action apparently must take place during the reduction with hydrogen, i. e., the promotor effect is manifested when platinic chloride is added just before the hydrogenation is started. The interpretation of the results is further complicated by the fact that in adding platinic chloride, poisons for the nickel catalyst are added, although it should be pointed out that using non-catalytically active metals, or completely plating out the platinum and removing the poisons resulted in completely reduced activity. Further, the type of catalytically active nickel appears to be a factor. On a weight basis, reduced nickel on kieselguhr is hundreds of times as active as is Raney nickel,[7] however, addition of platinic chloride to such a catalyst under the same conditions as Raney catalyst (temperature, pressure of hydrogen and ratio of catalyst to hydrogen acceptor) had no effect on its activity.

On the other hand, however, the effect is not limited to the hydrogenation of a single substance

(7) Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

(nitroguanidine), as is often the case in promoter catalysis. It has, indeed, been applied even more successfully to the hydrogenation of castor oil, linseed oil, nitrobenzene and benzaldehyde.

The application of the Raney nickel–platinic chloride catalyst to the hydrogenation of various types of organic compounds, as well as a more detailed investigation of the effects involved particularly with respect to other noble metal salts, is in progress in this Laboratory and will be reported in a subsequent paper.

Summary

Small amounts of platinic chloride added to Raney nickel catalyst immediately before the beginning of the hydrogenation have a definite and pronounced enhancing action which is not limited to the hydrogenation of nitroguanidine but is apparently applicable to the reduction of many types of organic compounds.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Reactions of Aldoxime Derivatives with Bases. III. The Reactions of Geometrically Isomeric Acetyl-3,4-methylenedioxybenzaldoximes with Certain Amines
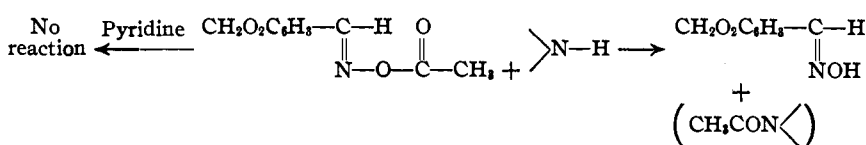
BY CHARLES R. HAUSER AND EARL JORDAN[1]

In continuation of our investigations[2] of the reactions of acyl-aldoximes with bases, a study has been made of the reactions of the two isomers of acetyl-3,4-methylenedioxybenzaldoxime with certain primary, secondary and tertiary amines.

It has been found that when the α-isomer is dissolved in n-butylamine, aniline, piperidine or diethylamine, and allowed to stand for a short time, it is converted into the corresponding α-aldoxime in yields of 90–99%; apparently these reactions are quantitative. On the other hand, the acetyl-α-aldoxime may be heated in pyridine solution at 97–100° for an hour and then recovered practically unchanged; also, it is relatively stable in triethylamine solution. The yields of aldoxime and recovered acetyl-α-aldoxime are given in Table I.

(1) This is from a portion of a thesis presented by Earl Jordan in partial fulfilment of the requirements for the Ph.D. degree at Duke University.

(2) See (a) Hauser and Sullivan, THIS JOURNAL, **55**, 4611 (1933); (b) Hauser and Jordan, ibid., **57**, 2450 (1935); (c) Hauser, Jordan and O'Conner, ibid., **57**, 2456 (1935).

The reaction of acetyl-α-3,4-methylenedioxybenzaldoxime with a primary or secondary amine may be represented as an aminolysis,[3] thus[4]

$$\text{No reaction} \xleftarrow{\text{Pyridine}} \begin{matrix} CH_2O_2C_6H_3\!-\!C\!-\!H \\ \| \\ N\!-\!O\!-\!\underset{\|}{C}\!-\!CH_3 \end{matrix} \;+\; \rangle N\!-\!H \longrightarrow \begin{matrix} CH_2O_2C_6H_3\!-\!C\!-\!H \\ \| \\ NOH \end{matrix} + \left(CH_3CON\!\langle \right)$$

The tertiary amines have no hydrogen atom attached to nitrogen and consequently are not capable of bringing about this reaction. The other possible decomposition, the elimination of acetic acid from the acetyl-α-aldoxime to form nitrile,[5] might occur very slowly in triethylamine solution at the boiling point of the

(3) This reaction is analogous to an ammonolysis of an ester; it is possible that the primary or secondary amine attacks the carbonyl group of the acetate, perhaps forming an intermediate addition compound which decomposes to form aldoxime and amide; the latter, however, has not been isolated.

(4) For references to evidence that α-aldoximes have the *syn* configuration, see note 2b.

(5) Although the acetyl-β-aldoxime in the presence of a base eliminates acetic acid to form nitrile much more readily than the α-isomer, it is possible for the latter, under certain conditions, to form nitrile or the corresponding acid; see reference 2b.

amine,[6] but this reaction does not occur in pyridine solution, at least not to an appreciable extent within an hour even at 97–100°.

