Novel Method for the Conversion of the Imino-group into the Carbonyl Group *via* Nitrosoimines;[1] Preparation of *S*-Alkyl Thiocarbamates from *S*-Alkylisothioureas

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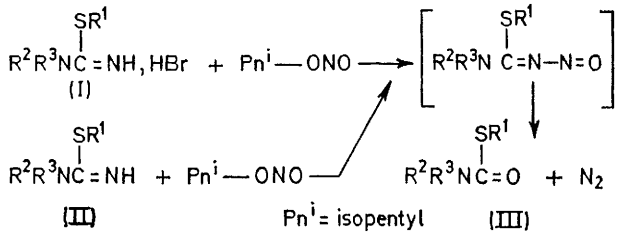
Summary *S*-Alkylisothiourea hydrobromides are converted into *S*-alkyl thiocarbamates with isopentyl nitrite under mild and anhydrous conditions *via* nitrosoimine intermediates.

S-ALKYLISOTHIOUREAS (II) and their hydrobromides (I) have been converted into *S*-alkyl thiocarbamates (III)[2] in good yields under rather mild and anhydrous conditions.

A mixture of (Ia) (17 mmol) and isopentyl nitrite (23 mmol) in benzene (50 ml) was heated at 50° for 2 h. Work-up provided recovered (Ia) (30%) and (IIIa), m.p. 46·0—46·8° [61% from (Ia) consumed]. Similar reactions of (Ib—f) gave (IIIb—f) in 86, 85, 66, 61, and 62% yields, respectively [31, 0, 41, 34, and 31%, (Ib—f), respectively, recovered]. Nitrogen was evolved quantitatively from (Ic) at 60° within 1 h.

Free base (IIc) (6 mmol), isopentyl nitrite (12 mmol), and acetic acid (12 mmol) reacted rapidly in benzene at 60°, with quantitative evolution of nitrogen in 5 min.



a; $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = Ph$
b; $R^1 = PhCH_2$, $R^2 = Et$, $R^3 = Ph$
c; $R^1 = PhCH_2$, $R^2 = R^3 = Ph$
d; $R^1 = Et$, $R^2 = Me$, $R^3 = Ph$
e; $R^1 = R^2 = Et$, $R^3 = Ph$
f; $R^1 = Et$, $R^2 = R^3 = Ph$

The reaction also proceeded in acetonitrile, but no reaction was observed in ethanol or with the hydrochlorides of (II).

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[1] For preceding paper in the series 'Chemistry of Nitrosoimines' see: K. Akiba, I. Fukawa, N. Nomura, and N. Inamoto, *Bull. Chem. Soc. Japan*, 1972, **45**, 1867.

[2] For other methods for the preparation of thiocarbamates see: T. W. Evans and W. H. Dehn, *J. Amer. Chem. Soc.*, 1930, **52**, 3645; H. Tills, *ibid.*, 1959, **81**, 714; R. G. Hiskey, F. I. Carroll, R. F. Smith, and R. T. Corbett, *J. Org. Chem.*, 1961, **26**, 4756.