

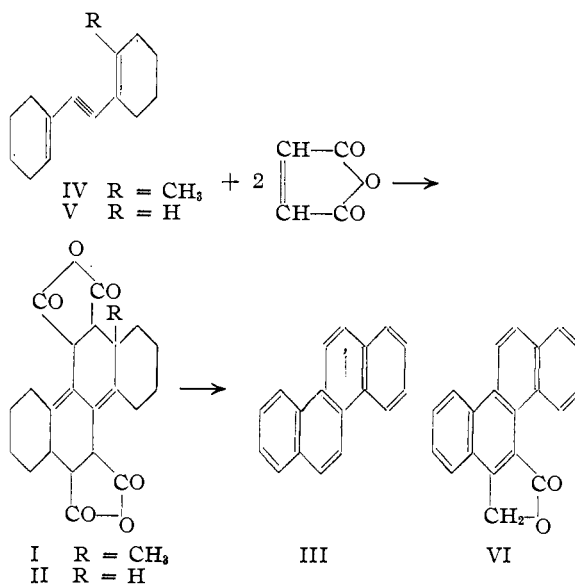
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The Synthesis of Condensed Ring Compounds. VI. The Dianhydride of a Tetradecahydrochrysene-5,6,11,12-tetracarboxylic Acid and a Homolog with an Angular Methyl Group¹

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All of the one hundred or more known naturally occurring steroids have an angular methyl group at carbon 13. Bachmann, Cole and Wilds² have reproduced this feature of the natural structures in their total synthesis of the sex hormone equilenin and its stereoisomers. It is important to devise procedures for the synthesis of non-benzenoid steroids with this 13-methyl group. We have been able to obtain a closely related ring analog, the dianhydride of a 6a methyltetradecahydrochrysene-5,6,11,12-tetracarboxylic acid (I), by means of the dienyne double addition reaction.³ We have also prepared the dianhydride of tetradecahydrochrysene-5,6,11,12-tetracarboxylic acid (II) by the same reaction. The position of the double bonds in I and II was chosen after a consideration of the process of formation and the ultraviolet absorption maxima.⁴ The character of the ring systems in I and II was demonstrated by dehydrogenation with the formation of chrysene (III). The formation of chrysene from I is evidence that the methyl group in I occupies an angular position, for if it did not, a methylchrysene should have been obtained. The formation of I and III can be represented by $IV \rightarrow I \rightarrow III$.

While the yield of hydrochrysene dianhydride (II) was a little higher (27%) than that of the steradiene dianhydride prepared by a similar reaction,³ it was not possible to push the yield of the methyl derivative above 2%. The yield of total ether-insoluble products was only one-third that from the other two dienyne double additions. Raising the temperature of reaction from 150 to 175° increased this yield of total ether-insoluble products from 15 to 23%. It appears therefore that the presence of a methyl group at a terminal carbon of the dienyne system retards the formation of the tetracyclic diene dianhydride to a great



extent, but does not prevent the addition completely. To a less extent the formation of the uncharacterized ether-insoluble by-products is also retarded. These observations are of interest in connection with a previous discussion⁵ of the mechanism of the dienyne double addition reaction. It has now been proved that the addition can proceed without any hydrogen being attached to one of the two terminal carbon atoms.⁶

In addition to chrysene, a second compound was isolated from the mixture obtained by the pyrolysis of II with platinized charcoal. Its elementary analysis and behavior toward alkali suggest that the compound may be a hindered lactone such as VI. The structure VI is more likely than the isomeric lactone structure in which the alternate carbonyl has been reduced to methylene, since it is to be anticipated that the carbonyl borne by carbon 6 in the hydrochrysene derivative II would be reduced in preference to the more hindered carbonyl on carbon 5. Furthermore, the lactone formulated in VI may be expected to resist saponification in view of the known re-

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(2) Bachmann, Cole and Wilds, *THIS JOURNAL*, **62**, 824 (1940).

(3) Butz and Joshel, *ibid.*, **63**, 3344 (1941).

(4) These observations were made by Dr. Russell E. Davis and Mr. Harry Bastron and are recorded in Table I of the preceding paper.³

(5) Butz, Gaddis, Butz and Davis, *J. Org. Chem.*, **5**, 384 (1940).

(6) A discussion of the bearing of this observation upon the question of the mechanism of the dienyne addition is postponed until another time.

sistance of chrysene-5-carboxylic acid to Fischer esterification.⁷

Experimental⁸

1,1'-Dicyclohexenylacetylene (V) was prepared by the method of Pinkney, *et al.*,⁹ and 2-methyl-1,1'-dicyclohexenylacetylene (IV) according to Marvel, *et al.*¹⁰ 1,1'-Dicyclohexanolacetylene was prepared by a new method¹¹ which gave a 70% yield of glycol when an efficient stirrer was used. In the preparation of 2-methyl-1,1'-dicyclohexanolacetylene it was found that a completely crystalline product was obtained, after the removal of more volatile contaminants, if the mixture from the Grignard reaction had been decomposed with ammonium chloride instead of acid.

