

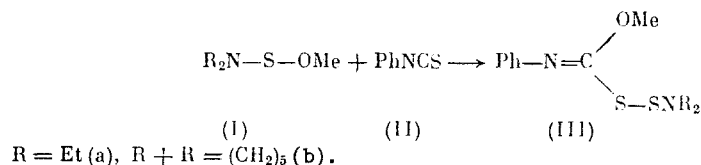
REACTION OF AMINOSULFENATES WITH PHENYL ISOTHIOCYANATE

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Sulfenamides and N,N'-thiobisamines react with phenyl isothiocyanate (II) to form the products of insertion into the S-N bond [1, 2]. There is no information on the reactions of aminosulfenates (I) and (II) in the literature.

We have shown that the reaction of (I) and (II) at 90°C over 200 h involves insertion at the stronger S-O bond and not at the S-N bond to give O-methyl-N-phenyl-S-(aminosul-fenyl)isothiocarbamates (III).



The structure of (III) isolated from the reaction mixture by chromatography on silica gel using hexane as the eluent was demonstrated by IR and PMR spectroscopy, chemical ionization and electron impact mass spectrometry, and elemental analysis.

Product (IIIa) was obtained in 49% yield, n_D^{20} 1.5915, R_f 0.64 (CHCl_3). IR spectrum (ν , cm^{-1}): 1630 (C=N), 1170 (C-O-C). PMR spectrum (δ , ppm): 1.12 g (CH_3), 2.77 q (CH_2), 3.88 s (OMe), 6.53-7.17 m (Ph). Found: m/z (CI): $[\text{MH}]^+$ (100%), 271.094. Calculated for $\text{C}_{12}\text{H}_{19}\text{N}_2\text{OS}_2$: 271.0939.

Product (IIIb) was obtained in 42% yield, n_D^{20} 1.6135, R_f 0.47 (CHCl_3). IR spectrum (ν , cm^{-1}): 1630 (C=N), 1170 (C-O-C). PMR spectrum (δ , ppm): 1.42 br.s [$(\text{CH}_2)_3$], 2.78 br.s (CH_2NCH_2), 3.83 s (OMe), 6.50-7.12 m (Ph). Found, m/z (CI): $[\text{MH}]^+$ (100%), 283.093. Calculated for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{OS}_2$: 283.0939. EI Mass spectrum: 282 (14) [M], 148 (25) [$\text{C}_5\text{H}_{10}\text{NS}_2$], 134 (100) [PhNCOMe], 119 (50) [PhNCO], 116 (23) [$\text{C}_5\text{H}_{10}\text{NS}$] ($\Delta m/m \leq 5 \cdot 10^{-6}$).

LITERATURE CITED

1. N. M. Heimer and L. Field, J. Org. Chem., 35, 3012 (1970).
2. G. Oertel, H. Malz, and H. Holtschmidt, Chem. Ber., 97, 891 (1964).