

Studies on Catalytic Action, XXI. Catalytic Reduction of the Nitriles.

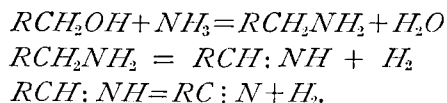
By

Shigeru Komatsu and Shigeo Ishida.

(Received November 10, 1927)

One of the present writers (S. K.) and T. Hara¹ have previously described the formation of the nitriles from primary alcohols and ammonia in the presence of reduced copper, while a mixture of diphenyl carbinol and ammonia, by the catalytic action of reduced copper, yields diphenyl ketimine.

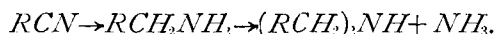
The mechanism for the formation of the nitriles, therefore, was explained with the following interpretation that the primary amines formed by dehydration from a mixture of primary alcohols and ammonia, were transformed into aldimines and then into nitriles by oxidation one after another in succession, shown in the schemes :



The formation of the ketimines from secondary alcohols and ammonia will be shown in a similar manner to that of the aldimines, from an analogy in their chemical structure.

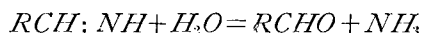
When our assumption of direct nitrile synthesis is admitted to be correct, the synthesis of the aldimines by partial reduction of the nitriles will be possible as suggested by the notion of the reversibility of the

¹ These Memoirs, **8**, 241 (1925).



According to Frebault¹, when benzonitrile and hydrogen were passed on reduced nickel heated to 200°, mono- and di-benzylamines were formed.

The conclusions drawn from the experimental results by many investigators of the catalytic reduction of the nitriles, will be warrant for our view of the formation of the aldimines as an intermediate reaction product, and the fact that the occurrence of aldehyde² in the reduction product of the nitrile is in favor of this view, since according to the investigation by V. Grignard² and his co-workers, the aldimine decomposes easily in contact with water into aldehyde and ammonia.



Such an idea for the formation of aldimines from nitriles was confirmed partially by the experiment by V. Grignard and R. Escourron³ in obtaining aldimines from nitriles by catalytic reduction of reduced nickel under reduced pressure.

An aldimine, therefore, should be prepared by partial reduction of a nitrile in presence of reduced copper prepared from a copper salt in the proper manner, since properly reduced copper, as we have frequently announced in this series of researches, carries out its catalytic functions similarly to reduced nickel.⁴

The catalyst which was used in the experiment was: Cu II, prepared from crystalline copper hydroxide obtained from basic copper nitrate; Cu III, from amorphous copper hydroxide; Cu V from black copper oxide formed from copper nitrate and 20% ammonia water.

In the reaction, 10 gram. of copper oxide were placed in a glass reaction tube and reduced with hydrogen at 180° as usual, and benzonitrile from Kahlbaum (B. p. 188°-189°) was passed with hydrogen over the catalyst heated at the required temperature. After the reaction was completed the reaction tube was cooled to room temperature and dry hydrogen gas was passed to sweep out completely any ammonia gas and other reaction products which might have remained in it. The liquid reaction product was condensed in the receiver connected with the reaction tube by an adapter, which contained dry ether and carried a spiral condenser cooled with a mixture of ice and the salt to condense any volatile matter. One end of the condenser was immersed into dilute hydrochloric

1 C. R., **140**, 1036 (1905).

2 Brunner & Rapin: Loc. cit.; Paal & Geram: Loc. cit.

3 C. R., **180**, 1885 (1925).

4 Refer: R. N. Pease & R. B. Purdum: J. Am. Chem. Soc., **47**, 1435 (1925).

acid in an absorption vessel to catch any ammonia gas generated by the reaction.

