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RING CONTRACTION IN 2,2,6,6-TETRAMETHYLPIPERIDIN-4-ONE WITH DICHLOROCARBENE UNDER PHASE TRANSFER CONDITIONS

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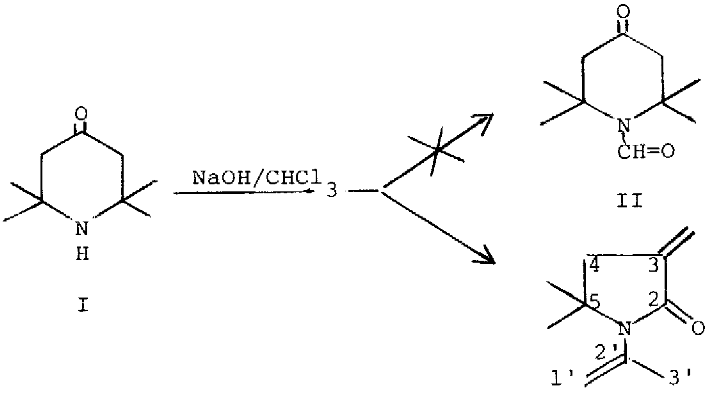
Summary: The preparation of a 5-membered lactam via a postulated dichloro-oxirane intermediate is described.

We have recently investigated the preparation of the substituted formamide II. It appeared that a convenient route to this material would involve the reaction of 2,2,6,6-tetramethylpiperidin-4-one (I) with dichlorocarbene generated under "Makosza-conditions" 1). Unexpectedly, however, the reaction took an entirely different course leading to N(2'-propenyl)5,5-dimethyl-3-methylene-pyrrolidin-2-one (III).



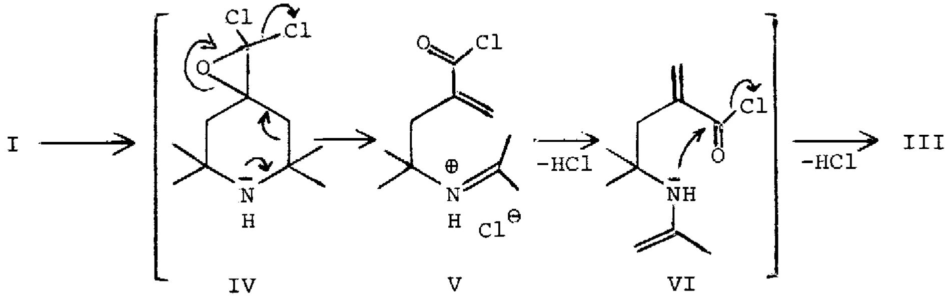
I

II

III

Thus, continued (overnight) stirring of a mixture of the amine I (0.1 mole), benzyl-trimethylammonium chloride (0.004 mole), 50% aqueous sodium hydroxide solution (25 ml) and chloroform (50 ml) gave III in 65% yield (b.p.: 115 - 117°C/ 12 torr. ^{1}H-nmr($CDCl_3$): 5.98 & 5.28 (m, vinyl-H cis and trans to C=O), 5.17 & 4.86 (m, H-C(1')), 2.67 (t, J = 2, H-C(4)), 2.00 (m, H-C(3')), 1.35 (s, CH_3-C(5)). ^{13}C-nmr($CDCl_3$): 166.6 (s, C(2)), 140.2 & 139.4 (s, C(3) and C(2')), 115.7 & 114.8 (t, CH_2=), 59.7 (s, C(5)), 42.2 (t, C(4)), 28.2 (q, CH_3-C (5)), 22.1 (q, C(3')). ms: m/e 165 (M^+). When the crude product was not distilled but purified by chromatography over a silica gel column the yield was nearly quantitative.

While further study of the reaction would be desirable it is not unreasonable to postulate[2)] initial addition of dichlorocarbene to the carbonyl group of I and an essentially irreversible Grob-type fragmentation[3)] of IV to V. Ring closure of the acid chloride VI to yield III seems a reasonable pathway.



References and Notes

1) J. Graefe, I. Fröhlich und M. Mühlstädt, Z. Chem. 14, 434 (1974).

2) H. Greuter, T. Winkler and D. Bellus, Helv. Chim. Acta 62, 1275 (1979). We are indebted to Dr. W. Breitenstein of CIBA-GEIGY Limited for valuable discussions on the reaction mechanism.

3) K. B. Becker und C. A. Grob, in The Chemistry of Double-Bonded Functional Groups, part II, Ed. S. Patai, Wiley Intersc., London 1977, p. 653.

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