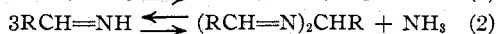
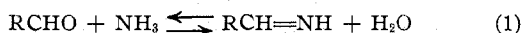


[A CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GOODYEAR TIRE &amp; RUBBER CO.]

## Hydrogenation of Aldehydes in the Presence of Ammonia

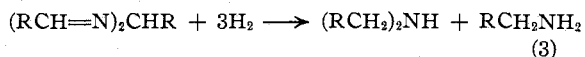
BY CHARLES F. WINANS\*

The catalytic hydrogenation of hydro-amides derived from aldehydes such as benzaldehyde, furfuraldehyde, and trimethylacetaldehyde is known to give rise to equimolecular amounts of the corresponding primary and secondary amines.<sup>1</sup> The chemical reactions in the formation of hydrobenzamide are considered to be

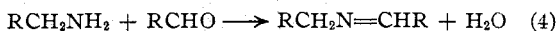


These reactions are reversible as shown by Lach<sup>2</sup> who obtained Schiff bases and ammonia by treating hydrobenzamide with amines. The result of adding excess ammonia to hydrobenzamide should be to displace the equilibrium to the left, giving larger amounts of benzalimine which is readily reducible with nickel catalysts to benzylamine. Such is the case, and at the same time there is always produced a small amount of dibenzylamine which arises from the hydrogenation of that hydrobenzamide which has not been decomposed by ammonia.

The addition of one mole of benzaldehyde to one mole of hydrobenzamide with subsequent hydrogenation gives rise to predominant amounts of dibenzylamine. In this case the mechanism is considered to be different, in that the reaction involves, first, the hydrogenation of hydrobenzamide



second, the reaction of benzaldehyde with benzylamine



and, finally, the hydrogenation of the Schiff base to dibenzylamine



The use of preformed hydrobenzamide is not necessary, since the hydrogenation of mixtures of benzaldehyde and ammonia gives the same results. Thus, a mixture of 2 moles of aldehyde and 1 mole of ammonia produces the secondary amine predominantly on hydrogenation. A ratio of 3 moles of aldehyde to 2 moles of ammonia gives

equimolecular amounts of primary and secondary amines, as if hydrobenzamide itself had been used. Finally, a mixture of one mole of aldehyde and one or more moles of ammonia produces mainly primary amine.

In this way a very effective method for controlling the type of hydrogenation product is made available. It is possible to obtain good yields only with those aldehydes which have no hydrogen on the alpha carbon atom. The use of aliphatic aldehydes should presumably lead to similar results, but the formation of tarry by-products through the aldol reaction or other condensation largely masks the production of amines.

Table I presents the results of several hydrogenations of benzaldehyde, *o*-methylbenzaldehyde, *o*-chlorobenzaldehyde, and furfuraldehyde with varying amounts of ammonia, showing the changes in proportions of products with changes in the aldehyde-ammonia ratio. Where low amounts of ammonia were used, the primary amine fraction contained some of the corresponding alcohol produced by direct hydrogenation of the aldehyde. Titration with standard acid gave the true amine content which is reported. In the other cases the products were substantially pure.

Table II gives summarizing data on the hydrogenation of preformed hydroamides in the presence of aldehydes or of ammonia. These results agree quite well with those of Table I for corresponding ratios of aldehyde and ammonia, and demonstrate that the proportions of products depend on the ratio of reactants and not on the method of addition.

### Experimental

All hydrogenations were carried out in a steel shaking autoclave of the type described by Adkins.<sup>3</sup> Hydrogen pressure as low as 20 atmospheres has been quite satisfactory although higher pressures up to 100 atmospheres generally were used. Raney nickel in the amount of 3% on the aldehyde was very active, and a single portion of catalyst could be used a dozen times or more in successive hydrogenations. Temperatures in the range of 40-75° have been effective in these conversions.

Ammonia was most conveniently added as a standard alcoholic solution in those cases where accurately measured amounts were needed. For additions of ammonia in ex-

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(1) Winans and Adkins, *THIS JOURNAL*, **54**, 306 (1932); **55**, 2054 (1933).

(2) Lach, *Monatsh.*, **9**, 695 (1888).

(3) Adkins, *Ind. Eng. Chem., Anal. Ed.*, **4**, 342 (1932).

