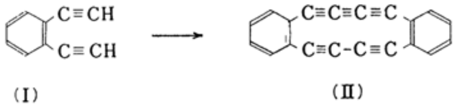
Another Example of the Formation of Highly Strained Cyclic Dimer of o-Diethynyl Compound[1]

By Mamoru Morimoto, Shuzo Akiyama, Sōichi Misumi
and Masazumi Nakagawa

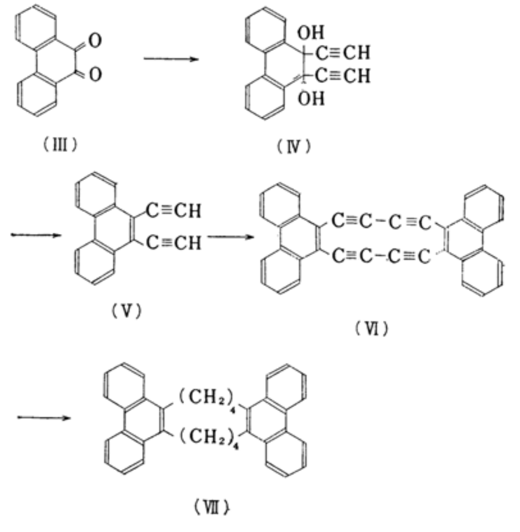
(Received October 23, 1961)

Recently, Raphael, Eglinton and their coworkers have studied the oxidative coupling of *o*-diethynylbenzene (I) by means of cupric acetate in pyridine, and the product was proved unexpectedly to be the highly strained cyclic dimer of I on the basis of chemical and physical evidence[2]. This result is rather surprising, because the starting material I has a rigid geometry favorable for the formation of strainless cyclic trimer[3].



(I) (II)

The present authors have carried out the oxidative coupling of 9, 10-diethynylphenanthrene (V) to confirm whether the forced



(III) (IV) (V) (VI) (VII)

---

[1] This paper is Cyclic Acetylenes VII. For the previous paper in this series see F. Toda and M. Nakagawa, This Bulletin, **34**, 874 (1961).

[2] O. M. Behr, G. Eglinton and R. A. Raphael, *Chem. & Ind.*, **1959**, 699; O. M. Behr, G. Eglinton, R. A. Galbraith and R. A. Raphael, *J. Chem. Soc.*, **1960**, 3614.

[3] W. Baker, J. F. W. McOmie and W. D. Ollis, ibid., **1951**, 200.

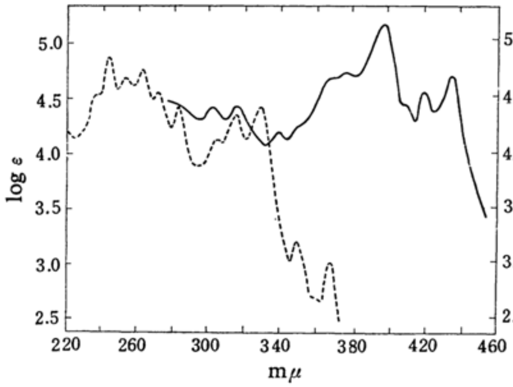


Fig. 1. The ultraviolet spectra of 9, 10-diethynylphenanthrene, V (----) and the cyclic dimer, VI (——).

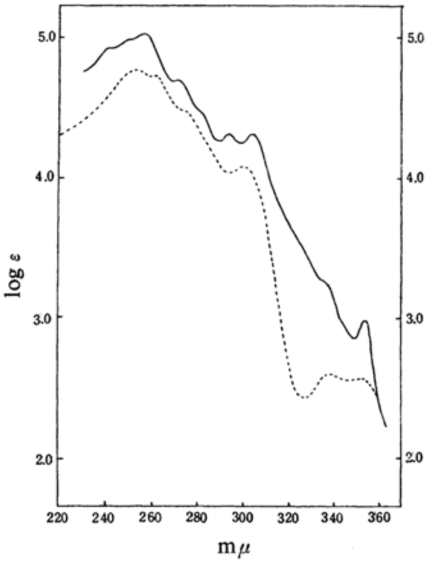


Fig. 2. The ultraviolet spectra of VII (——) and 9, 10-dimethylphenanthrene (----).

