[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Addition of Oxy Compounds to Acetylenic Alcohols[1]

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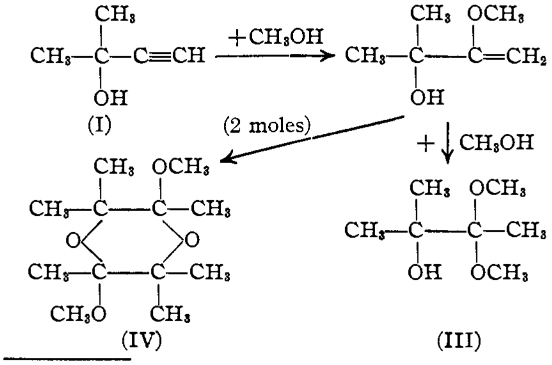
Introduction

Numerous examples of catalytic addition reactions of alcohols and carboxylic acids to acetylenic hydrocarbons have been reported from this Laboratory.[2] It was thought of interest to continue these investigations, particularly with acetylenes containing a reactive group in addition to the triple bond. The products found by the reaction of dimethylethynylcarbinol (I) and of the corresponding glycol, 2,5-dimethyl-3-hexyne-2,5-diol (II) with methanol and with acetic acid have now been investigated.

(I) and (II) were selected because they can be obtained readily by the reaction of acetone with sodium acetylide in liquid ammonia.[3,4] The carbinol (I) was obtained in yields up to 88%. High yields are favored by conducting the reaction at about −50° in the presence of excess acetylene. The glycol (II) was obtained as a by-product of the synthesis, in yields from 0–45%, depending on conditions. When excess acetylene is avoided in the reaction and the product aged for several days before hydrolysis, the yield of carbinol (I) is decreased and the yield of glycol (II) markedly increased.

As anticipated, certain anomalies in the behavior of these compounds toward methanol and acetic acid were noted.

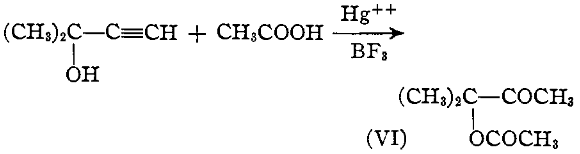
In the presence of small amounts of mercuric oxide and boron trifluoride, methanol reacted smoothly with dimethylethynylcarbinol (I) to form principally 3,3-dimethoxy-2-methyl-2-butanol (III). A small amount of 2,5-dimethoxy-2,3,3,5,6,6-hexamethyl-1,4-dioxane (IV) was obtained as a by-product. The reactions are indicated by the equations just given.



(IV) (III)

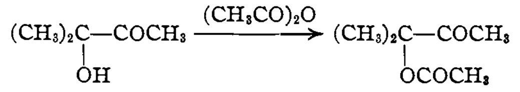
When heated with dilute acid both (III) and (IV) hydrolyze to 2-hydroxy-2-methyl-3-butanone, $(CH_3)_2C(OH)COCH_3$ (V), previously reported[5] by direct hydration of the carbinol (I). When boiled with methanol containing a trace of acid (IV) reacts to form (III).

The reaction of the carbinol (I) with glacial acetic acid is particularly unique; the hydroxyl group is acetylated and the triple bond hydrated.



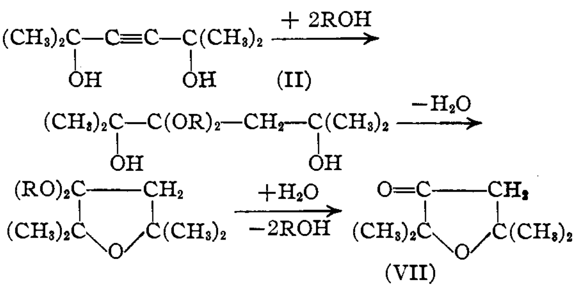
$$\underset{\displaystyle OH}{(CH_3)_2C}—C\equiv CH + CH_3COOH \xrightarrow[BF_3]{Hg^{++}} \underset{\displaystyle OCOCH_3}{(CH_3)_2C}—COCH_3 \quad (VI)$$

