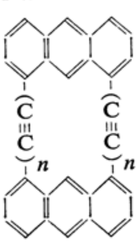
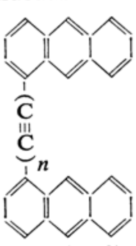
Cyclic Acetylenes. VIII. Synthesis of 1, 1'-Dianthryltetraacetylene. A Model Substance of a Cyclic Octaacetylene Containing Anthracene Nuclei*

By Shuzo AKIYAMA, Soichi MISUMI and Masazumi NAKAGAWA

(Received July 10, 1962)

The synthesis of the macrocyclic tetraacetylene (I) in which two anthracene nuclei constitute a part of the fully conjugated planar macroring has been reported by the present authors[1]. It is of interest to prepare the higher homologue of I in view of the unusual stability and the characteristic spectroscopic properties of I. The present paper concerns with the synthesis of 1, 1'-dianthryltetraacetylene (IV) which is a model substance of the cyclic octaacetylene (II), a higher homologue of I. The structural units of IV can be regarded as the same with that of II. Also a lower homologue of IV, 1 1'-dianthryldiacetylene (III) has been synthesized by the present authors[2]. Therefore, the comparison of the physical and chemical properties of these compounds with those of IV is also of interest.


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


III (n=2)
IV (n=4)

Benzanthrone was converted into 1-carboxyanthracene via two steps[2] and the carboxylic acid was esterified yielding the methyl ester (V). Reduction of the ester V by means of lithium aluminum hydride afforded 1-hydroxymethylanthracene (VI) in a good yield. 1-Bromomethylanthracene (VII) derived from VI was converted to 1-formylanthracene (VIII) by the Sommelet's method[3]. The aldehyde VIII was also prepared directly by the oxidation of the alcohol VI with chromium trioxide-pyridine[4] in a yield of 88%. The reaction of the aldehyde VIII with the Grignard derivative of tetrahydropyranyl ether of propargyl alcohol yielded the acetylenic glycol (IX). The glycol IX was treated with thionyl chloride and pyridine, and the dichloride X thus obtained was dehydrochlorinated without further purification with sodium amide in liquid ammonia. 1-Butadiynylanthracene (XI) was obtained in yellow needles. The diacetylene XI was found to be fairly stable substance and could be kept without decomposition for periods of days in a refrigerator. A dilute solution of XI in an organic solvent exhibits an intense lilac fluorescence. XI gave orange cuprous and orange-yellow silver salts indicating the presence of terminal acetylene. Also the infrared spectrum of XI exhibits strong bands at 3250 and 2210 cm^{-1} indicating the presence of ethynyl group and disubstituted carbon-carbon triple bond (Fig. 1). The electronic spectrum of XI was illustrated in Fig. 2.

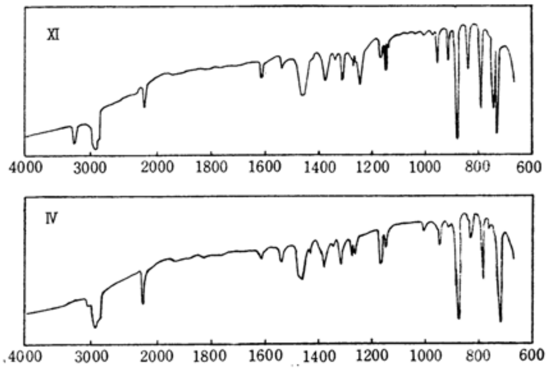


Fig. 1. The infrared spectra of 1-butadiynylanthracene (XI) and 1, 1'-dianthryltetraacetylene (IV) (Nujol mull).

The oxidative coupling of XI according to the procedure of Eglinton[5] yielded golden-yellow leaflets or needles. The structure of

---

* Although the present paper is concerned with acyclic acetylenes, it has been included in this series since the compounds and the reaction described here served as models for the synthesis of analogous cyclic derivative.

