Tetrahedron Letters No.8, pp. 585-586, 1970. Pergamon Press. Printed in Great Britain.

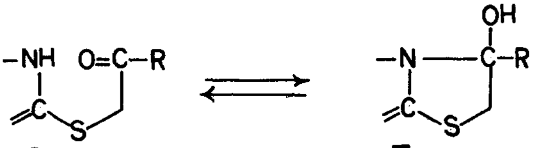
AMINO KETONE-CARBINOLAMINE TAUTOMERISM-RING SIZE EFFECT

Harjit Singh and Santokh Singh

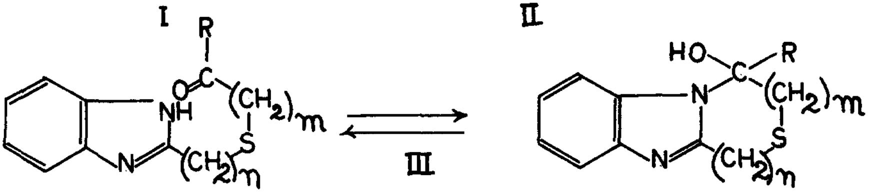
Department of Chemistry, Panjab University, Chandigarh, India

(Received in UK 5 January 1970; accepted for publication 16 January 1970)

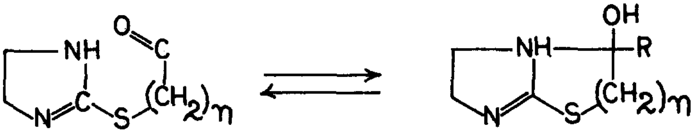
The amino ketones formed on treatment of α-halocarbonyl compounds with thioureas or cyclic systems where the ring N attached to the carbon carrying the thio function bears a mobile H present an interesting amino ketone-carbinolamine tautomerism (1,2). Conclusive evidences supported by I.R., N.M.R. data and chemical studies (3) have been presented in favour of the entire existence of the amino ketone tautomer (I) when R = aryl and for the predominance of carbinolamine tautomer viz. hydroxy thiazolidine (II) when R = H, alkyl in case of 2-thiobenzamidazolyl derivatives. During our study on such compounds we have found that the existence of carbinolamine tautomers, is also dependent upon the size of the ring to be formed and that it exists only when it involves the formation of five membered rings, whereas if the formation of higher membered rings is required, the amino ketone structure prevails.



I II



III



IV

(III) (B, n = o, m = 2); (C, n = 1, m = 1); (D, n = 1, m = 2) where the existence of carbinolamine tautomers requires the formation of six membered or seven membered rings were prepared by the condensation of 2-mercapto benzimidazole with β-chloro butanone-2 and 2-mercaptomethyl benzimidazole with α-chloro acetone and β-chloro butanone-2 respectively in aqueous sodium hydroxide solutions at room temperature. Whereas IIIA (n = 0, m = 1) exists as hydroxy thiazolidine structure (3), the amino ketone structure for IIIB, C and D were attested by their following spectral data : IIIB, ν_{max}^{KBr} 3425, 1695 cm^{-1} (-NH, C = O); δ 2.22 (s, CH_3), δ 3.13 (t, J = 7Hz, $-CH_2$), δ 4.6 (t, J = 7Hz, $-CH_2$), δ 7.2-7.6 (m, aromatic protons). IIIC, ν_{max}^{KBr} 3385, 1695 cm^{-1} (NH, C =O), δ 2.25 (s, CH_3), δ 3.36 (s, CH_2), δ 3.95 (s, $-CH_2$), δ 7.0-7.5 (m, aromatic protons). IIID ν_{max}^{KBr} 3375, 1700 cm^{-1} (NH, C = O), δ 2.08 (s, CH_3), δ 2.72 (s, 4H), δ 4.02 (s, 2H), δ 6.7-7.3 (m, aromatic protons), a broad signal centred at δ 7.9 (NH, exchanged with D_2O). Likewise IVA (n = 1) existed as hydroxy thiazolidine derivative (ν_{max}^{KBr} 3370, 1725 cm^{-1}, tertiary -OH) (4) and IVB (n = 2) favoured the amino ketone structure (ν_{max}^{KBr} 3320, 1700 cm^{-1}, -NH and - C == O).

Chemical evidence to these tautomeric structures is furnished by the fact that when capable of existence as carbinol amines they undergo facile dehydrations, characteristic of tertiary alcohols, whereas otherwise they require somewhat drastic conditions (unpublished). Conversely, these results can predict the conditions for such cyclodehydrations.

Acknowledgements :- The authors thank Dr. G.S. Sidhu for help in obtaining the N.M.R. spectra and the U.G.C. for financial assistance.

References

1. D.Bike in ''Advances in Heterocyclic Chemistry", Vol.1, Ed., A.R. Katritzky, Academic Press, Inc., N.Y. 1963, P. 167.
2. B.Stanovnik, M.Tisler and A.Vrbanic, J.Org.Chem., 34, 996(1969) and references therein.
3. A.E. Alper and A.Taurin, Can. J. Chem., 45, 2903(1967).
4. K.Nakanishi, Infrared Adsorption Spectroscopy , Holden Day, Inc., San Francisco, P. 138.
5. N.M.R. spectra were measured on varian A-60 instrument in $CDCl_3$ using TMS as internal reference and I.R. spectra were run on Perkin Elmer 337 grating infrared spectrophotometer. Satisfactory elemental analysis were obtained for new compounds.