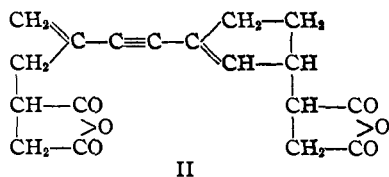


[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Condensed Ring Compounds. XI. A Tricyclic Compound by the Dienyne Double Addition Reaction¹

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From previous work on the addition of maleic anhydride and dialkyl fumarates to 1,5-dien-3-yne it would be expected that derivatives of cyclopenta[*a*]naphthitane² could be prepared from 1-cyclopentenylisopropenylacetylene. This hydrocarbon has now been prepared and has been found to react with two moles of maleic anhydride to give a crystalline compound, C₁₈H₁₆O₆, m. p. 168–170°. Structure I is very probable for this substance. The melting point is considerably lower than the melting points of the more highly symmetrical bicyclic and tetracyclic dienes previously prepared by this reaction. The absorption in the ultraviolet, however, is not affected by the lower degree of molecular symmetry and the value found, λ_{max}. 2500 Å., ε 18,000, lies just between that for a bicyclic adduct (λ_{max}. 2470 Å.) and those for a number of tetracyclic adducts (λ_{max}. 2560–2570 Å.).³ Other conceivable structures for the dianhydride can be excluded on the basis of this absorption maximum. For example, a di-succinic anhydride type of adduct containing a 1,5-dien-3-yne system (II) should show maximal absorption at about 2615 Å.⁴



II

In order to synthesize a 4,8-dimethyl derivative, isopropenyl-(2-methyl-1-cyclopentenyl)-acetylene⁵ was prepared. This combined with two

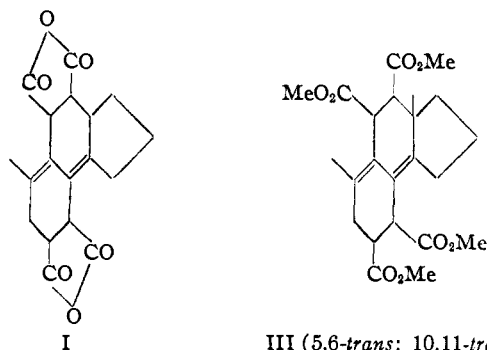
(1) This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not copyrighted.

(2) For nomenclature see the preceding paper on the dienyne double addition reaction, *THIS JOURNAL*, **64**, 1311 (1942). In deriving a synonym for decalin from *naphthalene*, it seems advantageous to drop the letters *al*. The numbering adopted for the tricyclic system is like that employed for related aromatic compounds (Patterson and Capell, "The Ring Index," Reinhold Publishing Corporation, New York, 1940, pages 345, 381).

(3) Butz and Joshel, *THIS JOURNAL*, **63**, 3345 (1941); **64**, 1311 (1942).

(4) Bastron, Davis and Butz, *ibid.*, **65**, 973 (1943). In view of the correspondence of the spectrum with the spectra of several other crystalline adducts from dienyne previously reported, we consider the 1,3-diene system and the presence of three rings in the dianhydride to be demonstrated. If opportunity had permitted, the further evidence from dehydrogenation and esterification, followed by hydrogenation of the tetraester, would have been sought as in the case of the other adducts.

(5) This may have contained some of the 5-methyl-1-cyclopentenyl isomer. See Joshel, Butz and Feldman, *THIS JOURNAL*, **62**, 3348 (1941).



I

III (5,6-*trans*; 10,11-*trans*)

moles of dimethyl fumarate to give a sirupy adduct, possibly III, which apparently was not pure enough to permit a demonstration of the ultraviolet absorption spectrum characteristic of conjugated dienes. The possibility that the liquid tetramethyl ester might give crystalline derivatives with hydrazine hydrate suggested a preliminary experiment in which *trans*-6,7-*trans*-11,12-tetracarboxymethoxy-8(14),9-chrysitadiene⁶ was treated with hydrazine hydrate. A poor yield of a dihydrazide was obtained. A pure hydrazide could not be obtained from the liquid adduct.