The reactions of acetyl-β-3,4-methylenedioxybenzaldoxime with amines have been carried out under several different sets of conditions. In general, with primary or secondary amines this isomer gives partly nitrile by elimination of acetic acid, and partly the corresponding β-aldoxime presumably by aminolysis;[3] but with tertiary amines it gives only nitrile. These reactions may be represented as follows

high yields of nitrile and no appreciable amounts of oxime; however, when the relatively weak base, aniline, is added to the acetyl-β-aldoxime in a similar manner, the latter dissolves without a noticeable rise of temperature, giving a high yield of oxime and no appreciable amount of nitrile. The yields of products obtained with these primary and secondary amines under these conditions are given in Table III. In this table are included also the yields of. nitrile obtained with the tertiary amines, pyridine and triethylamine; with the latter the reaction mixture becomes

The yields of nitrile and aldoxime obtained from the acetyl-β-aldoxime with a primary or secondary amine depend upon the relative rates of the two competing reactions. Similar to the reactions with alkali,[2b] an elevation of temperature accelerates the elimination of acetic acid to form nitrile more than the aminolysis to form oxime; also, these reactions are apparently dependent upon the basic strength of the amine used. In Table II are given the yields of products obtained by adding the acetyl-β-aldoxime in small portions to n-butylamine and to the much weaker base, aniline, at various temperatures. It can be seen that with n-butylamine the acetyl-β-aldoxime gives, below 0°, practically only oxime, between 20 and 45°, both oxime and nitrile; but at 78°, apparently only nitrile, no oxime being isolated at this temperature. With aniline at 25–30°, the acetyl-β-aldoxime gives apparently only oxime, and even at 97–100° this is the main product, the yield of nitrile being only 11%.

The difference in degree of reactivity of acetyl-α-, and acetyl-β-3,4-methylenedioxybenzaldoximes with various amines should be pointed out. Whereas the α-isomer merely dissolves in the amines listed in Table I without generating a noticeable amount of heat, the acetyl-β-aldoxime reacts vigorously with n-butylamine, piperidine, and diethylamine. When a few cubic centimeters of these amines are added, in 1-cc. portions, to gram samples of the acetyl-β-aldoxime, the reaction mixtures become hot immediately, producing

warm. The formation of nitrile from the acetyl-β-aldoxime and these tertiary amines is presumably quantitative over a considerable range of temperatures.

The yields of products obtained from the reactions of the acetyl-β-aldoxime with 1 M solutions of certain amines in water and in dioxane and with ammonia solutions, at 0 or 30°, are given in Table IV. It can be seen that with n-butylamine or piperidine both nitrile and oxime are obtained; in the reaction with aqueous piperidine the yield of nitrile is greater, and that of oxime correspondingly smaller at 30°, than at 0°.

It should be noted that with pyridine even in the presence of water the acetyl-β-aldoxime apparently gives only nitrile, whereas with triethylamine and water a small yield of oxime is obtained in addition to nitrile. In the latter case the formation of oxime presumably is due to the presence of hydroxyl ions since no oxime is found when the reaction is carried out in anhydrous dioxane solution; the concentration of hydroxyl ions in aqueous pyridine is apparently too small to produce an appreciable amount of hydrolysis before the acetyl-β-aldoxime is completely converted to nitrile.

Hantzsch[7] has previously reported that acetyl-β-aldoximes were decomposed by ammonium hydroxide to form β-aldoximes. We have found that with aqueous or alcoholic ammonia both nitrile and oxime are obtained except when the reaction is carried out at 0°; at this temperature with concentrated ammonia only oxime has been isolated.

(6) It can be seen from Table I that the melting point of the recovered product is somewhat lower than that of the pure acetyl-α-aldoxime.

(7) Hantzsch, *Ber.*, **24**, 20 (1891).

TABLE I

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-α-3,4-METHYLENEDIOXYBENZALDOXIME AND CERTAIN PRIMARY, SECONDARY AND TERTIARY AMINES

Amine	% yield	Oxime M. p., °C.[a]	Recovered acetyl deriv. % yield	M. p., °C.[a]
Primary				
n-Butylamine	91	108–110		
Aniline	98	108–110		
Secondary				
Piperidine	90	110		
Diethylamine	99	110		
Tertiary				
Pyridine At 25°			92	105
At 97–100[ob]			96	104–105
Triethylamine At 25°			96	104–105
At 89[ob]			99	95– 97

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for the α-aldoxime, 110°; for the acetyl-α-aldoxime, 105°. [b] This solution was heated for one hour.

