

bath at 140° for eight hours. The product was isolated as the free base by crystallization from 50% ethanol and water; yield, 2.0 g. (80%).

Other Heterocyclic Substituted Aminoquinaldines.—4-Chloro-6-methoxyquinaldine (0.02 mole) was mixed well with 0.022 mole of the desired heterocyclic amine, *i. e.*, 8-aminoquinoline, 8-amino-6-methoxyquinoline, thionine (0.011 mole), and 5-aminoindazole. The reaction mixture in each case was heated in an oil-bath at 160–175° for three hours. The products were isolated and purified by washing the residues with 5% sodium hydroxide then numerous crystallizations from 90% ethanol; yields, approximately 60 to 70%.

Summary

A relatively simple and economical process for the preparation of basically substituted propylamines has been reported.

4-Chloro-6-methoxyquinaldine has been condensed with a few basically substituted aliphatic amines and several heterocyclic amines to give the corresponding 4-substituted quinaldines.

DETROIT, MICH.
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[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Condensed Ring Compounds. VIII. Further Applications of the Dienyne Double Addition Reaction¹

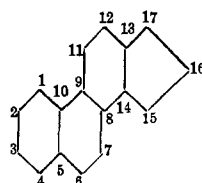
BY LEWIS W. BUTZ AND LLOYD M. JOSHEL²

Although it has not yet been found possible to realize the previously mentioned aim of adding ethylene to dienyne,³ the dienyne double addition reaction has been extended by the observation that methyl and ethyl fumarates can serve as dienophiles in this process. As was expected, the 6,7,11,12-tetracarbomethoxy-8(14),9-chrysitadiene (I)⁴ formed by the reaction of dicyclohexenylacetylene and methyl fumarate proved to be a stereoisomer of the tetramethyl ester (IV)⁵ prepared from the maleic anhydride adduct III.⁶ By analogy with the Diels–Alder synthesis, it is to be expected that maleic anhydride will yield products with *cis*-anhydride groups and that alkyl

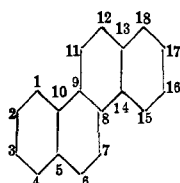
fumarates will yield *trans*-1,2-diester. The configurations of carbon 6 relative to carbon 7 and of carbon 11 relative to carbon 12 in these compounds may accordingly be considered as determined by the method of preparation. The other stereochemical relations illustrated have not been demonstrated but are suggestions partly based on the assumption that the rules developed for the Diels–Alder reaction⁷ may be applicable to the dienyne double addition reaction. We have not indicated any configurations at the various angular centers since these are entirely uncertain at the present time. The diene esters I, II, and IV all exhibit characteristic absorption spectra⁸ with molecular extinction coefficients of 24,000–24,500 at 2560–2570 Å.⁹

In addition to their different melting points, the contrast between I and IV is sharply illustrated by their respective behaviors toward hydrogen. IV, like the tetracarbomethoxysteradiene possessing the same configuration,⁸ readily absorbs one and only one mole of hydrogen in the presence of Adams catalyst with the formation in high yield of a compound of probable structure V. Under the same conditions, I absorbs no hydrogen whatsoever.

In view of the invariable presence of the 3-hydroxyl or 3-keto group in naturally occurring steroids, it is of interest that 4-methoxycyclo-