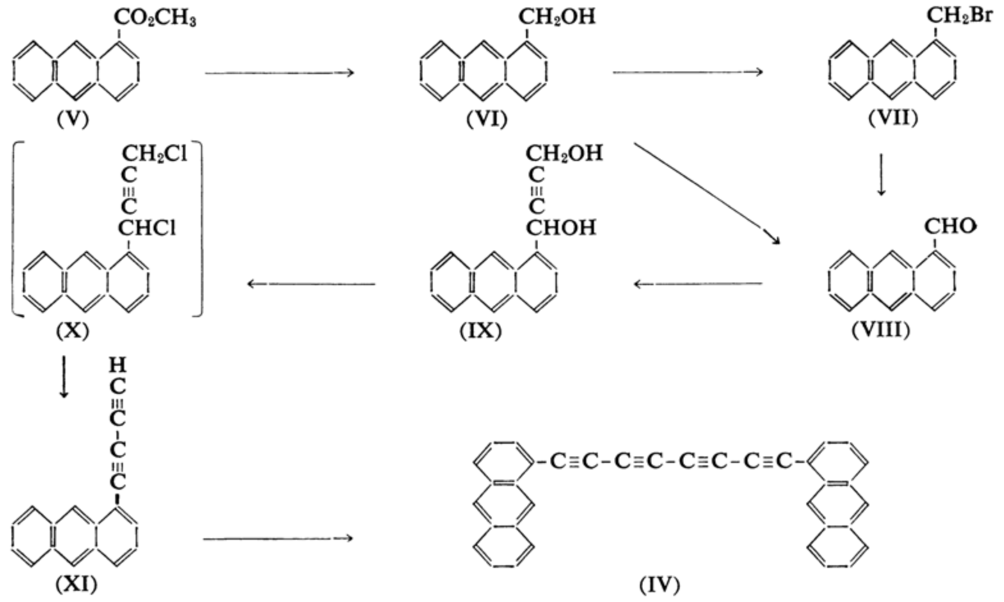
1) S. Akiyama, S. Misumi and M. Nakagawa, This Bulletin, 33, 1293 (1960).

2) S. Akiyama and M. Nakagawa, This Bulletin, 33, 1291 (1960).

3) Cf., M. Sommelet, *Compt. rend.*, **157**, 852 (1913); *Bull. soc. chim. France*, [4] **13**, 1085 (1913); S. J. Angyal, "Org. Reactions", Vol. VIII, J. Wiley & Sons, Inc., New York (1954), p. 197.

4) Cf., G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *J. Am. Chem. Soc.*, **72**, 422 (1953).

5) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **1959**, 886.



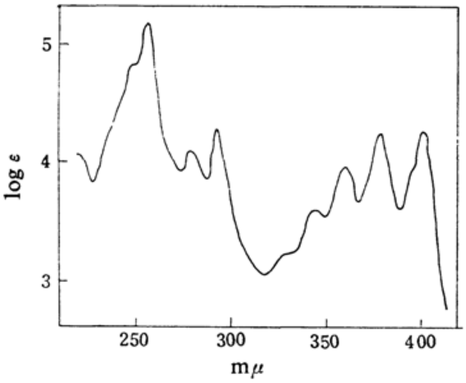


Fig. 2. The electronic spectrum of 1-butadiynylanthracene (XI).

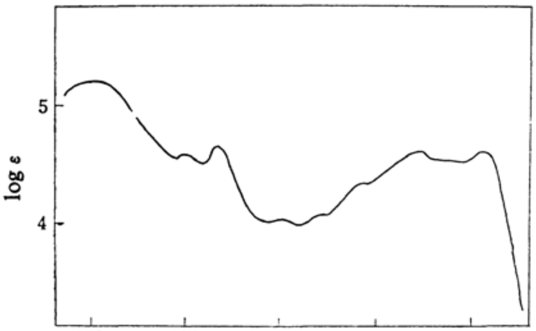


Fig. 3. The electronic spectrum of 1, 1′-dianthryltetraacetylene (IV).

