# *Cyclic Acetylenes. III.* Synthesis of 1, 1′-Dianthryldiacetylene. A Model Substance of a Cyclic Tetraacetylene Containing Anthracene Nuclei*

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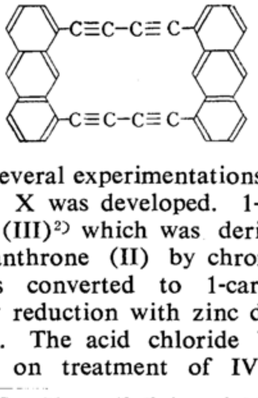
In the course of the synthetical studies on the cyclic tetraacetylene containing two anthracene nuclei (I)[1], the authors have studied the synthesis of 1, 1′-dianthryldiacetylene (X) as a model substance of I.



(I)

After several experimentations, the following route to X was developed. 1-Carboxyanthraquinone (III)[2] which was derived from 1, 9-benz-10-anthrone (II) by chromic acid oxidation was converted to 1-carboxyanthracene (IV)[3] by reduction with zinc dust in aqueous ammonia. The acid chloride V[4] which was obtained on treatment of IV with thionyl chloride was caused to react with diethyl ethoxymagnesiomalonate in toluene. The ketomalonate VI thus obtained was treated without further purification with a mixture of propionic acid and sulfuric acid to cause ester exchange and decarboxylation. The over-all yield of 1-acetylanthracene (VII)[5] from II was found to be 52%. The attempt to prepare VII by the reaction of dimethyl cadmium with V was found to be unsatisfactory.

The ketone VII was treated with phosphorus pentachloride in phosphorus oxychloride, and the crude chloride VIII was dehydrochlorinated with sodium amide in liquid ammonia yielding 1-ethynylanthracene (IX) as light yellow cubes. This substance decomposed gradually on standing at room temperature. The presence of a terminal acetylene was confirmed by the formation of yellow cuprous

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* For Part II, see F. Toda and M. Nakagawa, This Bulletin, 33, 230 (1960).

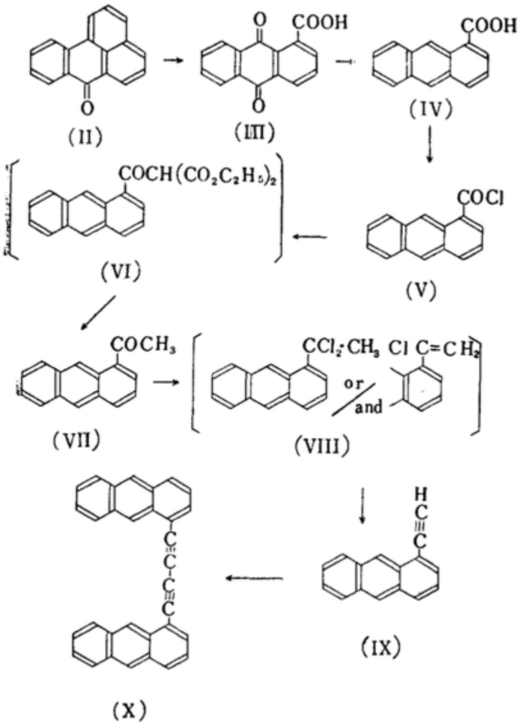
1) The following paper.

2) E. B. Barnett and J. W. Cook, *Ber.*, **57**, 1777 (1924).

3) C. Graebe and S. Blumenfeld, ibid., **30**, 1118 (1897).

4) J. W. Cook, *J. Chem. Soc.*, **1931**, 566; R. Scholl and J. Donat, *Ber.*, **62**, 1297 (1929).

5) VII can be obtained by the fractional recrystallization of a mixture with the 2-isomer which is the product of the direct acetylation of anthracene by the Friedel-Crafts reaction. The authors are grateful to Professor P. H. Gore for private communication suggesting the details of the above mentioned process. cf., P. H. Gore, *J. Org. Chem.*, **22**, 135 (1957).



and silver acetylides. Also the infrared spectrum of IX showed an absorption at 3270 cm$^{-1}$ indicating the presence of the ethynyl group as illustrated in Fig. 1.

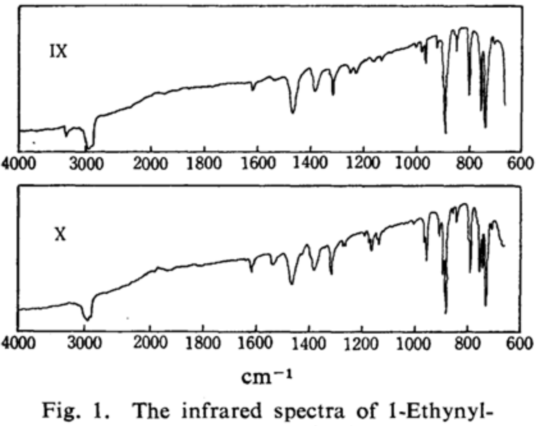


Fig. 1. The infrared spectra of 1-Ethynylanthracene (IX) and 1,1′-dianthryldiacetylene (X). (Nujol mull)

The oxidative coupling of IX according to the procedure of Eglinton[6] afforded fine yellow needles in almost quantitative yield. This was identified as X from its analytical data and the absence of free ethynyl absorption in the infrared spectrum (Fig. 1). X was found to be a stable substance and could be kept unchanged for a long time. X is slightly soluble in benzene and gives a greenish yellow solution with intense blue fiuorescence. The diyne X is almost insoluble in common organic solvents such as ethanol and petroleum benzine.

The ultraviolet spectra of IX and X will be discussed in the following paper comparing them with those of the analogous compounds.

