Cyclic Acetylenes. IV. Synthesis of a Cyclic Tetraacetylene Containing Anthracene Nuclei[*]

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There has already been discussion concerning the fact that a conjugated planar cyclic en-yne system may form a continuous molecular π-orbital overlapping the p-orbitals of the carbon atoms of the unsaturated linkages in the cycle(1). It is of interest to synthesize such a cyclic acetylene in order to establish experimentally the validity of the theoretical prediction, but the only member of this series known up to now is the completely conjugated planar eighteen membered monocyclic hexaene-triyne which was reported recently by Sondheimer and Wolovsky(2). They synthesized the hexaene-triyne by a prototropic rearrangement of the corresponding cyclic hexa acetylene which was prepared by the oxidative coupling of 1,5-hexadiyne. Another promising approach to the synthesis of a planar cyclic en-yne system is the oxidative coupling of a diethynyl aromatic compound in which the two ethynyl groups are directly attached to the proper positions of the aromatic nucleus. The rigid geometry of this type of molecule may be favorable to the ring formation by oxidative coupling as pointed out by W. Baker(3). The

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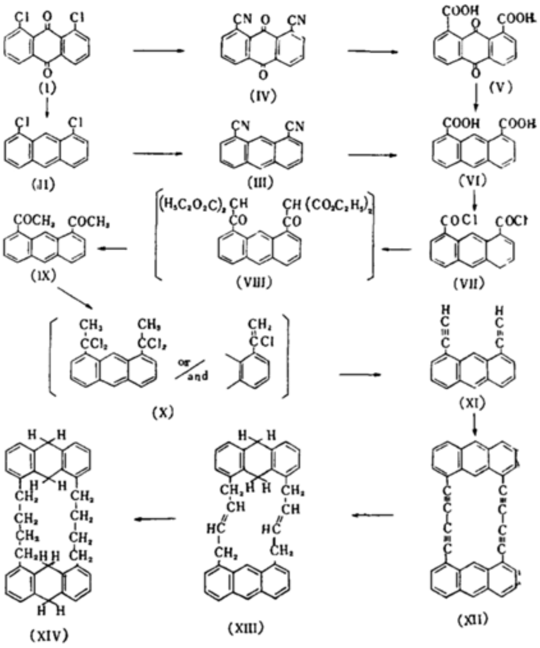
[*] For a preliminary report of a part of this work, see *Chem. & Ind.*, **1960**, 346.

1) T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

2) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 1771 (1959).

first attempt according to this principle has been reported by Eglinton and his coworker. They carried out the oxidative coupling of *o*-diethynylbenzene expecting the formation of a fully conjugated strainless cyclic trimer, the tribenzo derivative of cyclo-octadeca-triene-hexayne[4]. But unexpectedly the product was identified to be a highly strained cyclic dimer of *o*-diethynylbenzene[5].

We have synthesized a planar conjugated cyclic tetraacetylene containing two anthracene nuclei (XII) according to the following scheme. The starting material for our work was 1, 8-dichloroanthraquinone (I). The dichloroquinone I was reduced to 1, 8-dichloroanthracene (II)[6], and the reaction of II with cuprous cyanide in quinoline gave 1, 8-dicyanoanthracene (III). The attempt to obtain 1, 8-diacetylanthracene (IX) by the reaction of III with methylmagnesium iodide in anisol failed on account of the poor solubility and inert reactivity of III. Therefore, according to the results of the preliminary experiments[7], the route to the diacetyl compound IX via dicarboxylic acid VI was chosen. 1, 8-Dicarboxyanthracene (VI) was synthesized by the alkaline hydrolysis of the dinitrile III in ethylene glycol. The diacid VI was also prepared according to the procedure of Waldmann[8] by the reduction of 1,8-dicarboxyanthraquinone (V) which was derived from I via IV.



Treatment of VI with thionyl chloride in chlorobenzene afforded the diacid dichloride VII. VII was caused to react with diethyl ethoxymagnesiomalonate in xylene to yield the ketomalonate VIII. The curde VIII was heated without further purification with the mixture of propionic and sulfuric acid. Treatment of the reaction mixture resulted in 1, 8-diacetylanthracene (IX) as light yellow cubes.