Experimental⁷

1-Cyclopentenylisopropenylacetylene.—Four grams of fused and powdered potassium bisulfate was added to 10 g. of dimethyl-(1-hydroxycyclopentylethynyl)-carbinol⁸ (b. p. (5 mm.) 124°, in 76% yield). The mixture was heated at 160–180° for fifteen minutes, allowed to cool in an atmosphere of carbon dioxide, the water formed removed at reduced pressure, and the crude dienyne distilled. The fraction (4.7 g., 62% yield) boiling from 77–84° at 12 mm. (most of it boiled at 80–82°) was collected. The dienyne was redistilled at 81° and 13 mm. for analysis and ultraviolet absorption spectrum⁹; *n*_D²⁰ 1.5332.

Anal. Calcd. for C₁₀H₁₂: C, 90.8; H, 9.1. Found: C, 89.8; H, 9.0.

Other workers have observed that the values for carbon content of dienyne are usually low.¹⁰

The 5,6,10,11-Dianhydride of 8-Methyl-7,12-cyclopenta[*a*]naphthitadiene-5,6,10,11-tetracarboxylic Acid (I).—To 10.5 g. (1.75 moles) of twice distilled, hot (120°) maleic anhydride in a Claisen flask, through which carbon dioxide was being bubbled, was added 8.1 g. of redistilled 1-cyclopentenylisopropenylacetylene. The mixture was heated at 110–120° for two hours, after which it was rather fluid. Then the mixture was held at 150–160° for thirty

(6) Butz and Joshel, *THIS JOURNAL*, **64**, 1312 (1942).

(7) All melting points are corrected. Microanalyses by Dr. Carl Tiedcke.

(8) Zal'kind and Gverdtsiteli, *J. Gen. Chem.* (U. S. S. R.), **9**, 855 (1939); *C. A.*, **34**, 387 (1940).

(9) For the absorption curves of this and other 1,5,3-dienynes see ref. 4.

(10) Marvel, Mazingo and White, *THIS JOURNAL*, **62**, 1880 (1940); Marvel and Walton, *J. Org. Chem.*, **7**, 94 (1942).

minutes which caused it to become viscous. By the application of heat and reduced pressure, finally at 190° and 1 mm., 1.2 g. of maleic anhydride and 0.4 g. of dienyne were removed. The residue (15.9 g.) was taken up in ethyl acetate, the solution was concentrated, and ether was added. At this point a fine yellow, amorphous precipitate appeared which was filtered and dried (6.5 g.). Extraction of this material with boiling dibutyl ether gave 0.34 g. of crude dianhydride, m. p. 154–163°. The ether-ethyl acetate filtrate from the amorphous solid was heated on the steam-bath to remove the ether and some of the ethyl acetate. Crystals deposited from this solution after one week. These were filtered and washed with cold ethyl acetate, then with ether; 1.73 g., m. p. 162–169° (in open tube with slight yellowing). The yield of total crystalline material of this melting range was 13% on the maleic anhydride converted (88%). Recrystallization from benzene-petroleum ether gave white needles, m. p. 168–170° (without decomposition in evacuated tube); ultraviolet absorption in ethanol solution, λ_{max} 2500 Å.; ϵ , 18,000.¹¹
Anal. Calcd. for C₁₈H₁₆O₈: C, 65.8; H, 4.9. Found: C, 65.7; H, 5.0.

Dimethyl - (1 - hydroxy - 2 - methylcyclopentylethynyl) - carbinol.—This new glycol, b. p. (1–2 mm.) 122–123°, was prepared by a procedure similar to that employed for the preparation of dimethyl-(1-hydroxycyclopentylethynyl)-carbinol⁸; yield, 70%. It did not crystallize.

Anal. Calcd. for C₁₁H₁₈O₂: C, 72.5; H, 9.9. Found: 70.7; H, 10.3.