cyclic dimerization of *o*-diethynyl compounds is general or not in the Eglinton's reaction. 9, 10-Diethynylphenanthrene (V), which has a rigid geometry similar to I, was synthesized according to the method of Ried[4] with a slight modification as indicated in the foregoing chart. 9, 10-Diethynyl-9, 10-dihydroxy-9, 10-dihydrophenanthrene (IV) was obtained by the reaction of phenanthrenequinone (III) with sodium acetylide in liquid ammonia. The reductive aromatization of glycol IV afforded 9, 10-diethynylphenanthrene (V) in a reasonable yield. The oxidative coupling of V according to the procedure of Eglinton[2,5] furnished a fairly stable product which is found to be sparingly soluble in common organic solvents. The substance was recrystallized from a large amount of benzene or chlorobenzene yielding orange yellow fine needles. The color of the crystals changed to black on heating to ca. 290°C, but no fusion was observed even at 360°C. The analysis of the crystals suggests that the substance contains 1 mol. of solvent of crystallization. The absence of free ethynyl absorption in the infrared spectrum indicates the cyclic nature of this substance. A remarkable red-shift was observed in the ultraviolet spectrum of this substance as compared with that of V (Fig. 1). After removal of the solvent of crystallization by heating the substance to 110°C in vacuo, the analysis proved the molecular formula of the substance to be $(C_{18}H_8)_n$. The molecular weight of this hydrocarbon could not be determined by Rast's method owing to its poor solubility in camphor or other analogous solvents. Hydrogenation of the orange yellow crystals, $(C_{18}H_8)_n$ in benzene over palladium-on-charcoal furnished a colorless crystalline hydrocarbon, $(C_{18}H_{16})_n$. The determination of the molecular weight of the reduction product revealed the molecular formula of the hydrogenated product to be $(C_{18}H_{16})_2$. The ultraviolet spectra of the reduction product and 9, 10-dimethylphenanthrene[6] resembled closely in their absorption maxima, but the intensities of the former were found to be approximately double the relevant intensities of the latter (Fig. 2). From these observations the structure of VII, diphenanthro [9′, 10′-*a* ; 9′′, 10′′-*g*] cyclododeca-1, 7-diene was given to the reduction product. Therefore, the structure of the parent hydrocarbon, $(C_{18}H_8)_2$, was confirmed to be the highly strained cyclic dimer VI, diphenanthro [9′, 10′-*a* ; 9′′, 10′′-*g*] cyclododeca-1, 7-dien-3, 5, 9, 11-tetrayne.

The above-mentioned result is consistent with that of the oxidative coupling of *o*-diethynylbenzene, and can be regarded as the second example of an unusual cyclic dimerization. On the other hand, it has been reported that the oxidative coupling of aliphatic α, ω-diethynyl compounds under a similar condition results in the formation of the mixture of cyclic di, tri, tetra, penta and hexamer[7]. These facts strongly indicate that some specific cyclization mechanism operates in the Eglinton's coupling reaction of *o*-diethynyl compounds. The mechanism of the forced dimerization or the retardation of the cyclic

---

[4] W. Ried, H. J. Schmidt and A. Urschel, *Chem. Ber.*, **91**, 2472 (1958).

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

[6] W. L. Mosby, *J. Org. Chem.*, **19**, 299 (1954).

[7] F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

trimerization in the coupling reaction is not clear, but it seems to be probable to assume the formation of an intermediate copper complex containing *o*-diethynyl compound as ligand, in which the circumstance should be so favorable for the cyclic dimerization of the *o*-diethynyl ligands that the increase of strain energy can be overcome.

Experimental*

9, 10-Diethynylphenanthrene (V).—A hot solution of 9, 10-diethynyl-9, 10-dihydroxy-9, 10-dihydrophenanthrene (IV, 13 g., 0.05 mol.) in methanol (100 ml.) was added under stirring to a solution of stannous chloride dihydrate (22.5 g., 0.1 mol.) in concentrated hydrochloric acid (45 ml.) and water (30 ml.). The mixture was stirred for 1.5 hr. at 60∼65°C. After cooling the mixture, the flocculent brown precipitate was filtered, washed with water and dried in vacuo. The brown mass was dissolved in carbon tetrachloride (140 ml.) and the red solution was filtered through a short column of alumina (35 g.). The same solvent (500 ml.) was passed through the column. The colorless filtrate and the washing were combined, and the solvent was removed under reduced pressure at 45°C in an atmosphere of nitrogen to give yellow crystals (3.6 g., 32%). The analytical sample was prepared by recrystallizing the crude crystals from petroleum benzine (b. p. 60∼70°C). Pale yellow prisms, m. p. 130°C (decomp.).