The mechanism for this reaction is a matter of speculation. The product is identical with that obtained by Scheibler and Fischer[5] who acetylated the hydroxy ketone (V) with acetic anhydride.



$$\underset{\displaystyle (V)}{\underset{\displaystyle OH}{(CH_3)_2C}—COCH_3} \xrightarrow{(CH_3CO)_2O} \underset{\displaystyle (VI)}{\underset{\displaystyle OCOCH_3}{(CH_3)_2C}—COCH_3}$$

When either methanol or acetic acid reacted with the glycol (II) the triple bond was hydrated and the compound cyclized to form 2,2,5,5-tetramethyltetrahydro-3-furanone (VII). It is necessary for the triple bond to be saturated, at least partially, before cyclization can occur. The following mechanism is offered based on this fact (R is CH_3- or CH_3CO-).



(VII)

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[1] Paper XXXVII on the chemistry of substituted acetylenes and their derivatives: previous paper, THIS JOURNAL, **62**, 449 (1940).

[2] Hennion, Nieuwland, *et al.*, *ibid.*, **56**, 1130, 1384, 1802 (1934); **57**, 2006 (1935); **58**, 80 (1936).

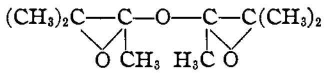
[3] Kreimeier, U. S. Patent 2,106,180 (1938).

[4] Campbell, Campbell and Eby, THIS JOURNAL, **60**, 2882 (1938).

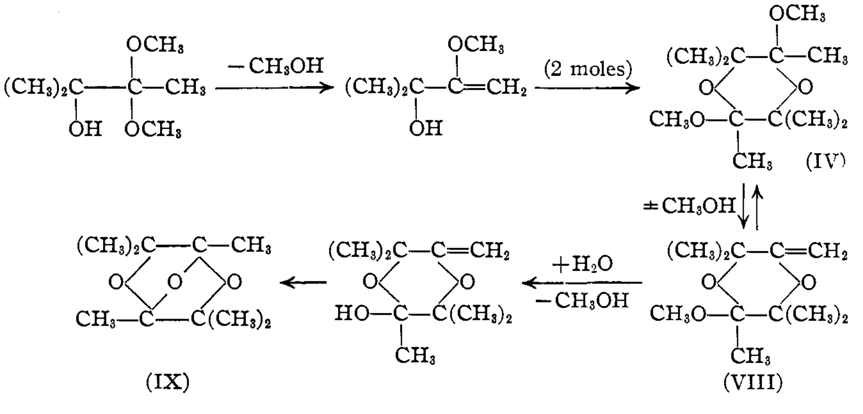
[5] Scheibler and Fischer, *Ber.*, **55**, 2903 (1922).

The product (VII) has been prepared previously[6] from the glycol (II) by heating with water in the presence of mercuric sulfate.

Since ketals are known to desaturate to vinyl ethers when heated with toluenesulfonic acid,[7] this reaction was applied to 3,3-dimethoxy-2-methyl-2-butanol (III). Methanol was eliminated upon heating with acid but the residue boiled over a wide temperature range. Two products were isolated, however, and their structures determined. The first of these was found to have the molecular formula $C_{10}H_{18}O_3$ as the structure 1,3,3,4,6,6-hexamethyl-2,5,7-trioxabicyclo[2-2-1]heptane (IX). This same compound was obtained by Scheibler and Fischer[5] upon treatment of the ketone (V) with phosphorus pentoxide. However, these investigators erroneously ascribed to this compound the structure



Distinction between these formulas was made by parachor measurement. Also the compound is unaffected by prolonged boiling with methanol containing toluenesulfonic acid, a fact which argues against the ethylene oxide structure. The second desaturation product was found to have a dioxane structure (VIII). These compounds are related in the following equations.



In the conversion of (VIII) to (IX) water is required. Presumably this is supplied by dehydration of (III) as a secondary reaction. In the presence of acid (VIII) adds methanol to its methylene group and reverts to (IV). When heated with a trace of acid (IV) loses methanol and yields (VIII) and (IX). These transformations confirm the mechanism cited above.

