The alkylidene or arylidene diacetamides thus formed are hydrolyzed by mineral acids, yielding the corresponding ammonium salt, the original aldehyde, and acetic acid. The melting point of ethylidenediacetamide was found to be 180° instead of 169° as reported by von Richter.

Experimental Part

A mixture of acetamide (2 moles), aldehyde (1 mole), and acetic acid (0.2 mole per mole of amide) are placed in a round-bottomed flask and quietly refluxed for about four hours. The reaction mixture, which generally has a brown color, is removed and placed on a steam-bath, where it is evaporated to dryness. The impure product is now taken up with just more than enough warm acetone required for solution. The solution is decolorized by norite. The product is now crystallized by evaporating off the solvent. This procedure usually yields small white needles; however, larger crystals were obtained by using alcohol (95%) as a solvent. The products are insoluble in benzene and ether, soluble in warm acetone, fairly soluble in alcohol and very soluble in water.

Summary

The condensations of acetamide with formaldehyde, acetaldehyde, propylaldehyde and benzaldehyde already studied by other authors have been repeated. Similar condensations have been carried out with butyl-, isovaleryl- and heptyl-aldehydes and the products are described. It is believed that the reaction is a general one.

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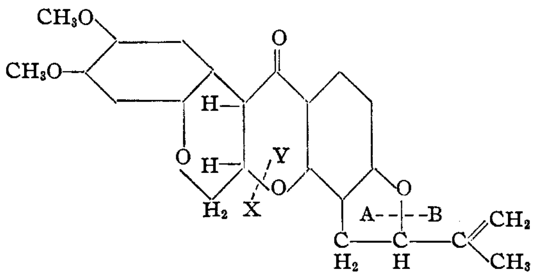
Note

Rotenone. XXVII. Note on the Hydrogenation of Rotenone

BY H. L. HALLER AND P. S. SCHAFFER

Hydrogenation of rotenone (I) with platinum oxide or palladium-barium sulfate catalysts results in the saturation of the double bond present in rotenone (formation of dihydrorotenone) and also in the cleavage of the furan oxide ring as indicated at A-B (formation of rotenonic acid).[1] The proportion of dihydrorotenone to rotenonic acid formed by one mole of hydrogen with these catalysts varies considerably. With a freshly prepared platinum oxide catalyst and in neutral solution, rotenonic acid pre-



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[1] LaForge and Smith, THIS JOURNAL, **51**, 2574 (1929); for the structure of rotenonic acid see *Chem. Rev.*, **12**, 181 (1933).

dominates. When the same catalyst is used a second time, however, more dihydrorotenone is formed than rotenonic acid. The addition of a small quantity of pyridine to the solvent with a catalyst which has been used for one reduction does not increase the amount of rotenonic acid formed. Our results, therefore, indicate that the "age"[2] of the catalyst rather than the temperature[3] at which the catalyst has been prepared determines the course of the hydrogenation with platinum oxide catalyst in neutral solution.

Hydrogenation of rotenone with palladium–barium sulfate catalyst in pyridine solution results in a quantitative yield of rotenonic acid.

With nickel catalysts, the course of hydrogenation of rotenone depends upon the nature of the nickel catalyst employed. Rotenone hydrogenated in butyl acetate solution at 90–105° and 35–60 lb./sq. in. pressure[4] with an active nickel catalyst supported on nickel enclosed in a nickel cage[5] gave no dihydrorotenone or rotenonic acid but dihydrorotenol[6] in a quantitative yield. With this catalyst, besides saturation of the double bond, cleavage of the dihydrobenzopyrone ring takes place as indicated at X-Y, with the formation of dihydrorotenol.

On hydrogenation of rotenone at room temperature and atmospheric pressure in neutral solution with a nickel catalyst prepared from a nickel–aluminum alloy[7] (Raney catalyst), dihydrorotenone was formed in excellent yields (more than 90%). Dihydrorotenol could not be detected in any of these experiments.

The Raney catalyst thus affords a practical way of preparing dihydrorotenone.

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[2] Farmer and Galley, *Nature*, **131**, 60 (1933).

[3] Takei, Miyajima and Ono, *Ber.*, **66**, 479 (1933).

[4] We are indebted to the firm of Derris, Inc., New York City, for having these experiments made.

[5] British Patent 162,370; British Patent 203,218; *J. Soc. Chem. Ind.*, **43**, 53 (1924); **46**, 444 (1927).

[6] LaForge and Smith, THIS JOURNAL, **51**, 2574 (1929).

[7] Covert and Adkins, *ibid.*, **54**, 4116 (1932).