SYNTHESIS OF 3-THIO-1,2,4-TRIAZINES FROM DIACETYL AND 4-SUBSTITUTED THIOSEMICARBAZIDES

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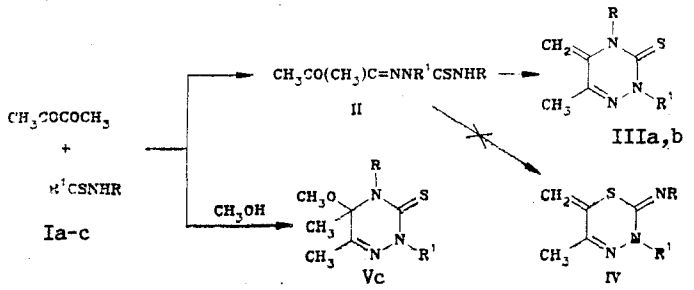
The reaction of thiosemicarbazides with α-bifunctional compounds is a widely used method for synthesis of 1,2,4-triazines and 1,3,4-thiadiazines but the use of 4-substituted thiosemicarbizides has not been described.

We have found that the semicarbazides Ia,b react with diacetyl to give the previously unknown 3-thio-5-methylene-1,2,4-triazines IIIa,b via the intermediate thiosemicarbazone II and demonstrated this in the case of IIa. Cyclization to III and not to the alternative 2-imino-6-methylene-1,3,4-thiadiazine ring IV was unambiguously proved by ^{15}N NMR which showed the presence of one imino and two thioamide nitrogen singlet signals at 312.0 (N_1), 169.1 (N_2), and 132.8 ppm (N_4), respectively.



I, IIIa R=CH_3, R^1=H; b R=R^1=CH_3; I, V c R=C_6H_5, R^1=H

Diacetyl 4-methylthiosemicarbazone (IIa) was obtained by dissolving 4-methylthiosemicarbazide (Ia) in a fivefold excess of diacetyl. After 1 h the precipitate was filtered off and recrystallized to mp 173-174°C (from ethanol) in 80% yield. PMR spectrum ($CDCl_3$): 1.98 (3H, s CH_3); 2.37 (3H, s CH_3); 3.21 (3H, d, J = 5.0 Hz, CH_3NH); 7.55 (1H, q, J = 5.0 Hz, HN_4); 8.82 ppm (1H, s, HN_2).

4,6-Dimethyl-3-thio-methylene-1,2,4-triazine (IIIa) was obtained by refluxing the hydrazone IIa (0.75 g, 4 mmole) over CaO (3 g) in benzene (150 ml) for 15 h. The CaO was filtered off and the benzene removed in vacuo to give product (82%) with mp 126-127°C (from methanol). PMR spectrum ($CDCl_3$): 2.05 (3H, s, CH_3); 3.48 (3H, s, CH_3N_4); 4.38 (1H, d, J = 2.0 Hz); 4.46 (1H, d, J = 2.0 Hz, CH); 9.85 ppm (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$): 18.7 (CH_3); 36.7 (CH_3N_4); 90.7 (CH_2); 134.3 (C_5); 146.1 (C_6); 170.7 ppm (C=S).

2,4,6-Trimethyl-3-thio-5-methylene-1,2,4-triazine (IIIb) was obtained by dissolving 2,4-dimethylthiosemicarbazide in a fivefold excess of diacetyl. After 2 h the diacetyl was removed in vacuo and the residue recrystallized to give the product (53%) with mp 102-104°C (from methanol). PMR spectrum ($CDCl_3$): 2.05 (3H, s, CH_3); 3.52 (3H, s, CH_3H_4); 3.73 (3H, s, CH_3N_2); 4.22 (1H, d, J = 3.0 Hz, CH); 4.36 ppm (1H, d, J = 3.0 Hz, CH). ^{13}C NMR spectrum ($CDCl_3$): 18.6 (CH_3); 36.6 (CH_3N_4); 45.5 (CH_3N_2); 88.9 (CH_2); 134.2 (C_5); 145.0 (C_6); 171.5 ppm (C=S).

