J.C.S. CHEM. COMM., 1974

A Convenient Synthesis of N-Isothiocyanatoimines

By CARSTEN BERG

(Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark)

N-ISOTHIOCYANATOIMINES constitute a new and highly reactive type of hydrazone derivative, and a small scale preparation of N-isothiocyanato-2,4-dimethylpentan-3imine (1) has been described.¹ We now report a more

Summary A new synthesis of N-isothiocyanatoimines has been developed which involves reaction of triethylammonium 3-alkylidenedithiocarbazate with thiophosgene.

convenient synthesis of N-isothiocyanatoimines based on the reaction of triethylammonium 3-alkylidenedithiocarbazate with thiophosgene. Reaction of the hydrazone² (2) (1 equiv.) and triethylamine (1.5 equiv.) in carbon disulphide gave







R² But PhCH₂ Me Ph

the triethylammonium 3-alkylidenedithiocarbazate (3). Thiophosgene (1 equiv.) in ether was added to a stirred, ice-cooled suspension of (3) (1 equiv.) in ether. The mixture was shaken with dilute NaOH (1 equiv.) and the ether layer washed with ice-water and dried

As compounds (4) are unstable¹ they were characterized by treatment of their ether solutions with methylamine. Evaporation yielded the corresponding 4-methylthiosemicarbazones (5), authentic samples of which were prepared from the hydrazones (2) and methylisothiocyanate. Compounds (5) prepared by the two routes were shown to be identical by comparison of their m.p.s.: (5a), 124-125°; (5b), 83-84°; (5c),³ 135-136°; (5d),⁴ 168-169°; and their i.r. and n.m.r. spectra.

	TA	BLE	
Compound	$v_{\rm NCS}/{\rm cm^{-1}}$ (4)	Half-life/h (4)	Yield (%) (5) ^a
a	1975	72	55
ь	1960	6	30
с	1980	3 0	60
đ	1960	24	41

^a Calculated from (3).

Compounds (4) could be isolated as oils by evaporation of the ether solution and were shown (n.m.r.) to be pure. They exhibit a strong i.r. absorption in the region 1950-2000 cm⁻¹ characteristic of N-isothiocyanatoimines.¹ From the intensities of the NCS absorptions the half-lives in CCl_4 (5%) at room temperature were established (see Table). The compounds formed by reaction of thiophosgene with (3) showed no NCS i.r. absorption.

(Received, 8th November 1973; Com. 1543.)

¹ U. Anthoni and C. Berg, Acta Chem. Scand., 1969, 23, 3602.
² A. Pross and S. Sternhell, Austral. J. Chem., 1970, 23, 989; R. J. Theis and R. E. Dessy, J. Org. Chem., 1966, 31, 624; L. I. Smith and K. L. Howard, Org. Synth., 1955, Coll. Vol. III, 352; G. Lock and K. Stach, Ber., 1944, B77, 293.
³ J. M'Lean and F. J. Wilson, J. Chem. Soc., 1939, 1048.
⁴ K. Sasse, Annalen, 1970, 735, 158.