170°C, 0.26 g. (19%) was obtained on addition of benzene (20 ml.) to the dark red oil. This substance was recrystallized 3 times from benzene-methanol to give pure VIII, light yellow leaflets. This material decomposed at ca. 210°C.

Found: C, 75.89; H, 5.24. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24%.

b) By the Method of Metalation with Phenyllithium. —An ethereal solution of phenyllithium (1.66 N, 90 ml.) was added during 20 min. to an ice-cooled solution of tetrahydropyranyl ether of propargyl alcohol (21.0 g., 0.15 mol.) in ether (20 ml.) under nitrogen atmosphere. The mixture was stirred for 30 min. at room temperature, then for 1 hr. under reflux. A solution of the dialdehyde (VII, 7.0 g., 0.03 mol.) in tetrahydrofuran (750 ml.) was added to the ice-cooled mixture and stirred for 4.5 hr. resulting in a dark red solution. At this stage, an aliquot of the reaction mixture gave negative test against carbonyl reagents. 4 N Sulfuric acid (300 ml.) was introduced to the reaction mixture under ice-cooling and the mixture was stirred for 3 hr. at 10°C. The organic layer separated was washed with saturated solutions of sodium chloride, sodium hydrogen carbonate and sodium chloride, successively, and dried over sodium sulfate. Evaporation of the solvent under reduced pressure gave a dark red viscous oil. Benzene (100 ml.) was added to the oil precipitating a light brown amorphous solid, 4.4 g. (42%). The solid was recrystallized twice from tetrahydrofuran-benzene to give pure VIII, m. p. ca. 210°C (decomp.), light yellow leaflets.

Found: C, 76.31; H, 5.24. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24%.

The infrared and ultraviolet spectra were proved to be entirely identical with those of the specimen prepared by the above-mentioned method a).

IR: 3260 (O-H), 1055, 1020 cm^{-1} (C-O) (KBr-disk).

UV $\lambda_{max}^{90\%EtOH}$ mμ (log ε): 254 (5.10), 300† (2.54), 315† (3.05), 329 (3.42), 345 (3.70), 362 (3.88), 381.5 (3.80).

1, 8-Bis-butadiynylanthracene (X).—A mixture of thionyl chloride (5.0 g., 0.042 mol.), dry pyridine (0.5 g., 6 mmol.) and tetrahydrofuran (10 ml.) was added dropwise during 1 hr. to an ice-cooled solution of the tetraol (VIII, 2.10 g., 6 mmol.) in tetrahydrofuran (100 ml.) under stirring. Stirring was continued for 30 min. at the same temperature, for 1.5 hr. at 20°C and finally for 10 min. under reflux. The dark red reaction mixture was concentrated to ca. 20 ml. under reduced pressure in an atmosphere of nitrogen. The solution of the crude tetrachloride thus obtained was added dropwise during 30 min. into a solution of sodium amide (prepared from sodium, 7 g., 0.3 g. atom) in liquid ammonia (250 ml.) at −70°C. After stirring for 2 hr., ammonium chloride (15 g.) was added and the ammonia was allowed to evaporate. The residual solid was repeatedly digested with petroleum benzine (b. p. 60~80°C, total 1.8 l.). The extract was washed with water and dried (sodium sulfate). The solvent was removed under reduced pressure in nitrogen atmosphere resulting in crude crystals, which were dissolved in benzene (40 ml.). The solution was passed through a thin layer of alumina (20 g.). Concentration of the filtrate afforded X, bright yellow fine needles, m. p. ca. 110°C (decomp.), 0.38 g. (23%). Crystallization from benzene-petroleum benzine gave the analytical sample with m. p. ca. 110°C (decomp.).

Found: C, 96.54; H, 3.79. Calcd. for $C_{22}H_{10}$: C, 96.33; H, 3.67%.

IR: 3280 (≡CH), 2200 cm^{-1} (-C≡C-), (KBr-disk).

Electronic spectrum, $\lambda_{max}^{95\%EtOH}$ mμ (log ε): 230.5 (4.13), 262 (5.16), 270.5 (4.71), 287.5 (3.84), 304 (3.90), 320 (4.01), 339† (3.46), 356 (3.75), 374 (4.09), 394 (4.30), 417 (4.30).