The same reaction can be used to prepare 5-alkoxy-3-thio-1,2,4-triazines if the condensation is carried out in the presence of the corresponding alcohol.

5-Methoxy-5,6-dimethyl-4-phenyl-3-thio-1,2,4-triazine (Vc). 4-Phenylthiosemicarbazide (Ic, 10 mmole) was dissolved in methanol (50 ml) and diacetyl (50 mmole) was added. After standing for 1 h the solvent was removed and the residue recrystallized to give the product

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(46%) with mp 138°C (from ethanol). PMR spectrum ($CDCl_3$): 1.24 (3H, s, CH_3); 2.00 (3H, s, CH_3); 3.20 (3H, s, OCH_3); 7.0-7.5 (5H, m, H_{arom}); 9.75 ppm (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$): 18.0 (CH_3); 25.1 (CH_3–C_5); 51.1 (CH_3O); 84.0 (C_5); 128.2-138.5 (6 signals, C_{arom}); 145.2 (C_6); 174.7 ppm (C=S). ^{15}N NMR spectrum ($CDCl_3$): 140.1 (s, N_4); 170.2 (d, J = 109.2 Hz, HN_2); 308.4 ppm (s, N_1).

TRICHLOROMETHYLATION OF BENZOXAZOLINE-2-THIONE AND BENZOTHIAZOLINE-2-THIONE BY CARBON TETRACHLORIDE IN THE PRESENCE OF ALUMINUM CHLORIDE

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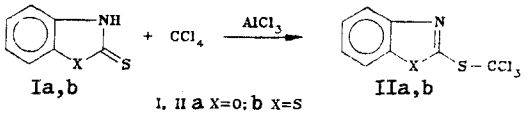
The reaction of benzoxazoline-2-thione (Ia) or benzothiazoline-2-thione (Ib) with carbon tetrachloride in the presence of aluminum chloride leads to high yields of 2-(trichloromethylthio)benzoxazole (IIa) or 2-(trichloromethylthio)benzothiazole (IIb) instead of the expected products of reaction of Ia,b in the benzene ring (as occurs with their oxygen analogs) [1].



Ia,b — I, II a X=O; b X=S — IIa,b

The products IIa,b were obtained by the addition of a threefold excess of $AlCl_3$ to a suspension of the corresponding thione in CCl_4, heating the reaction mixture at 80-90°C for 2 h, decomposition of the reaction mass with a mixture of ice and HCl, and fractionation of the organic layer in vacuo.

The mass spectra of IIa,b show characteristic peaks with m/z 118 $(M-SCCl_3)^+$ (IIa) and 134$(M - SCCl_3)^+$ (IIb). The UV spectra show absorption maxima near 280, 288 nm (IIa) and 280, 290, 300 nm (IIb)identifying them as S-alkylation products. By contrast, N-alkylbenzoxazoline-2-thiones [2] show absorption maxima near 308 nm and N-alkylbenzothiazoline-2-thiones [3] near 328 nm.

2-(Trichloromethylthio)benzoxazole (IIa). Yield 85%, bp 128-130°C (1 mm Hg). Mass spectrum, m/z: 267, 269, 271, 273 (M^+); 232, 234, 236 $(M - Cl)^+$; 150 $(M - CCl_3)^+$; 118 $(M - SCCl_3)^+$. UV spectrum λ_{max} (log ε): 280 (4.19), 288 nm (4.27).

2-Trichloromethylthio)benzothiazole (IIb). Yield 81 %. mp 93-95°C (from heptane). Mass spectrum, m/z: 283, 285, 287, 289 (M^+); 248, 250, 252, $(M - Cl)^+$; 166 $(M - CCl_3)^+$; 134 $(M - SCCl_3)^+$; UV spectrum, λ_{max} (log ε): 280 (4.07), 290 (4.00), 300 nm (3.90).

Elemental analytical data agreed with that calculated.

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