METHOD FOR THE PREPARATION OF THE 1,4-THIAZEPINO[2,3,4-i,j]QUINOLINE SYSTEM

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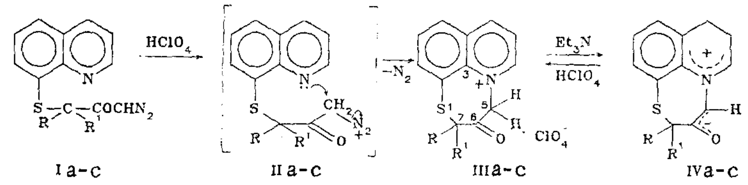
It is known that the acid-catalyzed intramolecular cyclization of diazo carbonyl compounds makes it possible to obtain four-, five-, and six-membered heterocycles [1-3], whereas systems that contain a condensed seven-membered heterocyclic ring could not be obtained by this method [4].

We have found that intramolecular cyclization of the intermediate diazonium ion (IIa-c) to give the 1,4-thiazepino[2,3,4-i,j]quinoline system (IIIa-c) occurs in the action of 60% perchloric acid on 1-diazo-3-(8-quinolylthio)propanones (Ia-c).



I–IV a $R=R'=H$, b $R=H$, $R'=CH_3$, c $R=R'=CH_3$

Thus, the successive addition of 0.5 ml of 60% perchloric acid and excess ether to 0.01 mole of the diazo ketone (Ia-c) in 5 ml of acetonitrile gave, after recrystallization from acetonitrile–ether (10:1), 1,4-thiazepino[2,3,4-i,j]quinolines IIIa-c. Compound IIIa, with mp 72-75°C, was obtained in 45% yield. IR spectrum (mineral oil): 1730 cm^{-1} (C=O). PMR spectrum (d_3-acetonitrile): 7.86-9.4 (6H, m, Ar), 6.56 (2H, s, 5-CH_2), and 4.25 ppm (2H, s, 7-CH_2). UV spectrum [water–acetonitrile (9:1)], λ_{max} (log ε): 242 (4.1), 270 (3.96), and 318 nm (3.69). Compound IIIb, with mp 68°C, was obtained in 50% yield. IR spectrum (mineral oil): 1725 cm^{-1} (C=O). PMR spectrum (d_3-acetonitrile): 7.86-9.4 (6H, m, Ar), 6.52 (2H, s, 5-CH_2), 4.28 (1H, q, J = 7 Hz, $CHCH_3$), and 1.6 ppm (3H, d, J = 7 Hz, $CHCH_3$). UV spectrum: [water–acetonitrile (9:1)], λ_{max} (log ε): 245 (4.05), 273 (3.95), and 321 nm (3.51). Compound IIIc, with mp 73°C, was obtained in 40% yield. IR spectrum (mineral oil): 1700 cm^{-1} (C=O). PMR spectrum (d_3-acetonitrile): 7.84-9.4 (6H, m, Ar), 6.59 (2H, s, 5-CH_2), and 1.7 ppm (6H, s, 2-CH_3). UV spectrum [water–acetonitrile (9:1)], λ_{max} (log ε): 246 (4.15), 270 (4.08), and 330 nm (3.75).

The cyclic structure of IIIa-c was also confirmed by their conversion to ylide systems IVa-c under the influence of basic agents with a characteristic shift of the absorption in the electronic spectra and the appearance of intense absorption in the visible region at λ_{max} 520-580 nm. Complete reversion to systems IIIa-c occurred when solutions of ylides IVa-c were treated with perchloric acid.

LITERATURE CITED

1. B. I. Christensen, N. I. Steinberg, and R. Hirshmann, Chem. Ind., No. 39, 1259 (1958).
2. A. K. Bose and P. Later, J. Am. Chem. Soc., 74, 4703 (1952).
3. L. Reichel and N. Hampel, Ann. Chem., 715, 159 (1968).
4. V. G. Kartsev, A. M. Sipyagin, N. F. Sepetov, and L. A. Sibel'dina, Khim. Geterotsikl. Soedin., No. 10, 1327 (1980).

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