Experimental

Preparation of Dimethylethynylcarbinol (I).—Using the procedure[8] previously described, 7.35 moles of sodium acetylide was prepared as a solution in 3–4 liters of liquid ammonia. This was cooled to −50 ± 5° by immersion of the flask in a carbice bath. Acetylene was passed in for ten minutes. Acetone (465 g., 8 moles) was then added during a period of thirty minutes. Meanwhile the admission of acetylene was continued. The ammonia was then allowed to evaporate (usually overnight), 1 liter of ether added, followed by sufficient iced 35% sulfuric acid to dissolve the solid. The water layer was separated and extracted with ether. The extract was combined with the original ether layer, the whole dried over anhydrous potassium carbonate and fractionally distilled. Fractions boiling between 60 and 102° were redried and redistilled. The yield of dimethylethynylcarbinol, b. p. 102–104°, was 545 g. (88%). Constants for a pure specimen were b. p. 103.8° at 757 mm.; n^{20}_D 1.4211; d^{20} 0.8623.

Preparation of 2,5-Dimethyl-3-hexyne-2,5-diol (II).—The above procedure was followed except that the reaction product was aged for one week after evaporation of the ammonia. The residue after distillation of the dimethylethynylcarbinol was crystallized several times from carbon tetrachloride. Yields varied, usually between 20 and 45%. Large white needles were obtained, m. p. 95°. The compound may be prepared in better yields by heating the sodium salt of the carbinol (I) for several hours in an atmosphere of ammonia.[9]

Preparation of 3,3-Dimethoxy-2-methyl-2-butanol (III).—The catalyst was prepared by heating together 4–5 g. of red mercuric oxide, 5 ml. of ether–boron fluoride, 5 ml. of methanol and 1–3 g. of trichloroacetic acid in a 2-liter 3-necked flask. The flask was provided with a reflux condenser, mechanical stirrer and dropping funnel. Reagent grade methanol (100 g.) was poured over the catalyst, the stirrer started, and 300 g. (3.13 moles) of dimethylethynylcarbinol in 300 g. of methanol added dropwise. The temperature was held at 45–55° by occasional cooling. After three hours the mixture was cooled to room temperature and 10 g. of powdered anhydrous potassium carbonate added with vigorous stirring. The sludge was allowed to settle overnight, the supernatant liquid decanted, excess methanol distilled and the residue fractionated at 50 mm. The yield was 371 g. (80%); colorless liquid, b. p. 81° at 50 mm.; n^{20}_D 1.4248; d^{20} 0.974; *MR* (calcd.), 39.34; *MR* (obsd.), 38.9.

Anal. Calcd. for $C_7H_{16}O_3$: C, 56.76; H, 10.81; mol.

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[6] Dupont, *Ann. chim.*, (8) **30**, 536 (1913).

[7] Killian, Hennion and Nieuwland, This Journal, **57**, 544 (1935).

[8] Hennion, *Proc. Ind. Acad. Sci.*, **48**, 116 (1938).

[9] Macullum, U. S. Patent 2,162,676 (1939).

wt., 148.13. Found: C, 57.15; H, 10.89; mol. wt., cryoscopic in benzene,[10] 149.

Hydrolysis with dilute sulfuric acid gave 2-hydroxy-2-methyl-3-butanone (V); b. p. 139° at 750 mm., 65° at 50 mm.; n^{20}D 1.4150; d^{20} 0.950; *MR* (calcd.), 26.83; *MR* (obsd.), 27.35.

Anal. Calcd. for $C_5H_{10}O_2$: C, 59.41; H, 9.78. Found: C. 58.82; H, 9.80.

Isolation of 2,5-Dimethoxy-2,3,3,5,6,6-hexamethyl-1,4-dioxane (IV).—A solid residue, partially organic, remained after the distillation of (III) described above. The solid was extracted with ether to yield an organic solid which was crystallized from methanol. The yield was 16 g. (4.4%), white rhombic crystals, m. p. 107°.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.02; H, 10.43; CH_3O, 26.72; mol. wt., 232.2. Found: C, 62.40; H, 10.50; CH_3O, 25.1; mol. wt., 235.

