

Catalytic Action of Reduced Copper on Benzaldoximes.

(On Beckmann's Rearrangement, XIII.)

By

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Chemists have mistakenly considered that ketoximes only, by treating with the so-called dehydrating agents undergo a rearrangement into acid amides, while aldoximes decompose into nitriles and water, despite the fact that there were important reports, but few, of the molecular conversion of benzaldoxime¹ into benzamide by the action of heat or concentrated sulphuric acid, and of cinnamyl aldoxime into isoquinoline².

The latter facts which were neglected by chemists, and the similarity in chemical character between aldoximes and ketoximes which might be anticipated from their chemical structures, have led the author to the endeavor of finding a suitable reagent which should bring about the Beckmann rearrangement on aldoximes with the consequent experimentation of the contact action of reduced copper on benzaldoximes, following the success with the ketoximes³, in the expectation of getting an analogous result.

18 gm. of α -benzaldoxime prepared according to the statement of E. Beckmann⁴, were passed with pure hydrogen on reduced copper

¹ J. Petraczek : Ber. D. Chem. Ges., **16**, 823 (1883) ; E. Beckmann : Ibid., **20**, 1507 (1887).

² E. Bamberger and C. Goldschmidt : Ibid., **27**, 1954 (1897).

³ These Memoirs, **6**, 245 (1923) ; **7**, 151 (1924).

⁴ E. Beckmann. Ber. D. Chem. Ges., **20**, 2766 (1887) ; **23**, 1684 (1890).

heated at 200°, and 13 gm. of reaction product were obtained with some ammonia. The reaction product (A) was treated with a sufficient quantity of absolute ether, the insoluble substance (B) filtered off, and then passed in dry ammonia gas to precipitate benzoic acid and again filtered. The filtrate (C) separated from the precipitate (D) was combined together with the product (B), and treated with dilute hydrochloric acid to get off completely some basic substances formed simultaneously with benzamide and other neutral substances, and the ethereal solution was evaporated to dryness, there remained an oily residue which was subjected to fractional distillation under 756 m.m.

The first fraction, B. p. 175–187° was confirmed in the usual way to consist chiefly of benzaldehyde with some benzonitrile. The second one, B. p. 187–191°, mainly composed of benzonitrile, gave on analysis the following result :

0.1204 gm. substance gave 0.0560 gm. H₂O and 0.3603 gm. CO₂.
0.1389 gm. substance gave 16.4 c.c. N₂ at 18°, 765 m.m.

	C	H	N
Calc. for C ₆ H ₅ CN	81.52	4.89	13.59
Found	81.61	5.20	13.80

The basic substance extracted from (B) and (D) with dilute hydrochloric acid, was identified to be benzylamine by transforming it into its hydrochloride, M. p. 215–228°. The yield was very small.

The solid substance (B) was recrystallised from a hot aqueous solution and confirmed to be benzamide from its melting point 129° and also from the analytical results :

0.1021 gm. substance gave 10.4. c.c. N₂ at 20°, 763.1 m.m.
0.1299 gm. substance gave 0.0659 gm. H₂O and 0.3298 gm. CO₂.

	C	H	N
Calc. for C ₆ H ₅ CONH ₂	69.39	5.83	11.57
Found	69.26	5.68	11.78

The ammonium salt (D) was transformed with hydrochloric acid into free acid, recrystallised in white crystals from the aqueous solution, melted at 121° and identified as benzoic acid.

Thus, α -benzaloxime, when passed with hydrogen on reduced copper heated at 200°, was transformed into benzamide, benzoic acid, benzonitrile, ammonia, benzaldehyde and benzylamine. β -Isomer

prepared by the following method was found to behave analogously with α -isomer, yielding the same reaction products.

β -benzaldoxime was prepared from α -isomer; the hydrochloride obtained at 19° from α -compound, melting at 51.5–57° by slow heating, and 52–94° by rapid heating, which was then decomposed with saturated sodium carbonate solution into free oxime, extracted with ether. It melts at 62–80° by slow heating and 110–114° by rapid.

The reaction products above mentioned, except aldehyde and the amine were regarded as formed from oximes by the Beckmann rearrangement. It was, therefore, tried to determine quantitatively the amount of the reaction products of both isomers in hopes of deducing some important conclusion thereby and the following results were actually obtained :

Sample used.	Total yield.	Yield of the reaction product.							
		Benzamide.		Benzoic acid.		Benzonitrile		Ammonia.	
α 15 grm.	13 grm.	2.0 grm.		0.8 grm.		0.9 grm.		0.35 grm.	
		wt. %	mol %	wt. %	mol %	wt. %	mol %		
		54	52	22	21	24	27		
β 10.5 grm.		1.0 grm.		0.75 grm.		0.62 grm.			
		wt. %	mol %	wt. %	mol %	wt. %	mol %		
		42	40	32	30	26	30		

It seems difficult to explain the chemical reaction for the formation of these compounds from benzaldoximes. If the explanation of the relation among benzamide, benzoic acid and benzonitrile proposed by S. Komatsu and M. Kurata¹ be accepted, it becomes easier to understand that benzaldoxime suffers an intermolecular transformation and converted into benzamide. Moreover, the fact noticed by Brady² that *m*-methoxy benzaldoxime on standing at ordinary temperature for a long time was transformed spontaneously into *m*-methoxy benzamide, supports the author's explanation for the behaviour of aldoximes toward the reagent above mentioned.

¹ These Memoirs. 7, 157 (1924).

² J. Chem. Soc. 123, 1791 (1923).

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The yield of benzoic and benzonitrile being in equal molecular relation in both α and β isomers, confirms not only Komatsu and Kurata's interpretation of the origin of these compounds, but suggests that a large part of β -benzaldoxime was first transformed into α -isomer and is suffered an isomeric change to benzamide by the catalytic action of reduced copper, which is then decomposed to benzonitrile and benzoic acid.

In other words, the formation of benzamide should be attributed to the Beckmann rearrangement of the oximes, and thus the before mentioned mistaken notion will be rectified.

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