[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

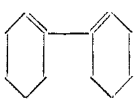
Synthesis of Certain Hydrogenated Phenanthrenes

BY E. E. GRUBER[1] AND ROGER ADAMS

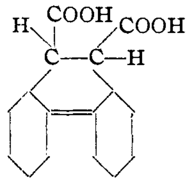
A recent communication by Barnett and Lawrence[2] describes the condensation of maleic anhydride and benzoquinone with the dienes obtained from the pinacols of cyclopentanone and cyclohexanone. A similar study has been under way for some time in the University of Illinois laboratories and occasion, therefore, is taken now to present some of these results which are closely related to the work of Barnett and Lawrence.

The British authors have neglected to mention that di-$\Delta^{1,1}$-cyclohexene (I) had previously been prepared by Wallach and Pauly[3] through dehydration of the corresponding pinacol with diluted sulfuric acid and indeed the yield by the latter procedure was found by us to be fully as satisfactory as that reported by Barnett and Lawrence using dehydrated alum as a catalyst.

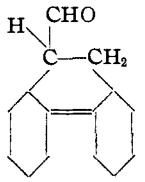
Condensation between maleic anhydride and the diene (I) mentioned, takes place readily with formation of the $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride (II).



I



II



III

The anhydride may be converted into the free acid, and the imide.

The diene (I) also readily condenses with acrolein with the formation of $\Delta^{4a,5a}$-dodecahydrophenanthrene-9-al (III), a product now being used by us in another investigation.

Experimental

1,1′-Dihydroxy-1,1′-dicyclohexyl.—In place of the aluminum used by Barnett and Lawrence in the synthesis of this compound, magnesium was employed.

To 94.6 g. of magnesium turnings and one liter of dry benzene in a 5-liter, two-necked flask (equipped with a reflux condenser and separatory funnel) was added 170 g. of mercuric chloride dissolved in 603 g. of dry cyclohexanone. Heat was applied to initiate the reaction, which then continued with increasing vigor until it was necessary to cool with an ice-bath. After the first vigorous reaction had subsided, the reaction mixture was heated on a steam cone for two hours, was broken up and 450 cc. of water was slowly added. Heating with occasional shaking was continued for about three hours longer. After filtering off the liquid, the residue in the flask was extracted with two 400-cc. portions of hot benzene. The combined filtrates were fractionally distilled *in vacuo*. About 308 g. of cyclohexanone was recovered. The fraction 140–175° (6.5 mm.) was chiefly the desired diol and was purified by recrystallization from high-boiling petroleum ether as white needles, m. p. 128.5–129.5°. Zelinsky[4] reports m. p. 128–129° and Barnett and Lawrence[2] report m. p. 130°. The yield was 35% based on cyclohexanone actually used.

It was found that by allowing the reaction to proceed as rapidly as possible and by avoiding a large excess of cyclohexanone, the major by-product cyclohexenylcyclohexanone was reduced in amount.

Di-$\Delta^{1,1}$-cyclohexene (I).—By heating under reflux for four hours a mixture of 132 g. of the dihydroxycyclohexyl in 600 cc. of 10% sulfuric acid,[2] then subjecting it to steam distillation, a colorless oil was obtained which was extracted with low boiling petroleum ether; b. p. 101–102° (5.5 mm.); d_{20} 0.9581; n^{20}D 1.5322; yield 88 g. (82%).

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid Anhydride (II).—A solution of 10 g. of dicyclohexene and 6 g. of powdered maleic anhydride in 12 cc. of benzene was warmed gently for a few minutes until the anhydride dissolved. After four hours of standing the solvent was evaporated and the oily crystalline mass thus obtained was washed with high-boiling petroleum ether and finally with 2 cc. of benzene. The anhydride was recrystallized from high-boiling petroleum ether and thereby obtained as colorless prismatic needles, m. p. 122.5–123.5°. Barnett and Lawrence[2] report the same m. p.; yield 5.5 g.

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.8; H, 7.74. Found: C, 73.5; H, 7.96.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid.—A solution of 20 g. of the powdered dodecahydrophenanthrene-9,10-dicarboxylic anhydride in 250 cc. of 5% sodium hydroxide was refluxed until the anhydride dissolved, filtered and cooled to about 5°, and then diluted with about 200 cc. of cold water. Dilute acetic acid was added slowly with stirring and the gummy precipitate was transferred to 250 cc. of hot glacial acetic acid, in which it solidified and then dissolved. Upon cooling it crystallized out as colorless prisms; m. p. 242° (bloc Maquenne); yield 12 g.

The aqueous solution from the neutralization was still milky and upon standing and diluting yielded more of the above acid in a white powdery form; yield 5 g.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.02; H, 7.97. Found: (I) C, 68.96; H, 8.37; (II) C, 69.41; H, 8.09.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9,10-dicarboxylic Acid Imide.—A mixture of 0.5 g. of anhydride and 5 cc. of

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[1] Part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Barnett and Lawrence, *J. Chem. Soc.*, 1104 (1935).

[3] Wallach and Pauly, *Ann.*, **381**, 112 (1911).