Found: C, 95.52; H, 4.46. Calcd. for $C_{18}H_{10}$: C, 95.54; H, 4.46%.

IR, 3260 cm^{-1} (-C≡CH). UV, $\lambda_{max}^{C_2H_5OH}$ 235 mμ (log ε=4.53), 242.5 (4.85), 252.5 (4.64), 261 (4.74), 271 (4.53), 282.5 (4.41), 303 (4.08), 315 (4.33), 328.5 (4.40), 348 (3.18), 366 (3.02).

Diphenanthro[9′, 10′ - *a* ; 9′′, 10′′ - *g*]cyclododeca-1, 7-dien-3, 5, 9, 11-tetrayne (VI). — 9, 10-Diethynylphenanthrene (V, 4.0 g.) was added under stirring to a mixture of cupric acetate monohydrate (60.0 g.) in pyridine (400 ml.). The mixture was stirred at room temperature for 3 hr., and then at 60°C for 4 hr. The green reaction mixture was cooled to room temperature and the stirring was continued for further 10 hr. The precipitate deposited was filtered, washed thoroughly with water to remove cupric acetate and pyridine, and the residue was washed with small amounts of ethanol and benzene, successively. The coupling product thus obtained was recrystallized twice from chlorobenzene or benzene yielding pure VI, tiny orange needles, 1.38 g., (33%). The determination of solvent of crystallization gave the following results. Benzene: 10.1∼11.4%; Chlorobenzene: 16.3∼18.2%. It was found that the solvent of crystallization can be removed by heating the crystals to 110°C in vacuo.

Found: C, 96.19; H, 3.61. Calcd. for $C_{36}H_{16}$: C, 96.40; H, 3.60%.

UV, $\lambda_{max}^{benzene}$ 300 mμ (log ε=4.42), 315 (4.42), 338 (4.21), 375 (4.72), 396 (5.51), 420 (4.56), 435 (4.70).

The solubility of VI in benzene was estimated to be 6.3 mg./l. at 10°C by a spectroscopic method.

Diphenanthro[9′, 10′ - *a* ; 9′′, 10′′ - *g*]cyclododeca-1,7-diene (VII).—VI (200 mg.) in benzene (600 ml.) was hydrogenated over 5% palladium-on-charcoal (160 mg.) until no change of the ultraviolet spectrum of the solution was observed. During the course of the hydrogenation the yellow color of the solution disappeared. The catalyst was filtered off, and digested with hot benzene (500 ml.). The solvent was removed under reduced pressure from the combined benzene solution to yield yellow solid (120 mg.). The solid was dissolved in benzene (25 ml.) and the solution was filtered through a short column of alumina (15 g.). The alumina layer was washed with benzene (75 ml.). Removal of the solvent from the combined filtrate and washing gave a yellowish solid contaminated with yellow liquid. A colorless solid (55 mg., m. p. 328∼333°C (decomp.)) was obtained on addition of a small amount of benzene-petroleum benzine (1 : 1) to the reduction products. This was recrystallized twice from benzene yielding pure crystals, m. p. 339∼340.5°C (decomp.).

Found: C, 92.77; H, 6.63. Calcd. for $C_{36}H_{32}$: C, 93.06; H, 6.94%.

Molecular weight determination (Rast's method in camphor): 445, 468, 487. $C_{36}H_{32}$=465.

IR, 2930, 2860 cm^{-1} (-CH_2-) (KBr-disk). UV, $\lambda_{max}^{tetrahydrofuran}$ 241 mμ (log ε=4.92), 256 (5.02), 272 (4.69), 292.5 (4.31), 304 (4.31), 353 (3.01).

The absorption intensity (256 mμ, ε=105800) was found to be approximately double of the relevant intensity of 9, 10-dimethylphenanthrene (253 mμ, ε=58900).

The financial support for this research was granted by the Ministry of Education, to which the authors thanks are due.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

---

* All melting points are not corrected. All ultraviolet and infrared spectra were measured with Hitachi autorecording spectrophotometers, EPS-2 and EPI-2 respectively. The analyses were performed by Mr. M. Okumiya in the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, Osaka University.