The liquid reaction product which was composed mostly of amines and some hydrocarbons, was dissolved with some ammonia in ether, and the ammonia was expelled from the solution by passing dry hydrogen gas. The ethereal solution after the ammonia gas had been completely removed, was treated with dry hydrochloric acid to precipitate the basic compounds, and the precipitate separated from the solution by filtration was well washed with ether and then dissolved in water. The content of the primary amine and ammonia in the aqueous solution, the latter substance generated from aldimines by the action of water, was estimated by van Slyke's method for the amino group determination, and the secondary amine-content was calculated by the difference of total nitrogen-content estimated by Kjeldahl's method and the content of the primary amine and ammonia. The imine-content in the solution was estimated indirectly from the determination of the aldehyde which formed from the imine, by means of phenylhydrazine and Fehling's solution as usual.¹

The ethereal solution separated from the basic compounds was distilled to get off ether only, and there remained some oily substance which was confirmed to be composed of aldehyde with unchanged nitrile. The results of the experiments are shown in the following table :

Table 1.

No.	Catalyst	Reaction temp.	Nitrile	Rate of passg. per. hr.	Reaction products		
					Amine salts	NH ₃	Toluene
1.	Cu. III	150°	12.6 gr	2.5 gr.	6.6 gr.	?	0
2.		150°	10.6 "	1.3 "	6.3 "	?	0
3.		185°	10.4 "	2.1 "	5.7 "	0.22	0.2
4.		190°—200°	11.2 "	2.3 "	2.3 "	0.53	3.5
5.		200°—210°					
6.	Cu. II	150°	9.7 "	2.0 "	6.2 "	0.37	0
7.		150°	5.8 "	1.9 "	3.8 "	0.24	0
8.		150°	8.6 "	1.2 "	6.9 "	0.50	0
9.	Cu. V	150°	12.9 "	2.0 "	2.4 "	0.14	0

¹ H. A. Spoehr: The carbohydrate economy of cacti, p. 31-38 (1919).

No.	Benzaldehyde	Unchanged nitrile	Nitrile changed
1.	0.2 gr.	5.7 gr.	7 gr.
2.	?	?	—
3.	4.0 "	4.0 "	6.6 "
4.	trace	2.1 "	8.3 "
5.	trace	1.2 "	10.0 "
6.	0.3 "	2.8 "	7 "
7.	trace	0.8 "	5 "
8.	0.1 "	1.2 "	7.4 "
9.	trace	7.0 "	7.0 "

Mol % of Bases.

No.	Catalyst	Temp.	NH ₃	Primary amine	Secondary amine	Aldimine
1.	Cu. III	150°	—	8.3	14	24.3
2.	"	"	"	"	"	"
3.	"	180°	—	2.6	20.5	23.1
4.	"	190°—200°	2	3.9	18.2	22.1
5.	"	200°—210°	3.1	0.5	7.7	8.2
6.	Cu. II	150°	3.1	16.6	15	31.6
7.	"	"	3.0	23.8	15.8	39.6
8.	"	"	4.0	5.6	30.5	36.1
9.	Cu. V	"	1.4	2.2	5.9	8.1

No.	Rate of pas:g. per hour	Nitrile changed	NH ₃	C ₆ H ₅ CHO	C ₇ H ₇ NH ₂	(C ₇ H ₇) ₂ NH	C ₇ H ₈ :NH
6.	2 gr.	7 gr. (72%)	3.1	0.3	16.6	15	6.9
7.	1.9 "	5 " (86%)	3.0	trace	23.8	15.8	8.8
8.	0.2 "	7.4 " (86%)	4.0	0.1	5.6	30.5	0.7

The reduction of benzonitrile, as will be seen in the table, proceeded in the presence of reduced copper to form benzaldimine, benzyl amine

and dibenzyl amine, and the yield of bases is favorable at low temperature, and also in presence of reduced copper Cu. II and Cu. III which are more adapted as oxidizing catalysts than other copper. At high temperatures nitrile was decomposed so as to form toluene and ammonia as noticed by Sabatier and Senderens on the catalytic reduction of the nitrile in presence of reduced nickel. When nitrile passed rapidly on the catalyst the aldimine as formed with a fruitful yield as will be seen in the experimental results, Nos. 1, 3 & 5. The yield of aldimine, not only depends upon the rate of passing of the nitrile on the catalyst, but on the nature of the catalysts as well, and Cu III and Cu II serve as suitable catalysts for this purpose.