TABLE I  
 HYDROGENATION OF ALDEHYDES WITH AMMONIA

Aldehyde	Moles	Yield of amine product, <sup>a</sup> %					
		<sup>1</sup> / <sub>4</sub> Eq. NH <sub>3</sub>		<sup>2</sup> / <sub>3</sub> Eq. NH <sub>3</sub>		1 Eq. NH <sub>3</sub>	
		Primary	Secondary	Primary	Secondary	Primary	Secondary
Benz-	3	11.8	80.8	30.5(91.6)	62.6(94.0)	89.4	7.1
<i>o</i> -Me-benz-	1.67	11.2	81.7	30.8(92.1)	63.1(94.5)	82.6	15.5
<i>o</i> -Chlorobenz-	0.5	3.6	84.6	.. ..	.. ..	87.5	7.6
Furfur-	1.5	12.2	65.5	30.3(91)	66.5(94.1)	79	6.0

<sup>a</sup> The figures in parenthesis are yields computed on the assumption of hydro-amide as starting material. All other figures are based on the aldehyde used.

TABLE II

## HYDROGENATION OF MIXTURES

Mixture	Moles	Product	Yield <sup>a</sup>
Hydrobenzamide	0.33	Benzylamine	30.7 (92.5)
		Dibenzylamine	60.9 (92.4)
Hydrobenzamide	0.33	Benzylamine	81
Ammonia	Excess	Dibenzylamine	8
Hydrobenzamide	0.37	Benzylamine	11.7
Benzaldehyde	0.37	Dibenzylamine	67
Hydrofuramide	0.75	Furfurylamine	29.4 (88.7)
		Difurfurylamine	62.8 (94.0)
Hydrofuramide	0.75	Furfurylamine	62.5
Ammonia	Excess	Difurfurylamine	12.4
Hydrofuramide	0.75	Furfurylamine	16.4
Furfural	0.75	Difurfurylamine	60.5

<sup>a</sup> Yield data are based on the aldehyde equivalent of hydro-amide used. Figures in parentheses are based on hydro-amide directly.

cess, the gas was led from a storage cylinder through high pressure connections directly into the autoclave.

A typical hydrogenation is described in detail. Three gram moles of benzaldehyde was added to a solution of 51 g. (3 moles) of ammonia in 300 ml. of cooled alcohol in the hydrogenation autoclave with 10 g. of Raney catalyst. Under an initial pressure of 90 atmospheres hydrogen

absorption started at 40° and in half an hour was complete at a final temperature of 70°. Distillation of the filtered reaction product gave 287 g. (89.4%) of benzylamine, b. p. 70–80° (8 mm.), and 21.7 g. (7.1%) of dibenzylamine, b. p. 140–150° (7 mm.).

Ethyl alcohol was used as reaction medium throughout because it is miscible with both starting materials and products. A solvent of this type is necessary to maintain homogeneity where water is one of the products.

**Acknowledgment.**—The writer is grateful to Messrs. L. B. Sebrell and R. P. Dinsmore of the Goodyear Tire and Rubber Company for their interest in this work and for permission to publish the results.

## Summary

The hydrogenation of aldehydes, such as benzaldehyde, containing no reactive hydrogen on the alpha carbon atom, in alcoholic ammonia solution may be accomplished at temperatures below 75°. By suitable control of the ratio of aldehyde to ammonia, the product may be predominantly primary amine or secondary amine.

AKRON, OHIO

RECEIVED OCTOBER 30, 1939

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF DUKE UNIVERSITY]

## Condensations Brought about by Bases. VII. The Acylation of Ethyl Isobutyryl-isobutyrate and the Cyclization of a 3,5-Diketo-ester by Means of Sodium Triphenylmethyl<sup>1</sup>

BY BOYD E. HUDSON, JR., AND CHARLES R. HAUSER

Ethyl isobutyryl-isobutyrate is readily synthesized in good yield either from the enolate of ethyl isobutyrate (prepared from the ester and sodium triphenylmethyl) and isobutyryl chloride,<sup>2</sup> or from ethyl  $\alpha$ -bromoisobutyrate and magnesium<sup>3</sup>;

(1) This work was supported in part by a grant from the Duke University Research Council.

(2) (a) See Hauser and Renfrow, *THIS JOURNAL*, **59**, 1826 (1937); (b) See also Hauser and Renfrow, "Organic Syntheses," Vol. XIX, John Wiley and Sons, Inc., New York, N. Y., 1939, p. 44.

(3) Salkind, *Chem. Zentr.*, **77**, II, 315 (1906); Zeltner, *Ber.*, **41**, 592 (1908).

the former method gives a purer product.<sup>4</sup>

Ethyl isobutyryl-isobutyrate (I) on treatment with sodium triphenylmethyl is converted into its sodium enolate, which is readily acylated. The enolate of (I) with acetyl chloride gives presumably compound (II), and with isobutyryl chloride gives compound (III).

In connection with the preparation of com-

(4) Ethyl isobutyryl-isobutyrate also has been prepared by the self-condensation of ethyl isobutyrate in the presence of sodium triphenylmethyl, see Ref. 2a, p. 1823.