

2. Mild pyridine acetylation of galactose oxime produces aldehydo-galactose oxime hexa-acetate, galactonic acid nitrile penta-acetate and the isomeric galactose oxime hexa-acetate (m. p. 106°; $[\alpha]_D -27^\circ$, CHCl_3). Vigorous acetylation produces the last two compounds.

3. Aldehydo-galactose oxime hexa-acetate undergoes nitrile formation but this behavior is not shown by the levorotatory oxime hexa-acetate.

4. The previously reported α -galactose oxime hexa-acetate is a mixture and accordingly the dependent proof that galactose oxime possesses an *alpha* ring structure is invalidated.

5. Mild acetylation of aldehydo-*l*-arabinose oxime tetra-acetate produces *l*-arabonic acid nitrile tetra-acetate.

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RECEIVED MAY 10, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Aldehyde-Amide Condensation. I. Reactions between Aldehydes and Acetamide

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The best known aldehyde-amide condensations are those that take place between urea and formaldehyde to give polymeric compounds. However, amides have been condensed with aldehydes to form bimolecular compounds. This is illustrated by the reactions of acetamide with formaldehyde,¹ acetaldehyde,² propylaldehyde³ and benzaldehyde.^{4,5}

These reactions have been found to be general for alkyl and aryl aldehydes, as the accompanying table will show. In each case, a small amount of acetic acid catalyzes the condensations, which take place according to the following equation



TABLE I

THE YIELDS ARE BASED UPON THE ACETAMIDE USED

Aldehyde	Product, diacetamide	M. p., °C.	Yield, %	Nitrogen analyses, %	
				Calcd.	Found
Form-	Methylene-	197.5-198	54	21.53	21.42
Acet-	Ethylidene-	180	44	19.42	18.97
Propyl-	Propylidene-	190-190.5	7.5	17.72	16.94
Butyl-	Butylidene-	189	11.5	16.28	16.17
Isovaleryl-	1-Methylbutylidene-4-	184	26	15.05	15.04
Heptyl-	Heptylidene-	171-172	6.5	13.08	13.18
Benz-	Benzylidene-	238	48	13.59	14.00

(1) G. Pulvermacher, *Ber.*, **25**, 304 (1892).

(2) V. v. Richter, *ibid.*, **5**, 477 (1872).

(3) A. Reich, *Monatsh.*, **25**, 933 (1904).

(4) K. Bulow, *Ber.*, **26**, 1973 (1893).

(5) Roth, *Ann.*, **154**, 72 (1870).

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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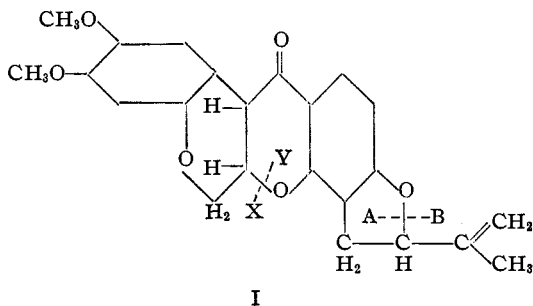
RECEIVED MAY 26, 1933
PUBLISHED AUGUST 5, 1933

Note

Rotenone. XXVII. Note on the Hydrogenation of Rotenone

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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-

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