1, 1′-dianthryltetraacetylene (IV) was given to the substance on the bases of its analytical data and the infrared spectroscopic evidences (the absence of free ethynyl absorption and the presence of acetylenic absorption at 2205 cm^{-1} (Fig. 1)). IV was found to be a very stable substance. IV showed no melting point, it decomposed on heating to ca. 245°C forming a black substance without the change of its crystal form. Like I and III, the tetraacetylene (IV) is slightly soluble or almost insoluble in common organic solvents. The electronic spectrum of IV was shown in Fig. 3. The electronic spectral properties of XI, IV and related compounds will be discussed in the following paper[6].

Experimental*

1-Methoxycarbonylanthracene (V).—1-Carboxyanthracene was refluxed with methanol in the presence of sulfuric acid yielding V, m. p. 104°C, (lit., m. p. 108°C[7]; m. p. 104°C[8]).

1-Hydroxymethylanthracene (VI).—The methyl ester (V, 30.6 g., 0.13 mol.) was reduced with lithium aluminum hydride (4.8 g.) in boiling ether (1.2 l.) using a Soxhlet type extractor. The refluxing of the reaction mixture was continued for further 1 hr. to complete the reduction after all of the ester V had been extracted (3 hr.). Ethyl acetate (6 ml.) and 5% aqueous sodium hydroxide (100 ml.) were added successively to the ice-cooled reaction mixture under vigorous stirring. The ether layer was separated and the residue obtained by the removal of the solvent was stirred with 10% aqueous sodium hydroxide (100 ml.) for 1 hr. The insoluble material was collected by filtration,

---

[6] S. Akiyama, S. Misumi and M. Nakagawa, This Bulletin, 35, 1829 (1962).

* All melting points were not corrected.

[7] E. A. Coulson, *J. Chem. Soc.*, **1930**, 1931.

[8] A. Sonoda, F. Ogura and M. Nakagawa, This Bulletin, 35, 853 (1962).

washed with water, 6 N hydrochloric acid and water, successively, yielding colorless fine fibrous crystals, m. p. 124~125°C, (26.0 g., 96%). This was recrystallized from ethanol to give pure VI, colorless long needles, m. p. 125~126°C.

Found: C, 86.63; H, 5.99. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81%.

IR: 3215 (O-H), 1030 cm^{-1} (C-O), (KBr-disk).

1-Bromomethylanthracene (VII).—To an ice-cooled mixture of VI (1.1 g., 5 mmol.), chloroform (20 ml.) and pyridine (0.2 ml.) was added phosphorus tribromide (0.6 g., 2.2 mmol.). The mixture was allowed to warm up to room temperature and kept at the temperature for 1 hr. with occasional shaking and then water was added. The chloroform layer was washed with water and dried over sodium sulfate. Evaporation of the solvent yielded crude VII, yellow needles, m. p. 111~113°C, (1.3 g., 93%). The crude material was recrystallized twice from carbon tetrachloride to give pure VII, yellow needles, m. p. 114~115°C. VII could not be kept without decomposition for a long time.

Found: C, 66.05; H, 4.04; Br, 29.30. Calcd. for $C_{15}H_{11}Br$: C, 66.04; H, 4.09; Br, 29.47%.

The Pyridinium Bromide.—Pale yellow leaflets, m. p. 225~227°C (decomp.).

Found: C, 68.27; H, 4.64; N, 3.92. Calcd. for $C_{20}H_{16}NBr$: C, 68.53; H, 4.60; N, 4.00%.

The Pyridinium Perchlorate.—Pale yellow leaflets, m. p. 235~237°C (decomp.).

Found: C, 64.94; H, 4.43; N, 3.93, Cl, 9.07. Calcd. for $C_{20}H_{16}O_4NCl$: C, 64.96; H, 4.36; N, 3.79, Cl, 9.59%.

An accurate analysis of chlorine could not be performed owing to an explosive decomposition of the salt in the combustion tube.