The crude chloride X which was obtained by the reaction of the diacetyl compound IX with phosphorus pentachloride in phosphorus oxychloride was dehydrochlorinated with sodium amide in liquid ammonia. 1, 8-Diethynylanthracene (XI) was obtained as yellow cubic crystals which melted at $150\sim151$°C with decomposition. XI was found to be a fairly unstable substance and could not be kept without de-composition for a long time. The infrared spectrum of XI shows an absorption at 3260 cm^{-1} indicating the presence of terminal acetylene as illustrated in Fig. 1. XI gives also red cuprous and yellow silver acetylides.

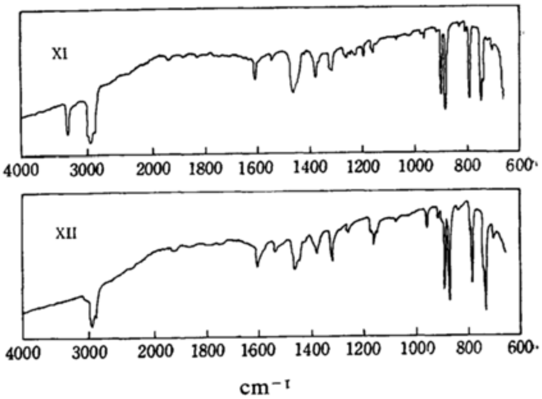


Fig. 1. The infrared spectra of 1,8-diethynylanthracene (XI) and the cyclic tetraacetylene (XII). (Nujol mull)

The oxidative coupling of the diethynyl compound XI, conducted according to the procedure of Eglinton[9], yielded orange crystals in a high yield. The structure of the cyclic tetraacetylene (XII) was assigned to the substance from the method of preparation and from the following evidences. The cyclic nature of XII was confirmed by the absence of free ethynyl absorption in the infrared spectrum (Fig. 1) and by the negative test against alcoholic silver nitrate solution. Various

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

[4] G. Eglinton and A. R. Galbraith, *Proc. Chem. Soc.*, **1957**, 350.

[5] O. M. Behr, G. Eglinton and R. A. Raphael, *Chem. & Ind.*, **1959**, 699; W. K. Grant and J. C. Speakmann, *Proc. Chem. Soc.*, **1959**, 231.

[6] H. Schilling, *Ber.*, **46**, 1066 (1913).

[7] The preceding paper.

[8] a) H. Waldmann and A. Oblath, *Ber.*, **71**, 366 (1938). b) H. Waldmann and R. Stengl, *Chem. Ber.*, **83**, 167 (1950).

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

methods for determining the molecular weight of XII were tried unsuccessfully as a result of the poor solubility of this substance in organic solvents. Reduction of XII with an excess of sodium in liquid ammonia yielded a substance with a composition $C_{36}H_{30}$ as a main product. The infrared spectroscopy of this material revealed the presene of a methylene group (ν_{as}: 2860, ν_s: 2920 cm^{-1}), unconjugated *trans*-ethylenic bond (δ_{CH}: 952 cm^{-1}) and 1, 2, 4, 5-tetrasubstituted benzene (δ_{CH}: 875 cm^{-1}) as illustrated in Fig. 1. From these evidences, the structure of XIII was assigned tentatively to the reduction product. Further hydrogenation of XIII in benzene over palladium on charcoal gave tiny colorless cubes with the empirical formula $(C_9H_9)_n$. The molecular weight of this substance could be determined accurately by Rast's method in camphor. The molecular weight thus determined (450; Calcd. for $C_{36}H_{36}$: 469) provided an unequivocal evidence regarding the dimeric cyclic acetylene for XII. The fully hydrogenated product shows no absorption at 875 cm^{-1} in the infrared spectrum, indicating the absence of the anthracene nucleus in the molecule. The infrared spectrum of this substance was illustrated in Fig. 2 together with that of XIII. The ultraviolet spectrum of the hydrogenated product also indicates the destruction of anthracene chromophor. From these observations structure XIV was given to the reduction product.