Sterane



Chrysitane

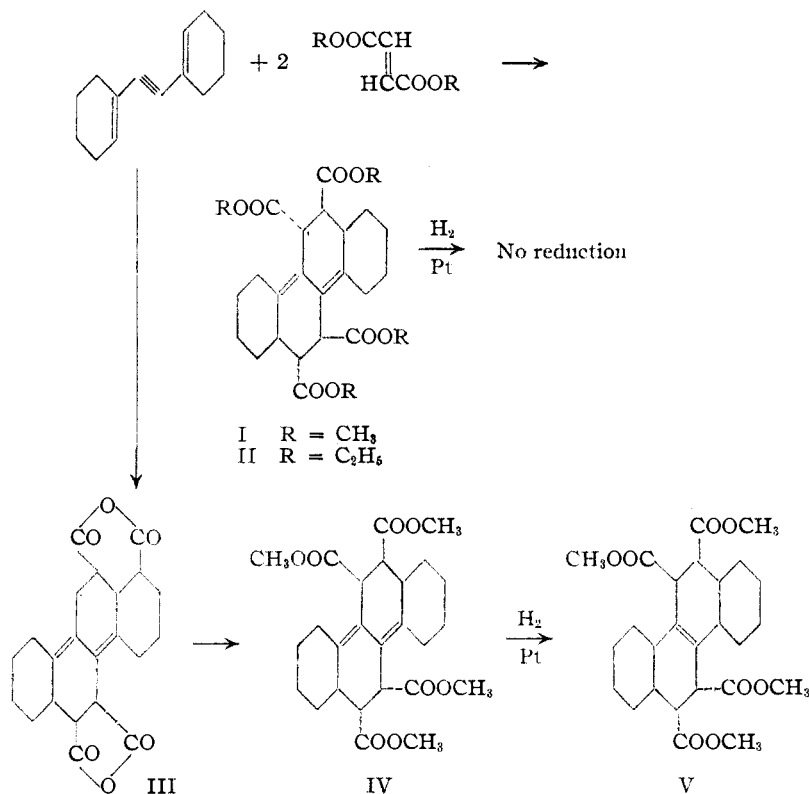
(5) This compound was prepared by Mr. Julian Feldman.

(6) Joshel, Butz and Feldman, *THIS JOURNAL*, **63**, 3348 (1941).

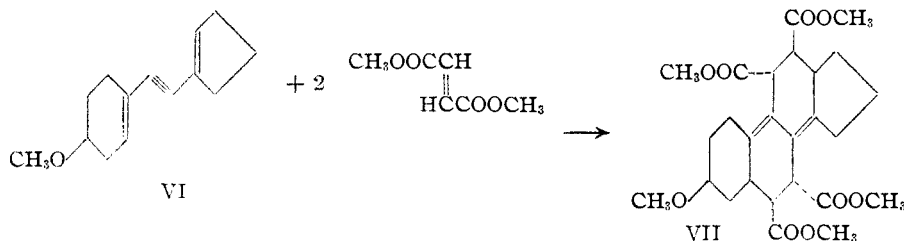
(7) Alder and Stein, *Angew. Chem.*, **50**, 510 (1937); Alder and Windemuth, *Ber.*, **71**, 1939 (1938).

(8) Butz and Joshel, *THIS JOURNAL*, **63**, 3344 (1941).

(9) The absorption spectra were determined by Dr. Russell E. Davis and Mr. Harry Bastron of this Bureau.



hexenylcyclopentenylnylacetylene (VI)¹⁰ combines with two moles of methyl fumarate to form 3-methoxy-6,7,11,12-tetracarboxymethoxy-8(14),9-steradiene (VII). In comparing this reaction with the dienyne double addition reactions described



above, it should be noticed that the introduction of the methoxyl group produces another asymmetric carbon atom and consequently the possible number of stereoisomeric products is doubled. This may account for the fact that the product of this reaction has not been obtained crystalline. It does contain the theoretical amounts of carbon and hydrogen, and exhibits an absorption spectrum characteristic of this class of compounds^{8,9} with a maximum at 2550 Å. ($\epsilon = 17,000$).

(10) Marvel and Walton, *J. Org. Chem.*, **7**, 88 (1942). We gratefully acknowledge Dr. Marvel's gift of a large sample of this dienyne.