Isopropenyl - (2 - methyl - 1 - cyclopentenyl) - acetylene.⁸—Fifteen grams of dimethyl-(1-hydroxy-2-methylcyclopentylethynyl)-carbinol and a mixture of 15 ml. of concentrated sulfuric acid and 37 ml. of water were heated for three hours at reflux. The reaction mixture was allowed to cool, water was added, and the hydrocarbon was extracted with ether. The ethereal solution was washed with water, 10% potassium hydroxide, saturated sodium chloride solution, and filtered through anhydrous sodium sulfate. Distillation of the residue after evaporation of the ether gave 4.5 g. (38%) of dienyne, b. p. (13–14 mm.) 85–95°. A cut, b. p. (14 mm.) 90°, n_{D}^{27} 1.5103, was taken for ultraviolet absorption determination.⁹

trans - 5,6 - trans - 10,11 - Tetracarboxymethoxy - 4,8 - dimethyl - 7,12 - cyclopenta[a]naphthitadiene (III) (?).—Isopropenyl-(2-methyl-1-cyclopentenyl)-acetylene,⁸ b. p. (13–14 mm.) 85–95° (4.5 g.), and 13 g. (3 moles) of dimethyl fumarate were heated together in a sealed tube filled with nitrogen for twenty-four hours at 190–200°. After removal to a distilling flask by means of acetone and evaporation of the acetone, 9.4 g. of dimethyl fumarate was distilled out of the product mixture at the water pump. The maximum conversion of fumarate to adduct was therefore 42%.

(11) We are indebted to Dr. R. E. Davis and Mr. H. Bastron of this Laboratory for these observations.

Removal of volatile products was completed by heating at 160° and 1 mm. The residue weighed 7.8 g.; only 5.4 g. of 1:2 adduct could result from the fumarate consumed. Attempts to crystallize this residue having failed, a small portion was sublimed at 110–120° and 10⁻³–10⁻⁴ mm. The sublimate was a clear, practically colorless glass, with a slight greenish tinge.

Anal. Calcd. for C₂₈H₃₀O₈: C, 63.6; H, 6.96. Found: C, 63.7; H, 6.94.

Although a 1:2 adduct, or a mixture of two or more isomers of this composition, is thus indicated, it was not possible to demonstrate the 1,3-diene grouping by absorption in the ultraviolet¹¹ because of the presence of some opaque impurity.

The main portion of the reaction product was heated at temperatures up to 260° at 1–2 mm. Nothing distilled. Treatment of this heated material with hydrazine hydrate on the steam-bath, refluxing of the products with methanol, and boiling of the residue from evaporation of the methanol with benzene gave a brownish solid which was soluble in water and insoluble in ethanol. The solid could not be crystallized and was not characterized.

Reaction of trans-6,7-trans-11,12-Tetracarboxymethoxy-8(14),9-chrysitadiene⁴ with Hydrazine Hydrate.—A mixture of 360 mg. of the tetraester and 0.6 ml. of hydrazine hydrate in 15 ml. of absolute methanol was heated at reflux for four hours. Nearly complete removal of the methanol, addition of a few drops of water, and cooling gave crystals. These were recrystallized from benzene containing a little methanol and in this way 50 mg. of colorless crystals with a little yellow oil was obtained. The oil was removed by a second crystallization from benzene-methanol; m. p. 161–168° (dec.). The analysis indicated that two of the four carbomethoxyl groups has been transformed to hydrazide groups.

Anal. Calcd. for C₂₄H₂₄O₈N₄: N, 11.8. Found: N, 11.21, 11.26.

Summary

The dienyne double addition reaction has been employed for the synthesis of a tricyclic compound. A derivative of cyclopenta[a]naphthitane (dodecahydrocyclopenta[a]naphthalene) has been prepared.

1-Cyclopentenylisopropenylacetylene, isopropenyl-(2-methyl-1-cyclopentenyl)-acetylene, dimethyl-(1-hydroxy-2-methylcyclopentylethynyl)-carbinol, and the dihydrazide of a dimethyl ester of 8(14),9-chrysitadiene-trans-6,7-trans-11,12-tetracarboxylic acid have also been prepared.

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