

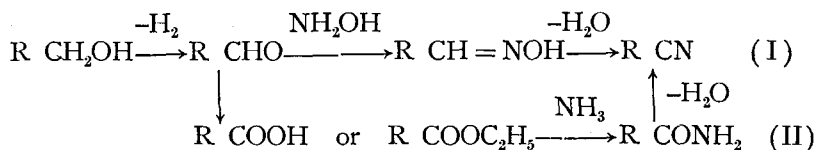
Studies on Catalytic Action, XVI. A New Synthesis of Nitriles.

By

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In synthetic chemistry, nitriles especially merit consideration as being an intermediate step in the synthesis of acids from alcohols. With the exception of the well-known methods of nitrile synthesis, by heating the alkyl halogen or a potassium alkyl sulphate with potassium cyanide¹, these compounds, however, were usually obtained from aldehydes and acids as will be seen in the following schemes (I) and (II).



Recently A. Mailhe² has contributed new devices to the last two processes for the preparation of nitriles, applying the catalytic action of thorium and aluminium oxides.

One of the authors (S. K.) and M. Kurata³ and also S. Yamaguchi⁴ have reported that aldoximes and acid amides yield, by the contact action of reduced copper, nitriles with acids accompanied as one of the reaction

¹ V. Meyer & P. Jacobson: *Lehrbuch Org. Chem.*, I, 474 (1907).

² *Bull. soc. chim.* (4), **23**, 18 (1918); **27**, 226 (1920); *C. R.*, **166**, 36 (1918); **170**, 813 (1920).

³ *These Memoirs*: **7**, 157 (1924).

⁴ *These Memoirs*.

products. Thus, in all of the methods of nitrile synthesis, aldehydes or acids, the oxidation products of alcohols, were used as a starting material; as to the direct synthesis from alcohols, however, we have not yet met with any information.

The present research, passing the vapour of primary alcohols, along with dry ammonia gas, over reduced copper at 300°, was, therefore, carried out by the authors, with the expectation of getting nitriles with fruitful results, since the catalyst, as we have discussed frequently in this series of research, acts on alcohols or nitrogenous compounds to oxidize into aldehydes or other compounds on the one hand, and on the other to dehydrate them.

30 gm. isoamylalcohol were passed in an interval of 5½ hours, at 300—350°, along with dry ammonia gas, over reduced copper (denoted by Cu I), obtained from 10 gm. of copper oxide by reduction at 200—220°, which was prepared from copper sulphate and equivalent quantity of caustic soda solution. The evolution of hydrogen gas was noticed during the reaction, and 34 gm. of the colourless reaction product were obtained which consisted of two layers; 27 gm. in the upper oily layer, and 7 gm. in the lower water one, the formation of the latter indicating that dehydration of alcohol took place during the reaction.

The aqueous layer was treated with ether to extract the basic and neutral substances dissolved in it, and the extract combined together with the oily reaction product and then treated with ether to extract the neutral substances after treating the mixture with acid sodium sulphite solution to remove the aldehyde formed by the contact oxidation of the alcohol. The ether was evaporated off from the ethereal solution and 24.5 gm. of the oily residue were obtained which was fractionated by distillation into following 4 portions:

	Fraction	Yield	Remark
1.	80—120°	0.3 gm	Mostly aldehyde
2.	120—126°	0.1 gm	
3.	126—131°	23 gm	Mostly nitrile
4.	residue & treatment loss 1.1 gm.		

The third fraction, B. p. 126—131°, (distils out mostly at 129—130°) was confirmed to consist of isovaleronitrile by converting into isovaleric acid by hydrolysis, and by analysis after it was purified by further fractional distillation (B. p. 127—128°). N = 16.7 (by Kjeldahl's method); the theory requires 16.9 for C₅H₉N: $d_4^{25} = 0.7861$; $n_D^{25} = 1.3850$.

Thus isoamylalcohol when passed, along with dry ammonia, over heated reduced copper, as the authors had expected, was transformed into isovaleronitrile with 83% of yield, and some quantity of hydrocarbons, iso-valeroaldehyde and basic compounds were obtained simultaneously as by-products.

Repeating the same experiment under similar conditions as above mentioned with other reduced coppers, prepared from (I) copper oxide obtained from copper sulphate and an excess of caustic soda solution (denoted by Cu II) (2) copper oxide resulting by ignition of copper nitrate (denoted by Cu III), both of which behave quite differently from the first catalyst and also from each other toward menthol¹, there resulted, contrary to our expectation, reaction products which do not manifest so markedly the difference in the activity of the catalysts as was indicated in the behaviour toward menthol, as shown in the following table.

	Reaction temperature	Substance (gram.) pass. per hour	Yield (%)		
			aldehyde	nitrile	base
Cu I.	300°	7	7	80	trace
Cu II.	300°	—	11	58	4.2
Cu III.	300°	6	18	38	1

Such a difference between the catalytic activities of the catalysts toward menthol and a mixture of alcohol and ammonia, would be ascribed to that caused on the structure of alcohols or to some other reason. The question which it is full of interest to discuss in detail, will be explained experimentally in another article.