The primary and secondary amines which occur with an aldimine in the reaction product, are formed abundantly at low temperatures, the favorable condition for their formation is entirely different from that of the secondary amine; the yield of the primary amine was proportionate to that of the aldimine, but keeps the inverse relation to the yield of the secondary amine. These facts seem to maintain a harmony with the explanation with regard to the formation of the secondary amine from the nitrile by catalytic reduction proposed by Braun and his co-workers.

The hypothesis that the secondary amine was formed by the interaction of the aldimine and the primary amine, is also held for the explanation of the transformation of cyclohexylamine into aniline and dicyclohexylamine in the presence of reduced nickel and copper.¹

Applying the catalytic reduction in the presence of reduced copper on acetonitrile (B. p. 81° - 82° , $n_D^{25}=1.3379$; $d_4^{25}=0.7772$) from Kahlbaum,

Table II

No.	Catalyst	Reaction temp.	Rate of passing per hr.	Nitrile	Reaction products			$C_6H_5NH_2$ HCl	$(C_2H_5)_2$ NHCl
					Nitrile unchanged	NH_3	HCl salts		
1.	Cu V	95° - 100°	1.8 gr.	9.8 gr.	3.0 gr.	?	0.4 gr.	6.5 %	5.3 %
2.		100° - 110°	1.9 "	9.5 "	4.4 "	0.06 gr.	0.5 "	6.4 "	?
3.		100° - 110°	2.3 "	7.0 "	1.1 "	?	0.5 "	14.9 "	65.6 "
4.		150°	2 "	11.0 "	1.4 "	0.23 "	0.8 "	9.1 "	75.5 "
5.		150°	2.6 "	8.8 "	2.3 "	0.17 "	0.8 "	16.1 "	59.2 "
6.		180°	2.5 "	13.8 "	2.4 "	0.58 "	4.1 "	16.6 "	45.6 "

¹ These Memoir, A. 8, 135 (1925)

and isovaleronitrile (B. p. 127°-128°, $n_D^{25}=1.3795$; $d_4^{25}=0.7924$) prepared by the writers from isoamyl alcohol and ammonia according to the method communicated by S. Komatsu and T. Hara¹, the following results, shown in Tables II and III, were obtained.

As will be seen in the experimental results shown in Tables II and III, any aldimine could be isolated in either case, while the primary and

Table III
Isovaleronitrile.

Catalyst	Reaction temp.	Rate of passing per. hr.	Nitrile		NH ₂	Aldehyde	HCl salts	RNH ₂	R ₂ NH
			passed	unchanged					
Cu IV	150°	3.2 gr.	8 gr.	4.3 gr.	0.2 gr.	0	1.4 gr.	13.9 %	65.5 %
Cu IV	"	3.6 "	9 "	4.4 "	0.33 "	0	1.2 "	12.9 "	60.3 "
Cu II	"	2 "	10 "	5.0 "	0.05 "	0	0.2 "	16.4 "	81.0 "
Cu II	"	2.4 "	8.5 "	?	0.06 "	trace	0.2 "	33.6 "	56.4 "

secondary amines were proved to occur in the reaction product, and the latter of the two substances predominated in it. The aliphatic nitriles by catalytic reduction in presence of reduced copper, as already noticed by P. Sabatier and Senderens,² were converted to primary and secondary amines, the reaction of the formation of these compounds being explained by assuming a momentary existence of an aldimine which being situated in a reactive state, in turn reacts with the primary amine which occurs side by side with the imine, to form a complex compound which will ultimately be decomposed into a secondary amine and ammonia.

April, 1927. Laboratory of Organic- & Bio-Chemistry.

¹ *Ibid.*, **8**, 241 (1925).

² *C. R.*, **140**, 482 (1905).