Experimental¹¹

trans-6,7-trans-11,12-Tetracarboxymethoxy-8(14),9-chrysitadiene (I).—Freshly distilled dicyclohexenylacetylene^{6,12} (5.6 g.) and dimethyl fumarate (10.0 g.) were heated under nitrogen in a sealed tube at 175° for twenty-four hours. On vacuum distillation of the product, 3.1 g. of the dienyne and 6.6 g. of the ester were recovered. The viscous, amber residue (5.4 g.) was crystallized from methanol furnishing 2.2 g. (15%, or 34% based on the dienyne consumed) of colorless prisms; m. p. 107–110°. A portion recrystallized for analysis melted at 111.6–112.6°.

Anal. Calcd. for C₂₆H₃₄O₈: C, 65.8; H, 7.2. Found: C, 65.8; H, 7.1.

Somewhat lower yields were obtained when the reaction was run at 200° for four hours or at 150° for forty-seven hours. Treatment at 150° for four hours resulted in almost quantitative recovery of the starting materials.

trans-6,7-trans-11,12-Tetracarboxymethoxy-8(14),9-chrysitadiene (II).—The above dienyne (7.0 g.) and diethyl fumarate (20 g.) were heated under carbon dioxide in a sealed tube at 175° for seven hours. On vacuum distillation of the product, 5.4 g. of the dienyne and 18.1 g. of the ester were recovered. The yellow, viscous residue (3.2 g.) was crystallized from ethanol-water furnishing 1.4 g. (7%, or 31% based on the dienyne consumed) of colorless prisms; m. p. 87–89.5°. The analytical sample melted at 90–91°.

Anal. Calcd. for C₃₀H₄₂O₈: C, 67.9; H, 8.0. Found: C, 68.3, 68.1; H, 7.6, 7.4.

cis-6,7-cis-11,12-Tetracarboxy-8(14),9-chrysitadiene.—Two grams of the dianhydride (III)⁶ was dissolved in 30 ml. of normal potassium hydroxide. The filtered solution was cooled in ice and acidified to congo red with hydrochloric acid. The fine, white powder was separated by centrifugation, washed with water, and dried, yielding 2.13 g. (97%) of tetra-acid; m. p. 256.5–258° dec. This acid does not lend itself to recrystallization so the crude product was analyzed.

Anal. Calcd. for C₂₂H₂₆O₈: C, 63.1; H, 6.3. Found: C, 61.4; H, 6.3.

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

(12) Pinkney, Nesty, Wiley and Marvel, *THIS JOURNAL*, **58**, 972 (1936).

cis-6,7-*cis*-11,12-Tetracarbo-methoxy-8(14),9-chrysitadiene (IV).⁵—A suspension of 3.0 g. of the tetra-acid in ether was cooled in ice and treated with an ethereal solution of diazomethane from 9 ml. of nitrosomethylurethan. Solution took place rapidly, and after standing a few minutes the solution was filtered, evaporated, and the residue crystallized from methanol, furnishing 2.85 g. of colorless ester, m. p. 121–122.5°, and 0.25 g. of slightly lower m. p. (91%). The mixed m. p. with the stereoisomeric ester (I) was 97–121°.

Anal. Calcd. for C₂₆H₃₄O₈: C, 65.8; H, 7.2. Found: C, 65.6; H, 6.8.

cis-6,7-*cis*-11,12-Tetracarbo-methoxy-8-chrysitene (V).—A solution of 1.01 g. of the tetra-ester (IV) in 20 ml. of acetic acid was shaken with hydrogen in the presence of 100 mg. of Adams catalyst. One molecular equivalent of hydrogen was absorbed in about four hours and then the rate of absorption became negligible. After the catalyst was filtered, the solvent was evaporated under reduced pressure and the residue crystallized from methanol, yielding 0.86 g. (85%) of colorless needles; m. p. 157–159°. A portion recrystallized for analysis melted at 158–159°.

Anal. Calcd. for C₂₆H₃₆O₈: C, 65.5; H, 7.6. Found: C, 65.4; H, 7.6.

When the stereoisomeric tetramethyl ester I was treated under the same conditions no hydrogen was absorbed beyond that required to reduce the catalyst, and an almost quantitative recovery of starting material was obtained from the reaction mixture.