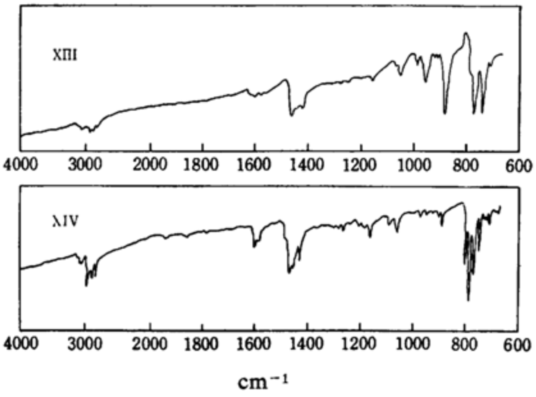

Fig. 2. The infrared spectra of $C_{36}H_{30}$ (XIII) and the hydrogenated product (XIV). (KBr-disk)

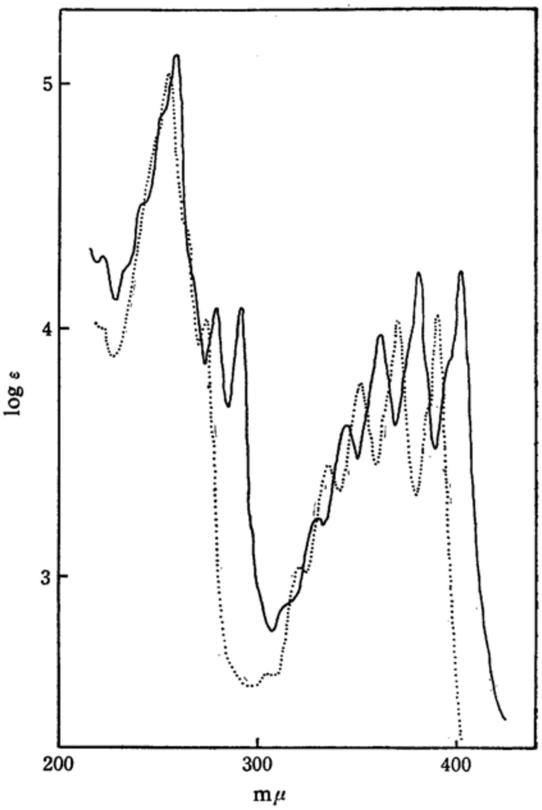

Fig. 3. The ultraviolet spectra of 1-ethynylanthracene (XVI, ……) and 1,8-diethnylanthracene (XI, ——).

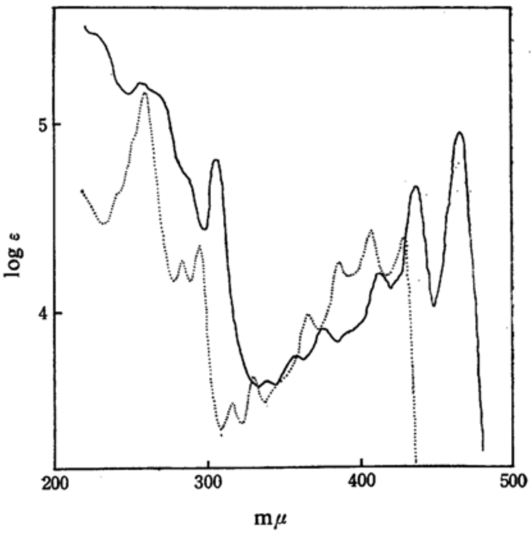

Fig. 4. The ultraviolet spectra of 1,1′-dianthryldiacetylene (XVIII, ……) and the cyclic tetraacetylene (XII, ——).

The high yield of the oxidative cyclic dimerization of XI to XII seems to reflect the favorable orientation of the ethynyl groups in XI. Examination of the bond angles of the compound XII readily verifies its planar and strainless nature. XII was found to be a very stable compound and can be kept without change for a long time in air and light. In an evacuated capillary tube, XII turned to black at a temperature over 370°C without the change of crystal form. XII is sparingly soluble in common organic solvents. The

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

Compound	$\lambda_{\max}$	ε	Solvent	Shifts in mμ from			
				XV	XVI	XI	XVII
Anthracene (XV)	374	7,460	C	—	—	—	—
1-Ethynylanthracene (XVI)	391	11,500	C	17	—	—	—
1,8-Diethynylanthracene (XI)	402	17,400	C	28	11	—	—
1,1′-Dianthryldiacetylene (XVII)	428	24,600	C	54	37	26	—
Cyclic tetraacetylene (XII)	465	91,200	B	91	74	63	37

C: cyclohexane, B: benzene.

solution in dimethylformamide, in which XII is slightly soluble, exhibits an orange yellow color with intense and characteristic green fluorescence.