For obtaining benzonitrile, by an analogous method, 50 gram. benzylalcohol were passed, along with dry ammonia gas, in an interval of 4.5 hours (11.5 gram. per hour) on reduced copper II, at 330°, and 57 gram. of the reaction product were obtained which consisted of two layers; 9 gram. of the upper layer and 48 gram. of the yellow lower one. The latter layer was treated with dilute hydrochloric acid to remove basic substances formed by the reaction, and then dried with anhydrous sodium sulphate, and then subjected to fractional distillation:

¹ These Memoirs:

	Fraction	Yield		Remark
		gram.	%	
1.	80—186°	2	5	Mainly toluene
2.	186—192°	33	82	Mainly nitrile
3.	residue	3	7.5	

The second fraction which consisted mostly of nitrile, was purified by fractional distillation and the analysis and the determination of the physical constants of the liquid boiling at 190—191° were made for the confirmation of its purity:

$N = 13.6$ and the theory requires $N = 13.6$ for C_7H_5N ; $d_4^{25} = 1.0009$; $n_D^{25} = 1.5218$.

The same experiment was repeated with reduced copper I and the results are shown in the following table.

	Benzylalcohol pass. per hour	toluene	benz- aldehyde	Yield (%)		
				benzoic acid	benzo- nitrile	residue
Cu I.	7.5 gram.	4	0	trace	84	5
Cu II.	11.5 gram.	5	0	trace	82	7.5

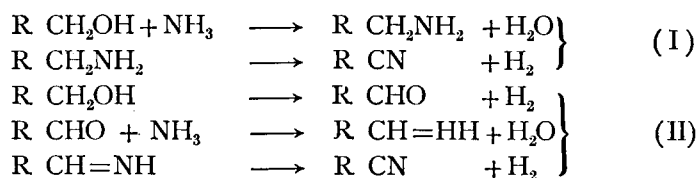
The reduced copper I, as indicated in the foregoing tables, was thus regarded by the authors as a convenient catalyst in preparation of nitrile from alcohol and ammonia, and accordingly acetonitrile, propionitrile and isobutyronitrile were prepared from the corresponding alcohols and ammonia with the aid of the same catalyst heated at 330°, and the experimental results are shown in the following table, with some physical constants of the reaction products after being purified by fractional distillation.

		Ethyl- alcohol	n-Propyl- alcohol	Isobutyl- alcohol
Total alcohol (gram.) passed		35	39	23
Alcohol (gram.) pass. per hour		10	6	5.7
Reaction product (gram.) total		38	46	25
nitrile layer		24	33	18
water layer		14	13	7
Yield %	{ nitrile	39	86	81
	{ aldehyde	trace	3	trace
	{ basic compounds	trace	trace	trace

	acetonitrile	propionitrile	isobutyronitrile
B. p.	81—83°	97—99°	103—105°
Nitrogen	Calc.	34.1	25.5
	Found (Kjeldahl)	32.5	24.1
d_4^{25}	0.7787	0.7771	0.7657
n_D^{25}	1.3358	1.3568	1.3660

It was suggested, from our experimental results, that the yield of nitrile would be greatly increased by passing the small quantity of alcohol, along with a brisk current of dry ammonia gas, on the heated catalyst, and also that pure nitrile free from alcohols remaining unchanged and associated with it, could be obtained by rectifying nitrile after treating the product with calcium chloride to fix the alcohol.

The mechanism of the direct synthesis of nitrile from alcohol and ammonia, in presence of the catalyst, may be explained by assuming an intermediate formation of amine or imine; in the former view, primary amine was regarded as being formed by the condensation of alcohol and ammonia (dehydration) as when thorium oxide was used as a catalyst, which then was oxidized by the catalytic action of reduced copper to nitrile, as was observed by P. Sabatier and Gaudion¹ in the catalytic oxidation with reduced nickel. According to the latter view, an aldehyde resulted from the alcohol by the contact action of the catalyst, which subsequently was transformed into imine and nitrile by the condensation and the oxidation which took place in turn, as will be seen in the following schemes:



The first view, however, was incompatible with the experimental results on the catalytic action of reduced copper on the amine observed by one of us (S. K.) and Ch. Tanaka², and consequently the second hypothesis becomes highly probable. For the confirmation of the idea, isovaleraldehyde was passed, along with dry ammonia gas, on reduced copper II, heated at 300°, and 5 grm. of pure isovaleronitrile were actually isolated from 18 grm. of the aldehyde and ammonia gas, with 2.5 grm.

¹ C. R., **165**, 224, (1917).

² These Memoirs,

of the unchanged aldehyde and 2.5 gm. of the fraction which boils above 130°.

In the same manner (1) 1.5 gm. of the aldehyde, 2.2 gm. of the nitrile and 1.3 gm. of the fraction boiling above 130°, were obtained from 18 gm. of the aldehyde and dry ammonia gas by passing the mixture on the reduced copper I, at 300°, and (2) 0.8 gm. of the aldehyde, 1.2 gm. of the nitrile from 10 gm. of the aldehyde and ammonia, using reduced copper III, as a catalyst at the same temperature.

Thus, the experimental results are in favor of the second hypothesis, in obtaining it the correct idea for the mechanism of the new nitrile synthesis. Moreover, our hypothesis will be confirmed to be correct in the new synthesis of ketimines from secondary alcohols and ammonia in presence of reduced copper, which will be discussed in detail in another article.

So far as we have experienced, reduced copper, when the mixture of alcohol or aldehyde and ammonia is brought into contact with the catalyst under the conditions described above, acts to promote simultaneously both reactions, dehydration and oxidation, and accordingly the reaction products in our cases are essentially different from both of those obtained from the mixture of alcohol and ammonia by the aid of thoria, and those which resulted by the catalytic action of alumina on the mixture of aldehyde and ammonia¹, though the catalytic action of reduced copper is partly alike to that of thoria and alumina.

The reaction between aldehydes and ammonia in presence of reduced copper will be studied further in our laboratory.

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¹ P. Sabatier: La Catalyse en Chimie Organique, 1920, 319.