

Short Communications

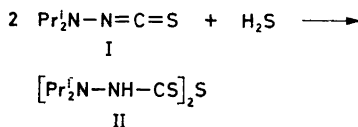
N-Isothiocyanatoamines

XI. The Preparation and Isomerism of *O*-Phenyl *N,N*-Diisopropylthiocarbamate

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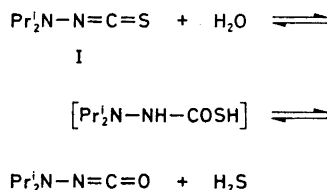
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Although dimerization of *N*-isothiocyanatoamines generally takes place readily¹ on standing at room temperature an outstanding exception appears to be *N*-isothiocyanatodiisopropylamine (I)² which can be stored in 96% ethanolic solution for several hours at 20°C. However, even in this case, as stated in an earlier communication,³ a colourless, crystalline compound slowly separates from the stock solution. This has now been identified as bis-(*N,N*-diisopropylthiocarbazoyl) sulfide (II) which can also be prepared by treatment of a solution of (I) with hydrogen sulfide.⁴



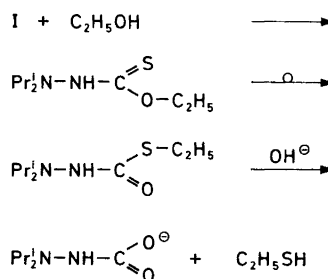
It is proposed that when II is formed from the ethanolic stock solution, the first step in the reaction is a slow hydrolysis of (I). The monothiocarbazic acid initially formed liberates hydrogen sulfide, which reacts with (I) to form II.

That hydrolysis is involved in the reaction is supported by the observation that hydrogen sulfide can be detected on boiling the ethanolic solution. The *N*-isocyanato-



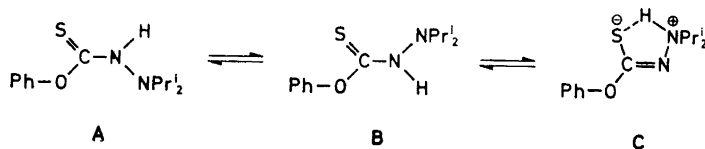
diisopropylamine formed by the reaction probably either dimerizes¹ or reacts with ethanol, but attempts to isolate a product have not been successful.

If an ethanolic solution of (I) is boiled for several hours with catalytic amounts of potassium hydroxide, a small yield of ethanethiolo is obtained. The following mechanism is proposed taking into account that initial attack of ethanol probably occurs at the carbon atom,⁵ and that rearrangement of similar thiocarbazates have been reported.⁶



Since the hydrolysis of (I) proceeds faster than the ethanolysis it might be inferred that the reactivity of (I) towards the OH group increases with the acidity of the proton. This supposition was supported by the observation that addition of small amounts of hydrochloric acid to the ethanolic solution of (I) resulted in an increased rate of formation of II. On heating (I) with phenol in 96% ethanol for a short

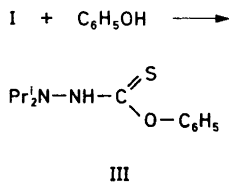
Table 1. Chemical shifts^a (τ , ppm) and coupling constants J (Hz) of the protons in the diisopropylamino group of *O*-phenyl-*N,N*-diisopropylthiocarbamate.



Solvent	Temp. °C	Form	%	CH ₃ (2)	CH (7)	$J_{\text{CH}_3-\text{CH}}$	$J_{\text{CH}-\text{NH}}$
CDCl ₃	ca. 40	A and/or B	55	8.86	6.74	6.4	—
		C	45	8.66 8.58	6.25 6.15	6.4	5.2
		A	40	8.86 8.78	6.65	6.4	—
CDCl ₃	-30	B	5	8.82	not obs.	6.4	—
		C	55	8.61 8.53	6.17 6.08	6.4	5.2
		A	85	8.87	6.74	6.4	—
CCl ₄	ca. 40	B	5	8.83			
		C	10	8.66	6.34	6.4	not. obs

^a The values given in the table are the centers of the multiplets, their multiplicities being given in parentheses.

time, *O*-phenyl-*N,N*-diisopropylthiocarbamate (III) was isolated in good yield.



To ensure that rearrangement of III to the *S*-phenylester had not occurred, the IR spectra of III in KBr and in CHCl₃ were recorded. Both in the solid state and in solution the absorption band characteristic for a C=O group was absent. The thioureide band⁷ indicative of the N-C=S group, was found at 1530 cm⁻¹ in KBr.

