CHEMISTRY LETTERS, pp. 653-656, 1979. Published by the Chemical Society of Japan

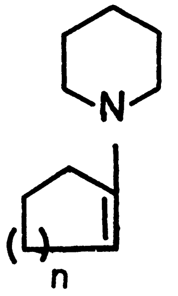
REACTION OF ENAMINE WITH CYCLOHEXENONE IN POLAR SOLVENT

Yash Karan SINGH and R. Balaji RAO
Department of Chemistry, Faculty of Science,
Banaras Hindu University, Varanasi - 221005, India

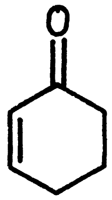
When 1-piperidino-1-cyclopentene was condensed with cyclohex-2-en-1-one in DMSO, 6-piperidinotricyclo $[5.2.2.0^{2,6}]$-undecan-8-one was obtained. However, with 1-piperidino-1-cyclohexene only Michael product was obtained. A tentative mechanism is proposed.

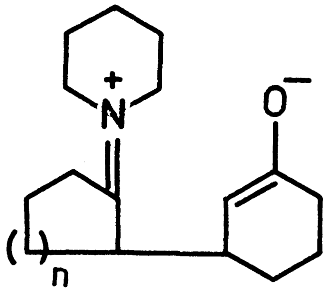
The reaction of enamines with α,β-unsaturated carbonyl compounds are well known1). We wish to report an unusual cyclisation of cyclohexenone with the piperidine enamine of cyclopentanone.

Equimolar amounts of piperidine enamine of cyclopentanone (1a, n=1) and cyclohex-2-en-1-one were dissolved in dry DMSO. The flask was flushed with nitrogen and heated in nitrogen atmosphere at 70°C for 8 days. The mixture was then poured into water and left overnight. Usual work up of the residue followed by extensive chromatography yielded a new compound A (m.p. 82.5°C) in 33% yield. *Anal*. Calcd. for $C_{16}H_{25}NO$, % : C, 77.73; H, 10.12; N, 5.66. Found : C, 77.77; H, 10.21; N, 5.96. The *I.R.* (Nujol) showed a peak at 1720 cm^{-1} indicating a carbonyl on 6-membered ring. The *N.M.R.* ($CDCl_3$) showed no vinylic protons. *Mass spectrum* : M/e : 248 (25%); 213 (13%); 150 (100%); 84 (14%). The analysis and mass spectrum suggest that the new compound is an addition product of (1a, n=1) and cyclohexenone. The structure of this new compound was finally solved as 5 by X-ray crystallography technique2). This compound could arise by the cyclisation of the intermediate 43). When the above reaction was carried out with the piperidine enamine of cyclohexanone (1b, n=2), no product corresponding to 5 could be obtained. The only identifiable product, after extensive chromatography, was the known diketone 64) (24%).

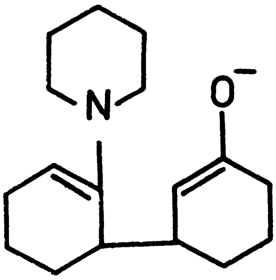


1 a: n=1
b: n=2

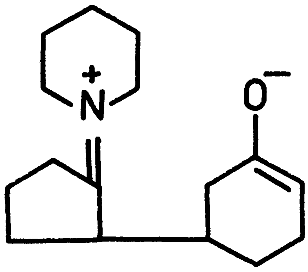




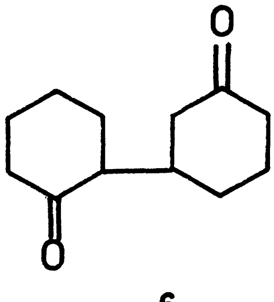
2 a: n=1
b: n=2



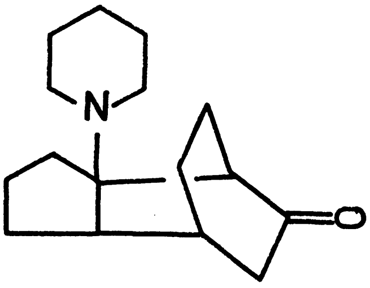
3



4

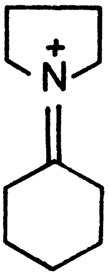


6

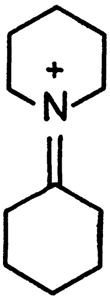


5

The above results could be rationalized on the basis of the stabilities of the intermediates 2a and 2b. To explain the faster rate of formation of the pyrrolidine enamine of cyclohexanone than the corresponding piperidine enamine, Stork et al. had suggested that the immonium ion 7 is more stable than 8[5]:



7



8

When n=1, the intermediate 2a has an immonium ion moiety analogous to 7. This, therefore would be more stable, permitting the enolate moiety to isomerise to 4 and finally cyclize. On the other hand, when n=2 the immonium ion intermediate 2b, which is analogous to 8, would be less stable. This would lead to deprotonation readily to give 3 and finally 6. It is of interest to note that no diketone was obtained when n=1 and no product corresponding to 5 was obtained when n=2.

This reaction was, however, found to be of very limited scope. Several other enamines failed to give compounds corresponding to 5.

Acknowledgement:

One of us (Y.K.S.) would like to thank C.S.I.R. (New Delhi) for S.R.F.

References

1) (a) J. Szmuszkovicz, Advan. Org. Chem., 4, 1 (1963).

   (b) G.H. Alt, Enamines : Synthesis, Structure and Reactions, 115 (1969).

   (c) Joseph V. Paukstelis, Enamines : Synthesis, Structure and Reactions, 169 (1969).

2) We thank Prof. K. Venkatesan, I.I.Sc., Bangalore, India for the X-ray analysis. Details of X-ray data would be published elsewhere.

3) An analogous mechanism has been proposed by N.L. Leonard and W.J. Musliner, J. Org. Chem., 31, 639 (1966) to explain the dimeric product obtained from cyclohexenone in presence of pyrrolidinium perchlorate.

4) M. Yasuda, Chem. Lett., 89 (1975).

5) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, J. Am. Chem. Soc., 85, 207 (1963).

(Received February 27, 1979)