3-Methoxy-*trans*-6,7-*trans*-11,12-tetracarbo-methoxy-8-(14),9-steradiene (VII).—Six grams of freshly distilled 4-

methoxycyclohexenylcyclopentenylacetylene (VI)¹⁰ and 10 g. of methyl fumarate were heated under nitrogen in a sealed tube for twenty-four hours at 175°. Upon vacuum distillation of the resulting mixture, 3.3 g. of dienyne and 6.3 g. of ester were recovered, leaving a viscous, amber residue in the flask (6.6 g., 45%). As yet this product has resisted all attempts at crystallization. It distills at 10⁻³ mm. (bath about 150°) yielding an almost colorless glass, which was used for analysis and absorption spectrum.

Anal. Calcd. for C₂₆H₃₄O₉: C, 63.7; H, 7.0. Found: C, 63.7; H, 6.9.

Summary

Dicyclohexenylacetylene combines with two moles of methyl or ethyl fumarate to form a 6,7-, 11,12-tetracarboalkoxy-8(14),9-chrysitadiene.⁴ A stereoisomeric tetramethyl ester was obtained via the adduct from this dienyne and maleic anhydride. The latter diene ester readily absorbs one mole of hydrogen whereas the diene ester from methyl fumarate absorbs no hydrogen under the same conditions.

A 3-methoxy-6,7,11,12-tetracarbo-methoxy-8-(14),9-steradiene was obtained from 4-methoxycyclohexenylcyclopentenylacetylene and methyl fumarate.

BELTSVILLE, MARYLAND

RECEIVED MARCH 4, 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH CAROLINA]

Vicinal Substituted Resorcinols. II. Alkylresorcinols. The Synthesis of γ -*n*-Hexyl, γ -*n*-Heptyl and γ -*n*-Octylresorcinols

BY ALFRED RUSSELL AND H. C. GULLEDGE¹

A series of the higher *n*-alkyl vicinal substituted resorcinols was prepared for the purpose of comparing their antiseptic properties with the well known isomeric 4-*n*-alkyl- and 5-*n*-alkylresorcinols. The lower alkyl vicinal resorcinols have previously been shown to have no value as antiseptics.² It is generally known that in the case of the 4-alkyl- and 5-alkylresorcinols, an increase in the number of carbon atoms in the alkyl group increases the antiseptic properties of the corresponding alkylresorcinol, reaching a maximum at hexylresorcinol.

Various investigators have prepared vicinal or 2-alkylresorcinols readily by the general scheme of Limaye.³ Russell, *et al.*,² however, were unable to prepare 2-*n*-hexylresorcinol by this scheme

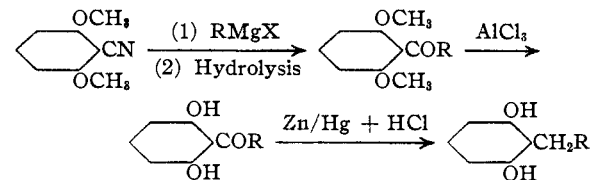
(1) Present address: Krebs Pigments Department, E. I. du Pont de Nemours and Company, Inc., Newport, Delaware.

(2) Russell, Frye and Mauldin, *THIS JOURNAL*, **62**, 1441 (1940).

(3) Limaye, *Ber.*, **67B**, 12 (1934).

due to the fact that the intermediate 4-methyl-7-caproyl-oxycoumarin did not undergo the Fries rearrangement.

Haller⁴ obtained 2-isoamylresorcinol in good yield from 2,6-dimethoxybenzotrile. The general scheme of Haller was chosen as the most likely route to the preparation of the higher vicinal alkylresorcinols since in this Laboratory 2,6-dimethoxybenzotrile had been prepared in fair yields (25%) from *m*-dinitrobenzene by a modification of Mauthner's⁵ method.



(4) Haller, *THIS JOURNAL*, **55**, 3032 (1933).

(5) Mauthner, *J. prakt. Chem.*, [2] **121**, 261 (1929).