A Convenient Synthesis of *N*-Isothiocyanatoimines

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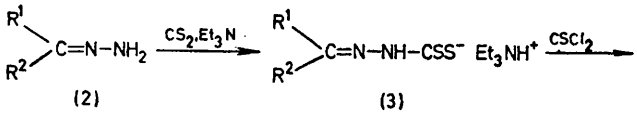
Summary A new synthesis of *N*-isothiocyanatoimines has been developed which involves reaction of triethylammonium 3-alkylidenedithiocarbazate with thiophosgene.

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

convenient synthesis of *N*-isothiocyanatoimines based on the reaction of triethylammonium 3-alkylidenedithiocarbazate with thiophosgene. Reaction of the hydrazone[2] (**2**) (1 equiv.) and triethylamine (1·5 equiv.) in carbon disulphide gave



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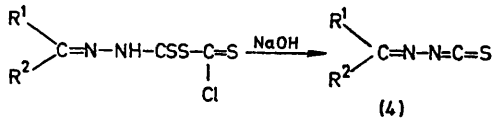

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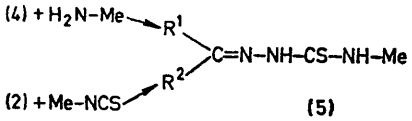

(5)

	a	b	c	d
R^1	Me	$PhCH_2$	Ph	Ph
R^2	Bu^t	$PhCH_2$	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 unstable[1] 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.

TABLE

Compound	ν_{NCS}/cm^{-1} (**4**)	Half-life/h (**4**)	Yield (%) (**5**)[a]
a	1975	72	55
b	1960	6	30
c	1980	30	60
d	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.

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