The ultraviolet spectra of 1-ethynylanthracene (XVI)[7], 1,8-diethynylanthracene (XI), 1,1′-dianthryldiacetylene (XVII)[7] and the cyclic tetraacetylene (XII) are illustrated in Figs. 3 and 4. The bathochromic shifts of the absorption maxima at the longest wavelength and the ε-values of these acetylenes as compared with anthracene are tabulated in Table I. The ε-value of XVII reduced to per acetylene-unit ($0.5 \times 24{,}600 = 12{,}300$) is approximately the same as that of XVI (11,500), whereas the ε-value of XII reduced per diyne-unit ($0.5 \times 91{,}200 = 45{,}600$) is much greater than those of XVII (24,600) and XI (17,400). The marked increase in the absorption intensities and the remarkable red-shift of the spectrum of XII indicate that the cyclic tetraacetylene can not be regarded as a simple derivative of anthracene. These ultraviolet spectroscopic properties and, at least to some extent, the unusual stability of XII seem to be attributable to an enhanced interaction of π-electrons of the acetylenic bonds with those of the aromatic system.

The syntheses of the same type of higher cyclic acetylenes are now being investigated.

Experimental**

1,8-Dichloroanthracene (II).—The reduction of I with zinc dust in aqueous ammonia[6] yielded a product consisting of mainly 1,8-dichloro-9,10-dihydroanthranol[10]. The reduction product was extracted with ethanol. The solvent was removed and the light yellow crystalline residue was recrystallized from carbon tetrachloride to give the pure anthranol, white needles, m. p. 136~136.5°C.

Found: C, 63.52; H, 4.03; Cl, 27.27. Calcd. for $C_{14}H_{10}OCl_2$: C, 63.41; H, 3.78; Cl, 26.80%.

I. R. max., Broad absorption near 3200 (-OH); 1180 cm^{-1} (C-O).

A catalytic amount of concentrated sulfuric acid was added to a solution of the anthranol in hot ethanol. Immediate precipitation of practically pure II, light yellow needles, m. p. 157~158°C, (values in literature, 156°C[6]; 160°C[11]) was observed.

Found: C, 68.04; H, 3.28; Cl, 28.96. Calcd. for $C_{14}H_8Cl_2$: C, 68.05; H, 3.26; Cl, 28.69%.

In practice it was found more convenient to treat the ethanol extract of the reduction product with a small amount of sulfuric acid without the isolation of the anthranol.

1,8-Dicyanoanthracene (III).—A mixture of II (50 g., 0.19 mol.), cuprous cyanide (60 g.) and quinoline (500 ml.) was stirred for 24 hr. under reflux. The cooled reaction mixture was filtered and the solid was washed with dilute hydrochloric acid, then treated with dilute aqueous sodium cyanide to dissolve cuprous cyanide, and was washed with water. The dried light brown powder was digested with nitromethane (250 ml.) to remove the resinous material on the powder. Recrystallization of the powder from acetic acid using active charcoal yielded III, long yellow needles, m. p. 299~304°C, 22 g. (48%). Further recrystallization of this material from acetic acid gave pure III, m. p. 304~306°C, (value in literature, m. p. 300.5°C[8]). III is soluble in concentrated sulfuric acid giving a greenish yellow solution.

Found: C, 83.69; H, 3.47; N, 12.13. Calcd. for $C_{16}H_8N_2$: C, 84.19; H, 3.53; N, 12.28%.

I. R. max., 2225 cm^{-1} (-C≡N).

1,8-Dicarboxyanthracene (VI).—*a) Hydrolysis of 1,8-Dicyanoanthracene (II).*—A mixture of II (10 g., 0.044 mol.), potassium hydroxide (125 g.) and ethylene glycol (270 ml.) was heated to 150~155°C under stirring until the evolution of ammonia ceased (ca. 70 hr.). The reaction mixture was neutralized with hydrochloric acid resulting in formation of a yellow precipitate. The precipitate was filtered, washed with water and dried, yielding yellow powder, 11 g. (94%), m. p. 341~345°C (decomp.). Recrystallization of this material from 95% ethanol resulted in pure VI, yellow needles, m. p. 347°C (decomp.). (value in literature, 345°C (decomp.)[8]).

Found: C, 71.84; H, 3.77. Calcd. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79%.

b) *Reduction of 1,8-Dicarboxyanthraquinone (V).*—1,8-Dicyanoanthraquinone (IV) which was obtained by the reaction of I with cuprous cyanide in benzyl cyanide[8a] was hydrolyzed to V by the reaction with sulfuric acid[8]. The reduction of V by means of zinc dust in aqueous ammonia yielded

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** All melting points are uncorrected. The infrared spectra were measured by the Nujol mull method otherwise special indication is given.

