

The Clemmensen Reduction of β -Diketones

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THE Clemmensen reduction of β -diketones has been under investigation as part of our study of carbon-carbon bond-forming reactions of the type

$$A^+ + B^+ \xrightarrow{2e} A-B.$$

Recent renewed interest in such reductions^{1,2} and the bearing of our early research results on the mechanism of the reduction process³ prompt the present communication.

Exposure of a refluxing aqueous, methanolic solution of hydrochloric acid and diketone (I)⁴ to zinc amalgam for fifteen minutes has led to the ketones (IIa⁵ and b⁶) in 43% and 18% yields, respectively. Longer reaction time increased the yield of (IIb) at the expense of (IIa), an observation in consonance with the known tendency of

α -hydroxy-ketones to be reduced by zinc and acid.⁷ The severe structural change involved in the conversion of (I) into (IIa) can be rationalized most readily by assuming the intermediacy of cyclopropanediol (III) and its subsequent acid-induced ring rupture. Since cyclopropanols have been shown to undergo cleavage in acid media with retention of configuration,^{8,9} the formation of only one diastereomeric hydroxy-ketone and, further, of the configuration depicted in (IIa) is not surprising.

The latest general review of the mechanism of the Clemmensen reduction³ offered an analysis of the reaction path of the reduction of dimedone (IVa),¹⁰ a well-documented example of the limited

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² M. Quadrat-I-Khuda, M. Manzoor-I-Khuda, and N. A. Jeelani, *Pakistan J. Sci. Res.*, 1964, **7**, 81

³ D. Staschewski, *Angew. Chem.*, 1959, **71**, 726.

⁴ G. B. Payne, *J. Org. Chem.*, 1961, **26**, 4793.

⁵ Y. N. Nazarov and A. A. Akhrem, *Zhur. obshchei Khim.*, 1958, **28**, 1791.

⁶ R. B. Turner, *J. Amer. Chem. Soc.*, 1950, **72**, 878.

⁷ *Inter alia*, W. T. Smith, Jr., *J. Org. Chem.*, 1951, **73**, 1883.

⁸ C. H. DePuy and F. W. Breitbeil, *J. Amer. Chem. Soc.*, 1963, **85**, 2176.

⁹ A. Nickon, J. H. Hammons, J. L. Lambert, S. J. and R. O. Williams, *J. Amer. Chem. Soc.*, 1963, **85**, 3713.

¹⁰ M. Quadrat-I-Khuda, *Nature*, 1933, **132**, 210; A. N. Day and R. P. Linstead, *J. Chem. Soc.*, 1935, 1063; M. Quadrat-I-Khuda and A. Mukherji, *J. Indian Chem. Soc.*, 1946, **23**, 435.