TABLE II

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-3,4-METHYLENEDIOXYBENZALDOXIME WITH n-BUTYLAMINE AND WITH ANILINE AT VARIOUS TEMPERATURES

Amine	Temp., °C.	Nitrile % yield	M. p., °C.[a]	Oxime % yield	M. p., °C.[a]
n-Butylamine	−10– −5	5	92–93	90	144
	20-30	15	92–93	81	140–141
	25–45[b]	29	93–94	59	142–143
	78 (b. p.)	94	93–94		
Aniline	25–30			92	145–146
	97–100	11[c]	93–94	82	109–110[d]

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for nitrile, 94–95°; for β-aldoxime, 146°. [b] In this case 5 cc. of n-butylamine was added all at one time to 1 g. of the acetyl-β-aldoxime; the heat of the reaction caused the temperature of the solution to rise from 25 to 45°. [c] In this case the nitrile might have been produced by a thermal decomposition of the acetyl-β-aldoxime. [d] In this case the β-aldoxime had changed to the α-isomer (m. p. 110°).

Experimental

Acetyl - α - and acetyl - β - 3,4 - methylenedioxybenzaldoximes were prepared according to methods previously described.[2a,b] Samples (1–2 g.) of these compounds were dissolved in 4–6 cc. of amine, the relative yields of oxime and nitrile produced from the β-isomer with certain primary and secondary amines being dependent upon the method of treatment. The solutions of n-butylamine, piperidine, diethylamine, pyridine and triethylamine, after standing at least an hour, were shaken with several volumes of crushed ice, and the mixtures filtered through sintered glass crucibles of the Gooch type.[2b] The precipitates were washed with water until free of amines, and then treated with cold 2 N sodium hydroxide to dissolve out oxime. The solid remaining in the crucible was identi-

TABLE III

PERCENTAGE YIELDS OF PRODUCTS OBTAINED BY ADDING A FEW CUBIC CENTIMETERS OF VARIOUS AMINES IN ONE-CUBIC CENTIMETER PORTIONS TO GRAM SAMPLES OF ACETYL-β-3,4-METHYLENEDIOXYBENZALDOXIME

Amine	Nitrile % yield	M. p., °C.[a]	Oxime % yield	M. p., °C.[a]
Primary				
n-Butylamine[b]	99	91–93		
Aniline			92	145–146
Secondary				
Piperidine[b]	99	92–94		
Diethylamine[b]	92	93–94		
Tertiary				
Pyridine	99	92–94		
Triethylamine	95	94–95		

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for nitrile 94–95°; for β-aldoxime 146°. [b] The reactions with these amines were vigorous, generating considerable heat.

TABLE IV

PERCENTAGE YIELDS OF PRODUCTS FROM ACETYL-β-3,4-METHYLENEDIOXYBENZALDOXIME WITH 1 M SOLUTIONS OF CERTAIN AMINES IN WATER, DIOXANE AND AMMONIA

Amine	Solvent	Temp., °C.	Nitrile % yield	M. p., °C.[a]	Oxime % yield	M. p., °C.[a]
n-Butyl-amine	Water	30	46	90–92	48	105–107[b]
n-Butyl-amine	Dioxane	30	42	93–95	56	143–144
Piperidine	Water	0	32	89–91	65	138–140
Piperidine	Water	30	63	92–94	28	110[b]
Piperidine	Dioxane	30	73	93–95	17	143–144
Pyridine	Water	30	99	94–95		
Triethyl-amine	Water	30	72	92–94	16	120–123
Triethyl-amine	Dioxane	30	97	93–95		
Ammonia	Water	30	36	93–95	55	144–145
Ammonia	Alcohol (95%)	30	39	93–95	60	143–144
Ammonia (14 M)	Water	0			95	146
Ammonia (14 M)	Water	30	28	92–93	65	123–125

[a] The melting points of these products were raised by recrystallization to those reported in the literature: for nitrile, 94–95°; for β-aldoxime, 146°. [b] On standing this oxime had changed to the α-isomer (m. p. 110°).

fied as nitrile or in certain cases as unchanged acetyl-α-aldoxime. The oxime was precipitated from the alkaline solution with carbon dioxide in the usual manner. In certain cases additional oxime was obtained from the amine filtrates by treatment with carbon dioxide.

The reaction solution obtained from aniline was dissolved in ether and extracted several times with small portions of cold 2 N sodium hydroxide. Oxime was precipitated from the alkaline solution by means of carbon diox-

ide. After drying with "Drierite," the ether solution was saturated with dry hydrogen chloride, the aniline salt filtered off, and the ether evaporated. A small amount of nitrile was obtained in this manner when the reaction had been carried out at 97–100°.

Blanks were run with β-3,4-methylenedioxybenzaldoxime in solutions of n-butylamine and pyridine; the oxime was recovered unchanged from these solutions.