[10] It has been reported that the reduction of anthracene with zinc dust in aqueous ammonia yields anthranol. Cf., H. R. von Perger, *J. prakt. Chem.*, **23**, 137 (1881).

[11] E. B. Barnett and M. A. Matthews, *J. Chem. Soc.*, **123**, 2549 (1923).

VI, m. p. 347°C (decomp.). This substance showed no depression of the melting point on admixture with the specimen prepared by route *a*).

Anthracene-1, 8-dicarboxylic Acid Chloride (VII).—The acid chloride (VII) was prepared according to the procedure of Waldmann[8b)]. Recrystallization of the crude product from toluene gave pure VII, orange needles, m. p. 255~257°C (decomp., in a sealed capillary tube). (value in literature, m. p. lower than 220°C (decomp.)[8b)]). VII gives yellow solution in concentrated sulfuric acid.

Found: C, 63.15; H, 2.80; Cl, 23.37. Calcd. for $C_{16}H_8O_2Cl_2$: C, 63.39; H, 2.66; Cl, 23.39%.

1, 8-Diacetylanthracene (IX).—1) *Malonation of the Acid Chloride (VII.)*—Diethyl ethoxymagnesiomalonate was prepared from magnesium (11 g., 0.46 gram atom), diethylmalonate (73.5 g., 0.46 mol.) and absolute ethanol (27.6 g., 0.6 mol.) in dry xylene (100 ml.). The excess of ethanol was removed by the azeotropic distillation with xylene. The solution of the malonate was added to the hot solution of VII (17 g., 0.057 mol.) in dry xylene (1.8 l.) in 30 min. under stirring. The mixture was refluxed for 1 hr. and decomposed with the addition of crushed ice (100 g.) and 4 N sulfuric acid (300 ml.). The organic layer was washed with water, and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure resulted in the crude ketomalonate (VIII) as an orange red oil.

2). *Ester Exchange and Decarboxylation of the Ketomalonate (VIII).*—The crude VIII was mixed with propionic acid (320 ml.) and concentrated sulfuric acid (4 ml.), and the mixture was refluxed for 4 hr. with a vigorous evolution of carbon dioxide. Sulfuric acid (4 N, 250 ml.) was added to the reaction mixture and the reflux was continued until no more evolution of carbon dioxide was observed. The mixture was distilled to remove a small amount of xylene with water, and poured onto ice-water (1 l.). The ice cooled mixture was filtered. The solid thus obtained was washed with water, and dissolved in benzene. The benzene solution was washed with dilute sodium hydroxide solution and water, successively. The dried solution was filtered through a short column of aluminum oxide, and the concentration of the filtrate resulted in IX, light yellow cubes, 7.4 g. (50%.), m. p. 176~179°C (Kofler block). Recrystallization of this substance from benzene resulted in pure IX, light yellow cubic crystals, m. p. 179~180°C. IX gives an orange red solution with concentrated sulfuric acid.

Found: C, 82.49; H, 5.49. Calcd. for $C_{18}H_{14}O_2$: C, 82.43; H, 5.38%.

I. R. max., 1675 cm^{-1} (C=O).

1, 8-Diethynylanthracene (IX).—*1) Chlorination of the Diacetylanthracene (IX).*—IX (5.25 g., 0.02 mol.) was mixed with phosphorus pentachloride (12.5 g., 0.06mol.) and phosphorus oxychloride (50 ml.), and the mixture was heated under reflux for 1.5 hr. With an evolution of hydrogen chloride, the mixture changed to a homogeneous dark red solution. The oxychloride was removed completely under reduced pressure. The dark red viscous oil was kept for several hours in a desiccator containing phosphorus pentoxide and potassium hydroxide.

2). *Dehydrochlorination of the Chloride (X).*—The crude chloride (X) in absolute ether (30 ml.) was added in 40 min. to a solution of sodium amide (prepared from sodium, 11.5 g., 0.5 gram atom) in liquid ammonia (500 ml.). The mixture was stirred for 2 hr. at the temperature of dry ice-ethanol bath. After evaporation of ammonia, water (250 ml.) was added cautiously to the reaction mixture and filtered to collect insoluble material. The dark brown solid obtained was digested with light petroleum (b. p. 60~80°C, 1.5 l.). The solution was washed with water and dried over anhydrous sodium sulfate. The solution was passed through a short column of alumina, and the filtrate was evaporated to yield XI, 1.65 g. (37%), m. p. 150~151°C (decomp., Kofler block). XI gave red cuprous, yellow silver and mercuric acetylides.

