Chemistry of Heterocyclic Compounds, Vol. 33, No. 5, 1997

FORMATION OF STABLE 1,2,4-TRIAZINE N-ADDUCTS

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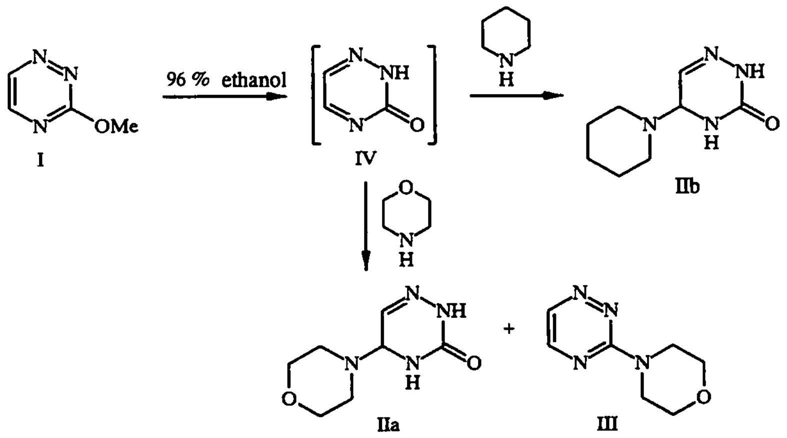
Amino adducts of 1,2,4-triazines at the $C_{(5)}=N_{(4)}$ bond have been detected only by spectral methods. Rykowski et al. [1, 2] have reported the oxidation of such adducts generated *in situ* by the action of potassium permanganate.

Reactions of 3-methoxy-1,2,4-triazine (I) with cycloalkylamines were found to give stable products of the addition of morpholine and piperidine to the 1,2,4-triazine ring. Thus, treating 3-methoxy-1,2,4-triazine (I) with morpholine in 96% aq. ethanol gave 5-morpholino-4,5-dihydro(2H)-1,2,4-triazin-3-one (IIa) and 3-morpholino-1,2,4-triazine (III). Heating triazine I with piperidine in ethanol at reflux leads to the analogous N-adduct (IIb). The formation of IIa and IIb probably occurs through the intermediate formation of 2H-1,2,4-triazin-3-one (IV), formed as a result of the hydrolysis of triazine I by the action of water in the ethanol solvent.

The structure of N-adducts IIa and IIb was established by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The assignment of the signals in the NMR spectra of IIa and IIb was carried out using homó- and heteronuclear double resonance. The physicochemical indices of by-product III were identical to the literature data for 3-morpholino-1,2,4-triazine [3].



5-Morpholino-4,5-dihydro(2H)-1,2,4-triazin-3-one (IIa) was obtained in 21% yield, mp 173-190°C (dec.). ^1H NMR spectrum in DMSO-d_6: 9.94 (1H, br. s, $^4J_{6,4}$ = 0.9 Hz, $N_{(2)}$—H), 7.74 (1H, br. s, $^4J_{6,4}$ = 0.9 Hz, $N_{(4)}$—H), 6.69 (1H, m, $^3J_{6,5}$ = 3.3, $^4J_{6,4}$ = 0.9 Hz, H-6), 4.60 (1H, m, $^3J_{5,6}$ = 3.3 Hz, H-5), 3.55 and 2.47 (8H, m, morpholine). Found: C, 45.8; H, 6.5; N, 30.3%. Calculated for $C_7H_{12}N_4O_2$: C, 45.9; H, 6.6; N, 30.6%.

5-Piperidino-4,5-dihydro(2H)-1,2,4-triazin-3-one (IIb) was obtained in 21% yield, mp 170-185°C (dec.). ^1H NMR spectrum in DMSO-d_6: 9.94 (1H, br. s, $^4J_{2,6}$ = 0.9 Hz, $N_{(2)}$—H), 7.67 (1H, br. s, $^4J_{4,6}$ = 0.9 Hz, $N_{(4)}$—H), 6.67 (1H, m, $^3J_{6,5}$ = 3.3, $^4J_{6,2}$ = $^4J_{6,4}$ = 0.9 Hz, H-6), 4.56 (1H, m, $^3J_{5.6}$ = 3.3 Hz, H-5), 2.48 and 1.43 ppm (10H, m, piperidine). ^{13}C NMR spectrum in DMSO-d_6: 152.97 ($^2J_{C(3)NH}$ = 5.2, $^3J_{C(3)H(5)}$ = 5.2 Hz, $C_{(3)}$), 136.01 ($^1J_{(C,H)}$ = 189.1, $^2J_{(C(6),H(5))}$ = 10.8, $^3J_{(C(6),NH)}$ = 6.7 Hz, $C_{(6)}$), 70.23 ($^1J_{(C,H)}$ = 152.4, $^2J_{(C(5),H(6))}$ = 12.0 Hz, $C_{(5)}$), 48.18 ($^1J_{(C,H)}$ = 132.9 Hz, α-C in piperidine) 26.47 ($^1J_{(C,H)}$ = 126.4 Hz, β-C in piperidine), 24.89 ($^1J_{(C,H)}$ = 126.2 Hz, γ-C in piperidine). Found: 52.5; H, 7.7; N, 30.4%. Calculated for $C_8H_{14}N_4O$: C, 52.7; H, 7.7; N, 30.8%.

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0009-3122/97/3305-0621$18.00

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