The products from the reactions of acetyl-β-aldoxime (1–2 g. samples) with 50 cc. of 1 M solutions of amine in water and in dry dioxane were isolated as follows: after standing several days at 0 or 30°, the solids were filtered off from the aqueous mixtures, and the oxime separated from nitrile by means of alkali; in certain cases additional oxime was obtained from the aqueous amine filtrate. The dioxane solutions were evaporated to dryness in an air-draft, and the residue treated with alkali. In the reactions with aqueous and alcoholic ammonia, oxime and nitrile were isolated in a similar manner.

It has been found also that certain other acetyl-β-aldoximes with aniline give only the corresponding oxime; the yields of this product from acetyl-β-benzaldoxime and acetyl-β-3-nitrobenzaldoxime were 85 and 99%, respectively.

Summary

1. A study has been made of the reactions of acetyl-α- and acetyl-β-3,4-methylenedioxybenzaldoximes with certain primary, secondary and tertiary amines.

2. It has been found that when the acetyl-α-aldoxime is dissolved in the primary or secondary amines it is converted to the corresponding aldoxime; this reaction appears to be quantitative. The acetyl-α-aldoxime, however, is stable in the presence of the tertiary amines under ordinary conditions.

3. The acetyl-β-aldoxime reacts with the tertiary amines to form only nitrile, but, in general, with primary and secondary amines to form both nitrile and β-aldoxime, the yields of these products depending upon the temperature of reaction and apparently upon the basic strength of the amine used.

DURHAM, N. C.   RECEIVED JUNE 10, 1936

The Alkaline Decomposition of Cellulose Nitrate.
I. Quantitative Studies[1]

BY W. O. KENYON AND H. LeB. GRAY

Previous workers have shown that the action of alkalies, especially potassium or sodium hydroxides, on aliphatic nitrates is not one of simple saponification regenerating the alcohol and forming sodium nitrate, but is a profound decomposition yielding also sodium nitrite and oxidation products of the aliphatic group. Thus, alkyl nitrates[2–5] give rise to ethers, alcohols, inorganic nitrates and nitrites, aldehydes and resinous bodies when treated with alkalies. Ethylene dinitrate[3,4,6] is stated to yield carbon dioxide, oxalic acid and glycol. The products of the alkaline decomposition of glycerol trinitrate[3,7–13] are

stated to include: ammonia, carbon dioxide, formic acid, acetic acid, oxalic acid, mesoxalic acid, alkali cyanides, alkali nitrates, alkali nitrites and intermediate peroxides. The presence of glycerol is affirmed[13] and denied.[7] From nitrated mannose,[8] the formation of nitrates, nitrites, oxalic acid and unidentified organic acids is reported. Glucose,[14–16] levulose and starch trinitrates are said to yield products from which the osazones of oxypyruvic acid or its homologs may be isolated. Partially denitrated carbohydrates were also found.

The products reported by various authors as formed by the alkaline decomposition of cellulose nitrate are naturally greater in number and more complex. These include inorganic nitrates and nitrites,[17,18] ammonia,[18] cyanide,[19] carbon dioxide,[20] oxalic,[17,21,3] malic,[21] glycolic,[21] trioxy-

(1) The material contained in this paper comprises a portion of a thesis presented by William O. Kenyon to the University of Rochester in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1935.

(2) Berthelot, *Ann. chim. phys.*, **53**, 447 (1860).

(3) Mixter, *Am. Chem. J.*, **13**, 507 (1891).

(4) Millon, *Ann. chim. phys.*, [3] **8**, 233 (1845).

(5) Nef, *Ann.*, **309**, 126 (1899).

(6) Henry, *Ann. chim. phys.*, [4] **27**, 243 (1872).

(7) Hay, *Moni. Sci.*, [3] **27**, 424 (1885).

(8) Hay, *Trans. Roy. Soc. Edinburgh*, **32**, 67 (1885).

(9) Berthelot, *Compt. rend.*, **131**, 519 (1900).

(10) Berthelot, *Chem. Ind.*, **19**, 1038 (1900).

(11) Klason and Carlson, *Ber.*, **39**, 2752 (1906).

(12) Berl and Delpy, *ibid.*, **43**, 1421 (1910).

(13) Railton, *J. Chem. Soc.*, **7**, 222 (1855).

(14) Berl and Smith, *Ber.*, **41**, 1837 (1908).

(15) Berl and Smith, *J. Soc. Chem. Ind.*, **27**, 534 (1908).

(16) Berl and Smith, *Moni. Sci.*, [4] **23**, 51 (1909).

(17) Hadow, *J. Chem. Soc.*, **7**, 201 (1855).

(18) Béchamp, *Compt. rend.*, **41**, 817 (1855).

(19) Will, *Ber.*, **24**, 400 (1891).

(20) Vohl, *Dinglers polytech. J.*, **112**, 236 (1849).

(21) Berl and Fodor, *Z. ges. Schiess- Sprengstoffw.*, **5**, 296 (1910).