Found: C, 95.49; H, 4.45. Calcd. for $C_{18}H_{10}$: C, 95.54; H, 4.46%.

I. R. max., 3260 cm^{-1} (-C≡CH).

U. V. max. (in cyclohexane), λ_{max} 258 mμ (log ε =5.13), 279 (4.08), 291 (4.08), 312 (2.87)*, 330 (3.22), 345 (3.60), 362 (3.98), 381 (4.22) and 402 (4.24). Asterisk indicates shoulder.

Oxidative Coupling of 1, 8-Diethynylanthracene (XI).—To the solution of XI (0.600 g., 0.0027 mol.) in pyridine (100 ml.) and methanol (8 ml.) was added cupric acetate monohydrate (12 g.), and the mixture was vigorously stirred for 4 hr. at 55°C. Stirring was continued for a further 3 hr. period at room temperature. The reaction mixture was filtered and the solid obtained was washed thoroughly with water, a small amount of benzene and ethanol, successively. The cyclic tetrayne XII almost free from inorganic contaminate was obtained as orange powder, 0.562 g. (95%). This substance decomposed over 370°C. A minor amount of XII of poor purity was obtained from the pyridine solution.

The crude XII was recrystallized 3 times from xylene and once from dimethylformamide yielding tiny orange cubes. These crystals decomposed over 370°C in an evacuated capillary tube without any change of the crystal form.

Found: C, 95.72; H, 3.61. Calcd. for $C_{36}H_{16}$: C, 96.40; H, 3.60%.

The unsatisfactory result in the analysis of carbon may be due to explosive decomposition of XII in the combustion tube forming a carbonaceous material difficult to burn.

U. V. max., λ_{max} 258 mμ (log ε=5.22) (in *n*-hexane), 307 (4.82), 340 (3.66), 358 (3.79), 376 (3.93), 413 (4.22), 437 (4.67) and 465 (4.96) (in benzene).

Reduction of the Cyclic Tetraacetylene (XII) with Sodium in Liquid Ammonia.—The mixture of XII (0.42 g., 0.0009 mol.), sodium (0.9 g., 0.039 gram atom) and liquid ammonia (150 ml.) was stirred for 7 hr. at the temperature of dry ice-ethanol bath. Ammonium nitrate was added to the reaction mixture, and ammonia was evaporated. Water was added to the residue and the light yellow powder formed was collected by filtration. The powder was digested with benzene to remove the insoluble material. The benzene solution was filtered through a thin layer of alumina (10 g.). Evaporation of the solvent afforded XIII, yellow needles, 0.20 g. (48%), m. p. 365~368°C (decomp., in an evacuated capillary tube, metal block).

Found: C, 93.24; H, 6.67. Calcd. for $C_{36}H_{30}$: C, 93.46; H, 6.54%.

I. R. max. (KBr-disk method), 2920, 2860 ($-CH_2-$), 952 (isolated trans-ethylenic bond), 875 cm^{-1} (tetrasubstituted benzene).

U. V. max., λ_{max} 257 mμ ($\log \varepsilon=4.91$) (in *n*-hexane), 318 (3.71), 332 (3.72), 348 (3.73), 368 (3.84) and 387 (3.89) (in benzene).

Catalytic Reduction of $C_{36}H_{30}$ (XIII).—The solution of XII (0.19 g.) in benzene (300 ml.) was shaken in hydrogen with palladium (5%) on charcoal (0.5 g.). The color and the fluorescence of the solution gradually disappeared in the course of the hydrogenation. The catalyst was filtered and washed with benzene. The filtrate was combined with the washing, and the evaporation of the solvent yielded XIV as fine colorless needles in almost quantitative yield. This was recrystallized from benzene to give pure XIV, m. p. 316~318°C, (in an evacuated capillary tube; metal block).

Found: C, 92.10; H, 7.67; Mol. wt. (Rast, camphor), 450. Calcd. for $C_{36}H_{36}$: C, 92.26; H, 7.74%; Mol. wt., 469.

I. R. max. (KBr-disk method), 2935, 2870 ($-CH_2-$), 735 cm^{-1} ($-(CH_2)_4-$).

U. V. max. (in ethanol), λ_{max} 256 mμ; λ_{min} 248 mμ.

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