1-Formylanthracene (VIII).—*a) By the Sommelet Method.*—The hydroxymethyl derivative (VI, 2.2 g., 0.01 mol.) was treated with phosphorus tribromide according to the above-mentioned procedure and the chloroform solution was washed with water and dried (sodium sulfate). A solution of hexamethylenetetramine (1.7 g., 0.012 mol.) in chloroform (15 ml.) was added to the dried solution and the mixture was refluxed for 3 hr. About half of the solvent was removed and the concentrated solution was chilled with ice. The hexamine-adduct deposited was filtered and washed with a small amount of chloroform affording pale yellow crystalline solid (3.3 g.). Water (30 ml.) was added to a solution of the adduct (3.3 g.) in acetic acid (30 ml.) and the mixture was refluxed for 1 hr., then 12 N hydrochloric acid (0.7 ml.) was added and refluxed for 5 min. The mixture was poured into water (200 ml.), extracted with benzene (100 ml.), and the extract washed with water and dried (sodium sulfate). Evaporation of the solvent under reduced pressure afforded yellow leaflets, m. p. 126~130°C (from ethanol), (1.1 g., 53%). Further recrystallization from the same solvent gave pure VIII, m. p. 131~132°C, (lit., m. p. 131~133°C[9], m. p. 126.5~127.5°C[10]).

Found: C, 87.16; H, 4.97. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89%.

b) By the Oxidation of VI with Chromium Trioxide-pyridine.—A solution of VI (4.2 g., 0.02 mol.) in dry pyridine (30 ml.) was added in one portion to an ice-cooled mixture of chromium trioxide (3.8 g., 0.08 mol.) and dry pyridine (80 ml.). The mixture was shaken for 30 min. in the cooling bath, then for 2 hr. at room temperature and then poured into water (1.5 l.); leaflets precipitated. The crystals were extracted with benzene (100 ml.) employing a Soxhlet type extractor. Evaporation of the solvent afforded VIII, yellow leaflets, m. p. 123~129°C, (3.6 g., 88%). Analytical specimen (m. p. 131~132°C) was prepared by one recrystallization from benzene.

Found: C, 87.36; H, 4.93. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89%.

IR: 2710 (-CHO), 1690 cm^{-1} (C=O), (KBr-disk).

UV $\lambda_{\max}^{\mathrm{MeOH}}$ mμ (log ε): 241.5 (4.80), 259.5 (4.63), 334† (3.16), 348 (3.48), 366 (3.69), 392 (3.76), 405† (3.71).

1-(1′, 4′-Dihydroxybut-2′-ynyl)-anthracene (IX).—To a solution of ethylmagnesium bromide (prepared from magnesium, 9.7 g., 0.4 g. atom and ethyl bromide, 49 g., 0.45 mol.) in tetrahydrofuran (150 ml.) was added a solution of tetrahydropyranyl ether of propargyl alcohol[11] (56 g., 0.4 mol.) in tetrahydrofuran (50 ml.) over a period of 30 min. under cooling with water and then the mixture was refluxed for 1.5 hr. A solution of the aldehyde (VIII, 20.6 g., 0.1 mol.) in the same solvent (460 ml.) was introduced during 1 hr. under cooling with water. After stirring for 10 hr. at 10°C, 4 N sulfuric acid (800 ml.) was added into the reaction mixture under cooling with water and stirred for 1.5 hr. The mixture was extracted with benzene (300 ml.). The extract was washed with 4 N sulfuric acid (100 ml.) and water, successively and dried (sodium sulfate). The most part of the solvent was removed under reduced pressure. The crystals deposited were filtered and washed with a small amount of benzene yielding crude IX, pale yellow fine crystals, m. p. 192~196°C, (18.4 g., 70%). This material was recrystallized from ethanol-benzene (4:1) to give pure IX, yellowish white leaflets, m. p. 204~205°C.

Found: C, 82.20; H, 5.50. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38%.

IR: 3220 (O-H), 1015, 1030 cm^{-1} (C-O), (KBr-disk).

UV $\lambda_{\max}^{95\%\mathrm{EtOH}}$ mμ (log ε): 254 (5.13), 302† (2.76), 312 (3.15), 327 (3.51), 342 (3.78), 359 (3.95), 378 (3.87).