The Oxidative Coupling of X.—To a mixture of finely powdered cupric acetate monohydrate (9 g.) and dry pyridine (30 ml.) was added a solution of the tetraacetylene (X, 0.35 g., 0.0013 mol.) in pyridine (10 ml.) and methanol (10 ml.) in one portion at 20°C. The color of the reaction mixture changed immediately to brownish black. The mixture was vigorously shaken for 1 min., and petroleum ether (100 ml.) was added to quench the reaction. The solid formed was filtered, washed with a small amount of petroleum ether and ethanol, and then thororoughly with water. The solid thus obtained was triturated successively with a minor amount of ethanol and benzene yielding reddish black powder (0.18 g.). The substance was digested with chlorobenzene (1.2 l.). The chlorobenzene solution was passed twice through a short column of alumina (15 g.) resulting in deep orange-red filtrate with fluorescence. Concentration of the solution under reduced pressure in an atmosphere of nitrogen resulted in deep red crystals. This was filtered, washed with a small amount of benzene yielding II, deep red fine needles, 0.06 g., (17%). II changed to a brownish black solid at ca. 160°C without fusion.

Found: C, 96.73; H, 3.31. Calcd. for $C_{44}H_{16}$: C, 97.04; H, 2.96%.

IR: 2190, 2140, 2110 cm^{-1} (-C≡C-), (Nujol mull).

Electronic spectrum $\lambda_{max}^{Tetrahydrofuran}$ mμ (log ε): 262 (5.26), 330† (4.41), 380 (4.33), 403† (4.30), 430 (4.53), 462 (4.71), 520 (4.31).

Catalytic Reduction of the Octaacetylene (II). —A suspension of II (0.04 g.) in pure benzene (500 ml.) was shaken in an atmosphere of hydrogen in the presence of 10% palladium-on-charcoal (0.1 g.). The progress of hydrogenation was followed by the change of the electronic spectrum. After 72 hr., no more change in the spectrum was observed. The catalyst was removed by filtration, and washed with benzene (250 ml.). The combined benzene solution was concentrated to 150 ml. and hydrogenated for 24 hr. in the presence of the fresh catalyst (0.05 g.). Further change of the spectrum could not be detected. The catalyst was removed and washed with the same solvent. The solvent was removed under reduced pressure giving light yellow solid. The solid was dissolved in petroleum benzine (10 ml.) and chromatographed on alumina (2.0 g.). Elution with petroleum benzine-benzene (3 : 1) afforded a light yellow

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† Dagger on the figure of the electronic spectral data denotes shoulder.

solution. After concentration of the eluate, a small amout of ethanol was added yielding a faint yellow amorphous substance. A benzene solution (2 ml.) of this substance was passed through a thin layer of alumina (1 g.) and eluted with benzene resulting in a light yellow eluate with blue fluorescence. The most part of the solvent was removed under reduced pressure and a minor quantity of ethanol was added yielding light yellow crystals. Recrystallization from benzene-ethanol gave XI, light yellow fine crystals, m. p. 122~125°C (0.01 g.).

Found: C, 91.27; H, 8.49. Mol. wt., 613 (Rast, in camphor). Calcd. for $C_{44}H_{50}$: C, 91.29; H, 8.71%. Mol. wt., 579.

IR: 2935, 2870, 1470 ($-CH_2-$), 770 (1, 2, 3-trisubstituted benzene), 875 cm^{-1} (1, 2, 4, 5-tetrasubstituted benzene), (KBr-disk).

UV $\lambda_{\max}^{\text{Tetrahydrofuran}}$ mμ (log ε): 235 (4.85), 259 (4.55), 284 (3.86), 295 (3.85), 308† (3.69), 327 (2.32), 334† (3.17), 351 (3.27), 369 (3.40), 389 (3.36).

The present study was partly supported by the grant-in-aid of the Ministry of Education, to which grateful acknowledgment is made. The present authors are also indebted to Messrs. Masakazu Okumiya and Osamu Saiki for performing the microanalyses.

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