## Experimental**

**1-Carboxyanthraquinone (III).**—The acid (III) was prepared by the chromic acid oxidation of 1,9-benz-10-anthrone (II) according to the method of J. W. Cook[2].

**1-Carboxyanthracene (IV).**—III was reduced by means of zinc dust and aqueous ammonia[3], m. p. 245°C, yellow rods (the reported value, m.p. 245°C[3]).

Found: C, 80.83; H, 4.63. Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.54%.

**1-Acetylanthracene (VII).**—IV was converted to the corresponding acid chloride V by the reaction with thionyl chloride. Diethyl ethoxymagnesiomalonate was prepared from diethyl malonate (48 g., 0.3 mol.), magnesium (7.3 g., 0.3 gram atom) and absolute ethanol (27.6 g., 0.6 mol.) in dry toluene (150 ml.). The excess of ethanol was removed by the azeotropic distillation with toluene. To the refluxed solution of the malonate a solution of crude V (24 g., 0.1 mol.) in dry toluene (400 ml.) was added in 30 min., and the stirring was continued for 3 hr. also under reflux. The reaction mixture was chilled with ice, and decomposed by the addition of 6 N sulfuric acid (100 ml.). The organic layer separated was washed thoroughly with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The crude ketomalonate VI was obtained as an orange-yellow oil. The crude product was mixed with propionic acid (80 ml.) and concentrated sulfuric acid (0.5 ml.), and the mixture was refluxed. After 3 hr., 4 N sulfuric acid (50 ml.) was added and the refluxing was further continued for 8 hr. to complete decarboxylation. A small amount of toluene was co-distilled out with water from the reaction mixture. The residue was diluted with water (300 ml.), and the mixture was extracted with benzene (100 ml.×6). The extract was washed with dilute sodium hydroxide and water, successively. The dried benzene solution was concentrated to 200 ml. and filtered through a short column of alumina (20 g.). Light yellow cubes, (15 g., 68%), m. p. 103~106°C were obtained on concentrating the filtrate. Recrystallization of the crude crystals from benzene afforded pure VII as light yellow cubes, m. p. 106~107°C (the reported value, m. p. 105~106°C[5]).

Found: C, 87.52; H, 5.50. Calcd. for $C_{16}H_{12}O$: C, 87.24; H, 5.49%.

I. R. max., 1670 cm$^{-1}$ (C=O).

**1-Ethynylanthracene (IX).**—The acetyl compound VII (10 g., 0.046 mol.) and phosphorus pentachloride (9.8 g., 0.068 mol.) was added to

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[6] G. Eglinton and A. R. Galbraith, *Chem. & Ind.*, 1956, 737; *J. Chem. Soc.*, 1959, 889.

** All melting points are uncorrected. The infrared spectra were measured by the Nujol mull method.

phosphorus oxychloride (70 ml.) and the mixture was refluxed for 1 hr. The mixture changed to a homogeneous dark red solution with an evolution of hydrogen chloride. Phosphorus oxychloride was removed completely under reduced pressure and the residual dark brown viscous oil was kept for several hours in an evacuated desiccator containing phosphorus pentoxide and potassium hydroxide.

The solution of the crude chloride in dry tetrahydrofuran (20 ml.) was added in 1 hr. to a solution of sodium amide (prepared from 11.5 g. of sodium) in liquid ammonia (500 ml.). After evaporation of ammonia, water (100 ml.) was added to the reaction product and extracted with ligh petroleum (b. p. 60~80°C, 1000 ml.). The extract was washed with water and dried over anhydrous sodium sulfate. The dried solution was filtered through a thin layer of alumina (40 g.). Concentration of the filtrate resulted in IX as light yellow cubes, 5.1 g. (55%), m. p. 88~90°C. This material was recrystallized from light petroleum or sublimed under high vacuum ($0.5\times10^{-4}$ mmHg) to yield pure IX, m. p. 90°C.

Found: C, 95.04; H, 5.10. Calcd. for $C_{16}H_{10}$: C, 95.02; H, 4.98%.

I. R. max., 3270cm$^{-1}$ (-C≡C-H).

U. V. max. (in cyclohexane), $\lambda_{max}$ 255 m$\mu$, (log $\varepsilon$ =5.05), 274.5 (4.04), 305 (2.60), 322 (3.03), 333.5 (3.44), 352 (3.78), 371 (4.04), 386 (3.68)* and 391 (4.06). Asterisk indicates shoulder.

**Oxidative Coupling of 1-Ethynylanthracene (IX).**—Cupric acetate monohydrate (40 g.) was added to the mixture of IX (1.89 g., 0.0094 mol.), dry pyridine (300 ml.) and methanol (20 ml.), and the mixture was stirred for 9 hr. at 55°C. The reaction mixture was filtered and the solid obtained was washed thoroughly with water. Yellow powder almost free from inorganic material was obtained, 1.45 g. (85%), m. p. 287~290°C (decomp.). The residue which was obtained by the concentration of the filtrate under a reduced pressure was digested with benzene. The benzene solution was passed through a short column of alumina and the filtrate was evaporated to yield yellow powder, 0.17 g. (10%), m. p. 289~291°C (decomp.). This was combined with the first crop and recrystallized from benzene to give pure X, yellow fine needles, m. p. 289~291°C (decomp.).

Found: C, 95.61; H, 4.47. Calcd. for $C_{32}H_{18}$: C, 95.49; H, 4.51%.

X gave no precipitate with an alcoholic silver nitrate solution.

U. V. max. (in cyclohexane), $\lambda_{max}$ 259 m$\mu$ (log $\varepsilon$ =5.16), 283 (4.27), 295 (4.35), 315.5 (3.52), 329 (3.66), 346 (3.64)*, 365 (3.99), 386 (4.26), 407 (4.42) and 428 (4.39). Asterisk indicates shoulder.

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