

Department of Chemistry,
State University of New York College at Geneseo

Quinazolines III (1). The Structures of the Products Obtained by the Condensation of *o*-Aminoacetophenone with Methyl Isocyanate and Methyl Isothiocyanate.

Richard F. Smith

In an extensive series of publications Gheorghiu and co-workers (2) have described the properties of the quinazolines obtained by the condensation of *o*-aminobenzaldehydes, benzophenones or their derivatives with isothiocyanates, and isocyanates, respectively. Recently, Metlesics and co-workers (3) have confirmed that the products obtained from these condensations are quinoid quinazoline derivatives (I) that readily undergo 1,4-additions. A recent review (4) also cited unpublished work that confirms the structure of the product resulting from the condensation of *o*-aminobenzaldehyde with methyl isocyanate as a quinoid quinazoline derivative (I, X = O; Y = H; R = CH₃). Doub and co-workers (5) have reported that *o*-aminoacetophenone condenses with methyl isothiocyanate to give a compound whose structure was tentatively assigned as 3,4-dihydro-3-methyl-4-methylene-2,1(*H*)-quinazolinethione (IIa). An alternative structure for IIa is IIIa which is structurally analogous to the products obtained from the reactions described above.

By the use of p.m.r. spectroscopy we have been able to confirm Doub's structural assignment as IIa and assign structure IIb to the hitherto unreported oxygen analog IIb. The deciding feature in each spectrum was the presence of an AB coupling pattern that was centered at 4.8 p.p.m. ($J = 2.5$ c.p.m.)

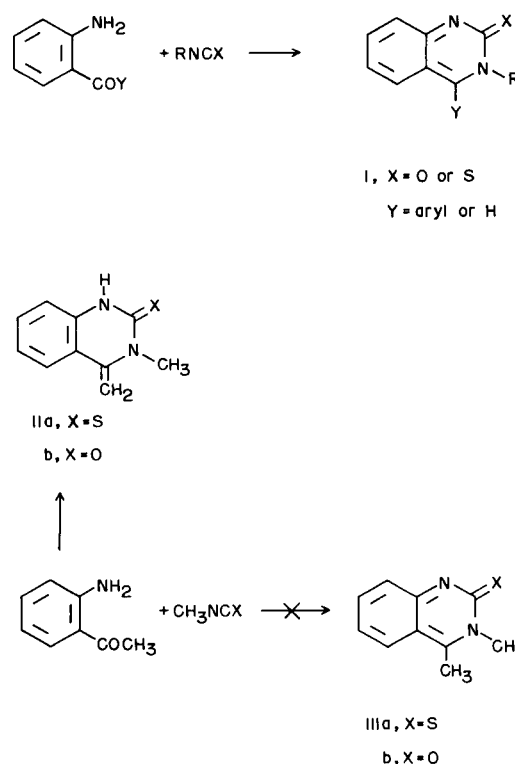


TABLE I

P.M.R. Spectra (a) of Quinazolinones

Compound	Aromatic Multiplet	3-CH ₃	1-H	4 - = C $\begin{matrix} \diagup \text{H} \\ \diagdown \text{H} \end{matrix}$
IIa	6.92-7.78	3.80	3.75	4.55 (doublet) and 5.08 (doublet) $J = 2.5$ c.p.s.
IIb	6.87-7.85	3.48	3.25	4.29 (doublet) and 4.90 (doublet) $J = 2.2$ c.p.s.

(a) Chemical shifts are expressed as p.p.m. relative to TMS. Spectra were determined with a Varian A60-A instrument in *N,N*-dimethylformamide solution.

for IIa and 4.6 p.p.m. ($J = 2.2$ c.p.m.) for IIb. These bands signal the presence of the 4-methylene group and their combined integrated intensity ratios were approximately one half those of the aromatic multiplets. The other features of the p.m.r. spectra were completely compatible with structures IIa and IIb and are recorded in the Table.

EXPERIMENTAL (6)

3,4-Dihydro-3-methyl-4-methylene-2,1(H)-quinazolinethione (IIa).

This compound was prepared by the published procedure (5) and recrystallized from ethanol as pale yellow crystals m.p. 221-223°, lit. 223-225°. The compound formed a bright yellow solution in concentrated sulfuric acid. The infrared spectrum exhibited strong intensity bands at 6.19, 6.52, 6.95, 7.55, 7.75, 8.95, 9.25, and 13.3 microns, medium intensity bands at 5.89, 6.10, 6.79, 8.05, 12.5 and 13.6 microns and weak bands at 3.15, 3.22, 3.30, 6.68, 7.25, 7.91, 9.75, 10.1, 10.6, 10.9, 11.5 and 11.9 microns.

Anal. Calcd. for $C_{10}H_{10}N_2S$: C, 63.12; H, 5.30; N, 14.73; S, 16.85. Found: C, 63.09; H, 5.41; N, 14.80; S, 16.96.

3,4-Dihydro-3-methyl-4-methylene-2,1(H)-quinazolinone (IIb).

A solution containing 2.5 g. of *o*-aminoacetophenone, 5 ml. of methyl isocyanate and 10 ml. of dry benzene was stirred at room temperature for 12 hours. Filtration afforded 2.9 g. of white crystals, m.p. 190-195°. Recrystallization from ethanol gave white crystals, m.p. 204-206°. The compound formed a bright yellow solution in concentrated sulfuric acid. The infrared spectrum exhibited strong bands at 5.97, 7.00, 7.30, 7.49, 12.9, 13.1, 13.2, 13.4. and 13.9

microns, medium intensity bands at 6.15, 6.79, 6.92, 7.89, 7.95, 9.30, 9.90, 11.7, 13.7 and 14.7 microns and weak bands at 3.15, 3.21, 3.30, 3.45, 6.28, 6.38, 7.15, 7.59, 8.15, 8.70, 9.00, 9.30, 9.80, 10.8 and 11.1 microns.

Anal. Calcd. for $C_{10}H_{10}N_2O$: C, 68.94; H, 5.79; N, 16.08. Found: C, 68.62; H, 5.82; N, 15.87.

Acknowledgment.

The author is indebted to Mr. Kenneth Fleischer of the Sterling-Winthrop Research Institute for the microanalyses and to Mr. William Jankowski of Varian Associates for determination of the p.m.r. spectra. The work was supported by a Grant-in-Aid from the Research Foundation of the State University of New York.

REFERENCES

- (1) Paper II, R. F. Smith, P. C. Briggs, R. A. Kent, J. A. Albright and E. J. Walsh, *J. Heterocyclic Chem.*, **2**, 157 (1965).
- (2) For leading references see: (a) C. V. Gheorghiu, *Ber.*, **76**, 994 (1943). (b) T. A. Williamson, "Heterocyclic Compounds" Vol. 6, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 371.
- (3) W. Metlesics, G. Silverman, V. Toome, and L. H. Sternbach, *J. Org. Chem.*, **31**, 1007 (1966).
- (4) W. L. F. Armarego, "Advances in Heterocyclic Chemistry", Vol. 1, A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p. 268.
- (5) L. Doub, L. M. Richardson, D. R. Herbst, M. L. Black, O. L. Stevenson, L. L. Bamas, G. P. Youmans and A. S. Youmans, *J. Am. Chem. Soc.*, **80**, 2213 (1958).
- (6) Melting points are uncorrected and were determined with a Mel-Temp apparatus. Analyses are by Mr. K. Fleischer of the Sterling-Winthrop Research Institute. Infrared spectra was determined in potassium bromide on a Perkin-Elmer Infracord instrument.

Received August 25, 1966

Geneseo, New York 14454