1-Butadiynylanthracene (XI).—To an ice-cooled mixture of the acetylene glycol (IX, 3.15 g., 0.012 mol.) in dry pyridine (4 g., 0.05 mol.) and tetrahydrofuran (100 ml.) was added under stirring a solution of thionyl chloride (6 g., 0.05 mol.) in tetrahydrofuran (10 ml.) over a period of 1 hr. The mixture was stirred for 0.5 hr. at 40°C and then refluxed for 1.5 hr. resulting in a dark red solution.

---

9) R. Walker, "Documentation of Molecular Spectroscopy", English Ed., 4504, 3/59, Butterworth Scientific Publications (London).

10) P. H. Gore, *J. Chem. Soc.*, **1959**, 1616.

† Dagger on the figures of the spectral data denotes shoulder.

11) H. B. Henbest, E. R. H. Jones and I. M. S. Walls, *J. Chem. Soc.*, **1950**, 3646.

Crushed ice was added to the solution and extracted with benzene (100 ml.). The extract was washed with aqueous sodium hydrogen carbonate and dried (sodium sulfate). The solvent was removed under reduced pressure in an atmosphere of nitrogen yielding the crude dichloride X as tarry viscous oil. A solution of the crude dichloride in tetrahydrofuran (25 ml.) was added dropwise into a solution of sodium amide (prepared from sodium, 5.8 g., 0.25 g. atom) in liquid ammonia (250 ml.) in the course of 1 hr. After stirring for 3 hr., ammonium chloride (10 g.) was introduced to the mixture and the ammonia was allowed to evaporate. The residue was repeatedly extracted with petroleum benzine (b. p. 60~80°C, total 1000 ml.). The extract was condensed, after being washed with water and dried (sodium sulfate), to ca. 300 ml. under reduced pressure in nitrogen atmosphere. The condensed extract was filtered through a thin layer of alumina (10 g.). The filtrate was again condensed under reduced pressure in nitrogen atmosphere to yield XI, yellow needles, (0.89 g., 33%) which decomposed at ca. 130°C forming a black solid without fusion.

Found: C, 95.38; H, 4.44. Calcd. for $C_{18}H_{10}$: C, 95.54; H, 4.46%.

IR: 3250 (≡C-H), 2210 cm^{-1} (-C≡C-), (Nujol mull).

UV $\lambda_{\max}^{n\text{-Hexane}}$ mμ (log ε): 249.5 (4.85), 257.5 (5.19), 279 (4.10), 294.5 (4.27), 330 (3.23), 345 (3.60), 361 (3.97), 380 (4.22), 402 (4.25).

Formation of IV by the Oxidative Coupling of XI.—Cupric acetate monohydrate (15 g.) was added to a solution of the diacetylene (XI, 0.79 g., 0.0035 mol.) in pyridine (100 ml.) and the mixture was stirred for 4 hr. at 45°C. The solid obtained by filtrating the reaction mixture was washed thoroughly with water affording tiny yellow crystals, 0.65 g. (82%). The crystals were found to be free from inorganic substance. The residue obtained by the concentration of the filtrate under reduced pressure was dissolved in benzene (80 ml.) and passed through a thin layer of alumina. Benzene was removed by evaporation yielding crude orange-yellow crystals, 0.05 g. (6%). The combined crystals were recrystallized thrice from benzene to give pure IV, golden yellow leaflets or needles. The crystals decomposed at ca. 245°C without fusion forming a black solid.

Found: C, 95.90; H, 4.10. Calcd. for $C_{36}H_{18}$: C, 95.97; H, 4.03%.

IR: 2205 cm^{-1} (-C≡C-), (Nujol mull).

UV $\lambda_{\max}$ mμ (log ε): 250 (5.20), (in tetrahydrofuran), 301 (4.59), 316.5 (4.65). 351† (4.05), 371† (4.30), 422 (4.60), 457 (4.61), (in benzene).

The authors are grateful to the Ministry of Education for the financial support. The microanalyses were performed by Messrs. Masakazu Okumiya and Osamu Saiki in the Microanalytical Laboratory of this Department, to whom the authors' thanks are also due.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka