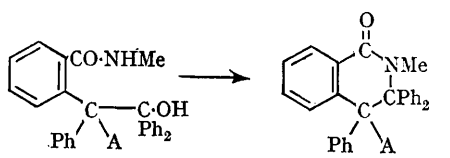
Concerted Mechanism in Acid-catalyzed Cyclodehydration of Certain Carbinol Amides and Phenylhydrazone to form Six- and Five-membered Rings

By CHUNG-LING MAO, FRED E. HENOCH, and CHARLES R. HAUSER*
(*Department of Chemistry, Duke University, Durham, N.C.* 27706)

WE report that the recently observed[1] cyclodehydration of the hydroxy-amide (Ia) with cold sulphuric acid to form the lactam (IIa) evidently involves participation of the amino-nitrogen, not linear dehydration followed by cyclization, since the deuterio-hydroxy-amide (Ib) has now been found to undergo this reaction without loss of deuterium to give (IIb).

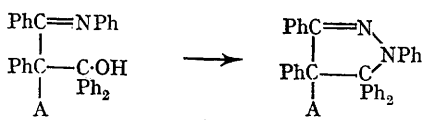
Similarly, the hydroxy-phenylhydrazone (IIIa) was found to undergo cyclodehydration with this acid to afford the pyrazoline (IVa), m.p. 193—195°. (correct analysis for $C_{33}H_{26}N_2$) and the deuterio-hydroxy-phenylhydrazone (IIIb) underwent this reaction without appreciable loss of deuterium to give (IVb).

The starting deuterio-hydroxy-amide (Ib) and the product (IIb) were each indicated by n.m.r. to contain 99% deuterium atoms per molecule. The starting deuterio-hydroxy-hydrazone (IIIb) and the product (IVb) were indicated by n.m.r. to contain 92 and 90% deuterium atoms per molecule, respectively. In the acidic medium at 0°, (IVb) lost 40% of its deuterium within 1 hour. The hydroxy-phenylhydrazone (IIIa) was prepared by *C*-condensation of dipotassiodeoxybenzoin phenylhydrazone with benzophenone, and (IIIb) was synthesized similarly.[2]



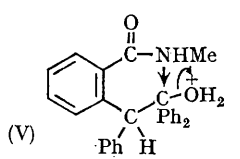
(Ia) A=H
(Ib) A=D

(IIa) A=H
(IIb) A=D

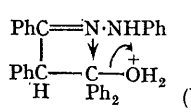


(IIIa) A=H
(IIIb) A=D

(IVa) A=H
(IVb) A=D



(V)



(VI)

These concerted cyclodehydrations, which may be indicated by (V) and (VI), seem remarkable since corresponding carbinols are known to

undergo very rapid acid-catalyzed dehydrations to form olefins. For example, 1,1,2,2-tetraphenylethanol, which would be (Ia) without the *ortho*-substituent, affords tetraphenylethylene.[3]

Work is in progress on other such concerted cyclodehydrations to form five- and six-membered rings; these reactions are not only of theoretical interest but also of synthetic value.

This work was supported by the National Science Foundation of the United States of America.

(*Received, October 3rd,* 1968; *Com.* 1354.)

[1] I. T. Barnish, C. L. Mao, R. L. Gay, and C. R. Hauser, *Chem. Comm.*, 1968, **10**, 564.
[2] See F. E. Henoch, K. G. Hampton, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1967, **89**, 463.
[3] See A. Gandini and P. H. Plesch, *J. Chem. Soc.*, 1965, 6019.