[4] Zelinsky, *Ber.*, **34**, 2801 (1901).

concentrated aqueous ammonia was heated slowly under reflux to about 250–300°. At this temperature the reaction reached a homogeneous melt. Anhydride, which sublimed into the condenser, was pushed back with a glass rod. After cooling, 95% alcohol was added and the solution filtered. Addition of water to the alcoholic solution precipitated a light tan solid, m. p. 145–150° (yield 0.3 g.). For purification it was dissolved in ethyl alcohol and water added to the hot solution until almost cloudy. Upon cooling prismatic needles separated. After recrystallizing three times from benzene and low boiling petroleum ether, the product formed colorless needles, m. p. 182–183°.

Anal. Calcd. for $C_{16}H_{21}O_2N$: N, 5.40. Found: N, 5.36.

$\Delta^{4a,5a}$-Dodecahydrophenanthrene-9-al (III).—A mixture of 17 g. of the dicyclohexene in 15 cc. of dry benzene and 6 g. of pure acrolein was heated under reflux for twenty-two hours at 50–60°. The benzene and the unreacted acrolein were removed and the residue fractionally distilled in vacuo. After distilling off all of the unreacted dicyclohexene (up to 126° (6.5 mm.)), the residue was dissolved in a small amount of ether and shaken with a 10% solution of sodium bisulfite. The solid which formed was filtered, washed with a little alcohol and decomposed with warm dilute aqueous sodium carbonate. The oil which separated was extracted with ether. The aldehyde was a colorless oil and was distilled in an atmosphere of nitrogen, b. p. 136–137° (4 mm.); yield, 4.2 g. (20%).

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.50; H, 10.65. Found: C, 82.87; H, 10.49.

The semicarbazone, purified from dilute alcohol, melted at 179–180°.

Anal. Calcd. for $C_{16}H_{25}ON_3$: N, 15.21. Found: N 14.99.

Summary

Addition of maleic anhydride and acrolein to di-$\Delta^{1,1}$-cyclohexene gives the hydrogenated phenanthrene derivatives, $\Delta^{4a,5a}$-dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride and $\Delta^{4a,5a}$-dodecahydrophenanthrene-9-al.

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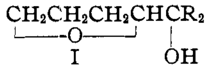
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Preparation and Reactions of Tertiary Tetrahydrofurylcarbinols

BY A. L. DOUNCE, RALPH H. WARDLOW[1] AND RALPH CONNOR[2]

Two methods are available for the synthesis of tertiary tetrahydrofurylcarbinols (I): (1) the action of the appropriate Grignard reagent upon ethyl tetrahydrofuroate, obtained by the hydrogenation of ethyl furoate over nickel, or (2) the reaction of the Grignard reagent with ethyl furoate, followed by the hydrogenation over nickel of the furyldialkylcarbinols thus obtained. Both of these methods have been used for the preparation of tetrahydrofuryldiethylcarbinol (II) and tetrahydrofuryldi-*n*-butylcarbinol (III). The former method gave

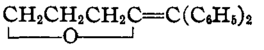

$\underbrace{CH_2CH_2CH_2CH}_{O}\underset{OH}{C}R_2$

I

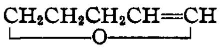
II, R = $—C_2H_5$
III, R = n-C_4H_9
IV, R = $—C_6H_5$

in over-all yields of 71% (II), 50% (III) and 77% (IV) and is to be preferred to the latter, which gave 52% (II) and 45% (III). Because of the well-known tendency[3] for hydrogenolysis of the carbon–oxygen bond in the α-position to aromatic nuclei, the latter method is not applicable to such compounds as IV.

Dehydration of these carbinols was readily accomplished by heating with magnesium sulfate until the theoretical amount of water had distilled. The product obtained by the dehydration of tetrahydrofuryldi-*n*-butylcarbinol (III) was a mixture of isomers which could not be separated by fractional distillation. With tetrahydrofuryldiphenylcarbinol (IV), however, the sole product isolated was 1,1-diphenyl-2,5-epoxy-1-pentene (V). The structure of the latter was established by the isolation of benzophenone and γ-butyrolactone from the hydrolysis of the ozonide; examination of the ozonolysis products failed to show any evidence of the formation of a dihydropyran during the dehydration.


$\underbrace{CH_2CH_2CH_2C}_{O}{=}C(C_6H_5)_2$

V


$\underbrace{CH_2CH_2CH_2CH{=}CH}_{O}$

VI


$\underbrace{CH_2CH_2CH_2C}_{O}{=}CH_2$

VII

The fact that no ring enlargement occurred under the conditions used in the dehydration of IV is in contrast to the results of Paul,[4] who obtained a dihydropyran (VI) by the catalytic dehydration of tetrahydrofurfuryl alcohol at 370–380°. Fur-

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[1] A portion of this communication is abstracted from the thesis submitted by Ralph H. Wardlow in partial fulfilment of the requirements for the degree of Master of Science at Cornell University in June, 1933.

[2] Present address, Harrison Laboratory, University of Pennsylvania, Philadelphia, Pa.

[3] *Cf.* Covert, Connor and Adkins, THIS JOURNAL, **54**, 1660 (1932).

[4] Paul, *Bull. soc. chim.*, [4] **53**, 417 (1933); *ibid.*, 1489 (1933); *Compt. rend.*, **196**, 1409 (1933); *Bull. soc. chim.*, [5] **2**, 311 (1935); *ibid.*, 745 (1935).