The NMR spectrum of III was recorded, in CDCl₃ and in CCl₄, at intervals from -30°C to 40°C. The most typical patterns arising from the isopropyl groups are summarised in Table 1. The signals in the NMR spectrum recorded at -30°C in CDCl₃ con-

sisted of five doublets from the CH₃ protons. Each doublet showed an apparent spacing of 6.4 Hz. However, only three septuplets were observed, each exhibiting the same coupling constant for the CH protons. These observations suggest an equilibrium between at least three structures A \rightleftharpoons B \rightleftharpoons C (see Table 1) for the following reasons.

A partially resolved triplet at $\tau=0$ ppm is assigned to the NH proton. The coupling constant $J_{\text{CH}-\text{NH}}=5.2$ Hz is identical with the separation between the two septuplets at the lower field ($\tau=6.17$ ppm and $\tau=6.08$ ppm). When the deuteriochloroform solution was shaken with deuterium oxide the two septuplets collapsed, verifying that the doubling arises from coupling of the NH proton with the neighbouring CH proton. This is only possible for the polar structure C. Magnetic nonequivalence of the methyl groups is expected in compounds with such a structure.⁸ The two doublets for the CH₃ protons at lower field ($\tau=8.61$ ppm and $\tau=8.53$ ppm) are therefore interpreted as being due to

nonequivalence of the methyl signals of the isopropyl group in the polar form C. The nonequivalence Δ , *i.e.* the difference between the centers of the CH_3 doublets, is 4.8 Hz at -30°C and decreases with increasing temperature, (4.6 Hz at 40°C) consistent with observations on related compounds.⁸

The three doublets at higher field must therefore arise from one (our both) of the nonpolar forms A or B. An examination of related compounds⁹ suggests the more stable to be the A form, in which the diisopropylamino group is *cis* to the phenoxy group. In the A form magnetic nonequivalence of the methyl groups is expected to occur because of steric hindrance from the phenoxy group. It was therefore deduced that the two doublets ($\tau=8.86$ ppm and $\tau=8.78$ ppm) separated by 4.8 Hz at -30°C but coalescing at -15°C (see below) arise from the A form. The separation $\Delta=4.8$ Hz at -30°C accordingly reflects the nonequivalence, at this temperature, of the CH_3 groups in the A form.

The unassigned doublet at $\tau=8.82$ ppm therefore arises from the B form in which the diisopropylamino group is *trans* to the phenoxy group. From the integrated CH_3 signals it is seen that the B form amounts to *ca.* 5% only, and the CH septuplet of the B form is not observed due to the low intensity.

The nonequivalence of the CH_3 groups in the A form decreases with increasing temperature. A substantial separation $\Delta=4.6$ Hz is still observed at -20°C , but in the interval from -20°C to -15°C the nonequivalence of the methyl groups in the A form disappears. At the same time the methyl doublet from the B form disappears. Since the results obtained using CCl_4 as solvent indicates that the rotation is still hindered at this temperature (*i.e.* both an A and a B form exist) it appears most probable that the methyl doublet arising from the B form becomes hidden under the CH_3 signals from the A form. At temperatures exceeding -10°C only one sharp CH_3 doublet from the A and the B forms and the two doublets for the CH_3 groups in the polar C form are observed. (Table 1, CDCl_3 , 40°C).

By recording the spectrum in CCl_4 at 40°C it was observed, that the ratio between the polar and the nonpolar forms is changed in favour of the nonpolar forms.

Three doublets corresponding to the methyl proton signals of the A, B, and C forms are observed, but magnetic nonequivalence of the methyl groups is not present in any of the three forms. This solvent effect will be discussed elsewhere,⁹ as well the effects of association.

Experimental. Conditions and equipment used for the physical measurements were those described in part II of this series.¹⁰

Bis-(N,N-diisopropylthiocarbazoyl)sulfide (II). The crystalline material which had separated from the stock solution of (I) in 96% ethanol over a period of one month was filtered off and recrystallized from ethanol to constant melting point, ($150-151^\circ\text{C}$). The identity was established by mixture melting point and by comparison of IR and NMR spectra with those obtained from the authentic material.⁴

O-Phenyl-N,N-diisopropylthiocarbazate (III). An ethanolic solution of equimolar amounts of phenol and (I) was heated close to the boiling point for a few minutes and left overnight. On evaporation of the solvent a crystalline residue was left which was recrystallized from ether to give a 40% yield of colourless crystals, m.p. $103-104^\circ\text{C}$. (Found C 61.55; H 7.99; N 10.98. Calc. for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{OS}$: C 61.87; H 7.99; N 11.10).

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