The Dianhydride of Tetradecahydrochrysene-5,6,11,12-tetracarboxylic Acid.—A mixture of 45.3 g. of the dienyne V (obtained in 90% yield by dehydration of the glycol with sulfuric acid) and 93 g. of freshly distilled maleic anhydride was heated in a sealed tube in an atmosphere of carbon dioxide for three hours at 150°. After cooling, the material was removed from the tube by dissolving in acetone, the acetone was evaporated, and 1.5 liters of dry ether was added. After standing overnight the yellow precipitate (52 g.) was filtered and this material was extracted with ethyl acetate for several hours in a Soxhlet apparatus. This treatment removed almost all of the colored and amorphous material. On crystallization of the residue (m. p. 243–247°, 25.4 g., 27%) from dioxane, colorless needles, m. p. 251–254° (in vacuum), were obtained; 18 g., 19%. For ultraviolet absorption maximum see reference 3.

Anal. Calcd. for C₂₂H₂₂O₆: C, 69.1; H, 5.8. Found: C, 69.2; H, 5.6.

Pyrolysis of the Tetradecahydrochrysene-5,6,11,12-dianhydride in the Presence of Platinized Charcoal.—A mixture of 0.96 g. of the dianhydride and 0.15 g. of 30% platinized charcoal¹² was heated at 280–350° for two and a half hours, during which time 14 millimoles of gas was collected (theoretical quantity, 22.5 millimoles). After cooling, the mixture was extracted with benzene, the solvent distilled off, and the residue distilled at 1 mm. The product so obtained was a mixture which was difficult to separate into pure components. Treatment with hot aqueous ammonia or hot 0.5 N potassium hydroxide, as well as passage of a benzene solution through activated alumina, failed to remove a yellow material. Separation by fractional crystallization from benzene-ethanol was rather difficult, but colorless plates of chrysene were so obtained in small yield, m. p. 253–254°; m. p. not depressed by authentic chrysene.

One substance which accompanied the chrysene was isolated, also in small yield, as yellow needles from ethyl acetate, m. p. 271.8–272.4°. The compound does not reduce

Tollens reagent for aldehydes. It is insoluble in 20% aqueous potassium hydroxide even after three hours refluxing; solution takes place in 50% aqueous potassium hydroxide after short heating, but acidification does not effect reprecipitation. The compound readily goes into solution in refluxing 10% iso-amyl alcoholic potassium hydroxide¹³ and after steam distillation of the alcohol, reprecipitation occurs on acidification of the filtered solution.

Anal. Calcd. for C₂₀H₁₂O₂: C, 84.5; H, 4.3. Found: C, 84.3, 84.2; H, 4.4, 4.3.

Formulation as VI agrees with the known properties of this compound.

The Dianhydride of 6a-Methyltetradecahydrochrysene-5,6,11,12-tetracarboxylic Acid.—Fifty-two grams of the dienyne IV and 130 g. of maleic anhydride, heated at 150° for four hours in four sealed tubes under carbon dioxide, gave 15% of material relatively insoluble in ether. From this 2.0 g., 1.9%, of pure crystalline dianhydride was obtained by crystallization from dioxane; m. p. 278–280° (in vacuum).

Anal. Calcd. for C₂₃H₂₄O₆: C, 69.7; H, 6.1. Found: C, 69.5; H, 6.2.

Although many variations in experimental conditions were tried, the yield of crystalline dianhydride could not be increased. In one run, four hours at 175°, 23% of total ether-insoluble products was obtained. For ultraviolet absorption maximum see reference 3.

Conversion of the Methylhydrochrysene Dianhydride to Chrysene.—A mixture of 0.99 g. of the dianhydride from IV and 0.50 g. of 30% platinized charcoal¹² was heated at 250–330° for two and a half hours. During this time 16 millimoles of gas was collected (theoretical quantity, 22.5 moles). After cooling, the mixture was extracted with benzene and acetone, the solvents were evaporated, and the residue was distilled at 1 mm. After a second vacuum distillation, passage of a benzene solution through a column of activated alumina, and several crystallizations from acetone and benzene-ethanol, chrysene was obtained as plates with blue fluorescence, 18 mg., m. p. 251–253°. After one more crystallization, it melted at 253–254°, not depressed by authentic chrysene.

Summary

The dianhydrides of a tetradecahydrochrysene-5,6,11,12-tetracarboxylic acid and a 6a-methyltetradecahydrochrysene-5,6,11,12-tetracarboxylic acid have been prepared by the dienyne double addition reaction.

The angular methyl compound has the methyl group in a position corresponding to the 13-position in steroids. Since it has been possible to prepare three different tetracyclic compounds by the dienyne double addition reaction, it is probable that the closely related 13-methyl steroid can also be obtained from the appropriate dienyne.

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(7) Fieser and Joshel, *THIS JOURNAL*, **62**, 1211 (1940).

(8) All melting points are corrected.

(9) Pinkney, Nesty, Wiley and Marvel, *ibid.*, **58**, 972 (1936).

(10) Marvel, Mozingo and White, *ibid.*, **62**, 1880 (1940). We are greatly indebted to Dr. Marvel for a gift of 2-methyl-1,1'-dicyclohexanolacetylene.

(11) Babayan, Akopyan and Gyuli-Kevkhyan, *J. Gen. Chem. (U. S. S. R.)*, **9**, 1631 (1939).

(12) Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).

(13) *Cf.* Fleck and Palkin, *THIS JOURNAL*, **60**, 2621 (1938).