

CYCLOPROPANONES. IV.¹

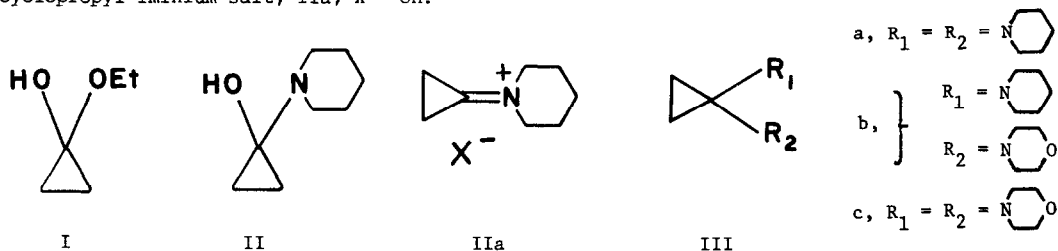
1-PIPERIDINOCYCLOPROPANOL AND RELATED SYSTEMS

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(Received in UK 23 November 1969; accepted for publication 31 March 1970)

We recently reported^{1c} that the ethyl hemiketal of cyclopropanone (I) provides a source of the parent ketone for reactions with nucleophilic reagents. We have now found that 1-piperidinocyclopropanol (II) may be readily prepared by a slight variation in the method employed for the synthesis of I. Compound II, a crystalline product easily purified, may have considerable potential in synthesis since it appears to undergo reactions expected of the cyclopropyl iminium salt, IIa, X = OH.



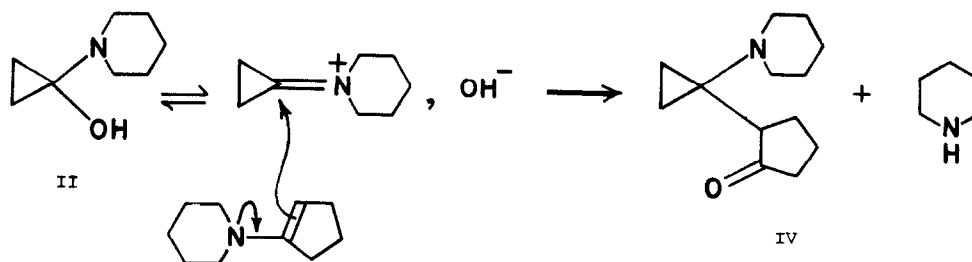
A solution of cyclopropanone was prepared by distilling ethereal diazomethane into a saturated solution of ketene in ether at -78° .^{2,3} After removal of the cooling bath, piperidine was added over a period of five minutes. Rapid extraction with saturated aqueous NaHCO_3 followed by removal of solvent gave II⁴ (50%) m.p. $81-82^\circ$. $\nu_{\text{max}}^{\text{KBr}}$ 3420, 3175, 2950, 2860, 2840 cm^{-1} ; τ_{CDCl_3} 6.80 (s, 1H), 7.24 (m, 4H), 8.50 (m, 6H), 9.21 (m, 4H).

Treatment of II at 25° with piperidine (one equiv.) for 2 1/2 hr yielded (95%) 1,1-bis-piperidinocyclopropanol, (IIIa)⁴, m.p. $32-34^\circ$; $\nu_{\text{max}}^{\text{KBr}}$ 3100, 3025, 2950, 2870, 2810 cm^{-1} ; τ_{CDCl_3} 7.43 (m, 8H), 8.56 (broad s, 12H), 9.31 (s, 4H); mol. wt. (mass spectrum) 208. With morpholine, two products were obtained. The first substance is 1-morpholino-1-piperidinocyclopropane (IIIb)⁴ (55%), a colorless oil; $\nu_{\text{max}}^{\text{film}}$ 3100, 3020, 2950, 2860, 2830, 2810 cm^{-1} ; τ_{CDCl_3} 6.33 (t, $J=6\text{Hz}$, 4H), 7.31 (m, 8H), 8.54 (m, 6H), 9.30 (s, 4H); mol. wt. (mass spectrum) 210. The second product is 1,1-bis-morpholinocyclopropane (IIIc)⁴ (35%), m.p. $89-92^\circ$; $\nu_{\text{max}}^{\text{KBr}}$ 3100,

3025, 2960, 2870, 2840, 2820 cm^{-1} ; τ_{CDCl_3} 6.35 (m, 8H), 7.40 (m, 8H), 9.27 (s, 4H); mol. wt. (mass spectrum) 212. In addition, a trace of IIIa was formed.

Reaction of II with dry HCl in ether yielded 1-piperidinocyclopropanol hydrochloride, m.p. 126.5–127.5°. $\nu_{\text{max}}^{\text{KBr}}$ 3150, 2950, 2900, 2865, 2840, 2525 cm^{-1} . The nmr spectrum of this product (H_2O) shows all four cyclopropane protons as a sharp singlet. In CDCl_3 , the spectrum contains peaks at τ 6.60 (t, $J=5\text{Hz}$, 4H), 8.00 (m, 6H), and an A_2B_2 pattern of cyclopropane protons at 8.55 (broad m, 2H) and 8.78 (broad s, 2H). The above nmr evidence is in accord with the occurrence of a rapid equilibration (in H_2O) between the hydrochloride of II and the corresponding iminium salt, IIa, $X = \text{Cl}$, permitting the cyclopropyl protons to become equivalent.

Support for the participation of IIa, $X = \text{OH}$, in the addition of nucleophiles to II was found in reactions with enamines. When II was refluxed for 72 hr with an excess of 1-piperidino-1-cyclopentene, 1-(2-cyclopentanoyl)-1-piperidinocyclopropane (IV)⁴ (75%) was obtained; $\nu_{\text{max}}^{\text{film}}$ 1747, 1625 cm^{-1} ; τ 7.48 (m, 4H), 8.0 (m, 7H), 8.60 (m, 6H), 9.40 (A_2B_2 , 4H); mol. wt. (mass spectrum) 195.



Acknowledgments

This work was supported by Grant GM-07874 from the U.S. Public Health Service.

References

1. For previous papers in this series, see a) H.H. Wasserman and D.C. Clagett, Tetrahedron Letters, 7, 341 (1964). b) H.H. Wasserman and D.C. Clagett, J. Amer. Chem. Soc., **88**, 5368 (1966). c) H.H. Wasserman, R.E. Cochoy and M.S. Baird, J. Amer. Chem. Soc., **91** 2375 (1969).
2. W.J.M. von Tilberg, S.E. Schaafsma, H. Steinberg, and Th. J. DeBoer, Rec. Trav. Chim., **86**, 417 (1967).
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4. Satisfactory elemental analyses were obtained for all new compounds.