Preparation of 2-Acetoxy-2-methyl-3-butanone (VI).—Dimethylethynylcarbinol (126 g., 1.5 moles) was treated with glacial acetic acid (180 g., 3 moles) in the presence of mercuric oxide and boron fluoride as described above for the reaction with methanol. After completion of the reaction the product was neutralized with sodium carbonate solution and extracted with ether. The ether layer was dried over calcium chloride, the ether removed by distillation, and the residue fractionated *in vacuo.* There was obtained 105.5 g. (49% yield) of product, a colorless liquid with amyl acetate like odor: b. p. 93° at 50 mm.; n^{20}D 1.4180; d^{20} 1.008; *MR* (calcd.), 36.2; *MR* (obsd.), 36.0.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.29; H, 8.39; mol. wt., 144.1. Found: C, 58.00; H, 8.65; mol. wt., 145.

This compound was prepared also according to the procedure of Scheibler and Fischer.[5] The yield was 69%.

Preparations of 2,2,5,5-Tetramethyltetrahydro-3-furanone (VII).—The glycol (II) (100 g., 0.7 mole) reacted with methanol (100 ml., 2.5 moles) with the catalyst and under the conditions described above. There was obtained 77 g. (77% yield) of product, a colorless, stable liquid of camphoraceous odor: b. p. 71° at 50 mm.; n^{20}D 1.4197; d^{20} 0.9255; *MR* (calcd.), 38.60; *MR* (obsd.), 38.8; mol. wt. (calcd.), 142; mol. wt. (found), 143.

The melting point of the semicarbazone was 190°, in agreement with the value of Dupont.[6]

Similarly (II) with acetic acid gave (VII) in 78% yield.

Thermal Desaturation of 3,3-Dimethoxy-2-methyl-2-butanol (III).—The ketal (351.5 g., 2.38 moles) was placed in a 1-liter round-bottomed flask, 0.1 g. of *p*-toluenesulfonic acid added, and the flask attached to a 1 × 30 cm. indented column with variable take-off. Distillation was begun by heating the flask in an oil-bath. Heating for eight hours at 150–180° gave 110 g. of distillate boiling at 64°. The residue was neutralized by shaking with powdered anhydrous potassium carbonate. Subsequent distillation gave several fractions: A, 115 g., b. p. 123–165° at 750 mm.; B, 67 g., b. p. 78–82° at 50 mm.; C, 5.5 g., b. p. 82–110° at 50 mm.; D, 33 g., b. p. 110–112° at 50 mm.; E, 10 g., residue.

Fraction A proved to be an intractable mixture which continued to boil over a wide temperature range, even after numerous distillations. However, redistillation with toluenesulfonic acid gave further quantities of methanol and fractions B and D.

Fraction B distilled at 165° at 750 mm. and at 81–82° at 50 mm.; n^{20}D 1.4199; d^{20} 0.972. The compound is assigned the bicyclic structure (IX) based on analysis and parachor.[11]

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.47; H, 9.68; mol. wt., 186.14; *MR*, 48.91; [P], 424.2. Found: C, 64.50; H, 9.75; mol. wt., 186; *MR*, 48.4; [P], 420.35. The parachor calculated for the structure of Scheibler and Fischer[5] is 449.2.

Fraction D redistilled at 110–112° at 50 mm.; n^{20}D 1.4533; d^{20} 0.979. The compound is given structure (VIII) based on its reactions and the following.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.95; H, 10.08; CH_3O, 15.50; mol. wt., 200.16; *MR*, 55.26. Found: C, 65.85; H, 10.34; CH_3O, 14.67; mol. wt., 199.5; *MR*, 54.75.

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Summary

The reactions of methanol and acetic acid with dimethylethynylcarbinol and 2,5-dimethyl-3-hexyne-2,5-diol are described. These reactions are more complex than the corresponding ones with acetylenic hydrocarbons.

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[10] All molecular weights reported in this paper were determined in the same manner.

[11] Ray, *J. Indian Chem. Soc.*, **12**, 764–767 (1935), gives the parachor constant for a bridged six-membered ring which was used. Other values are those of Sugden.