

Thermal Rearrangement of O-Thiocarbamoylated Hydroxamic Acids: a 1,3 Radical Shift

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Summary The rearrangement of *N*-aroyl-*N*-methyl-*O*-(*NN*-dimethylthiocarbamoyl)hydroxylamines (II) probably proceeds by a radical cage mechanism as shown by kinetic measurements and CIDNP effects in the n.m.r. spectra of the products.

In a previous communication¹ we presented evidence in support of a radical mechanism for the thermal rearrange-

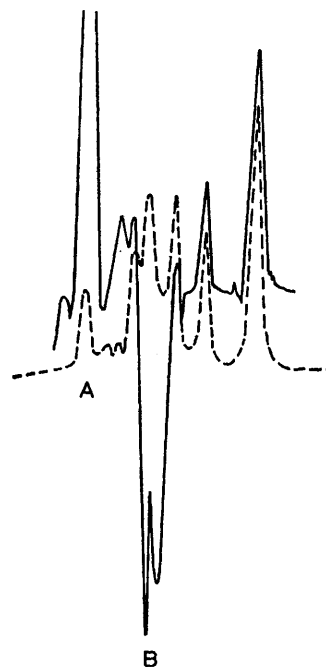
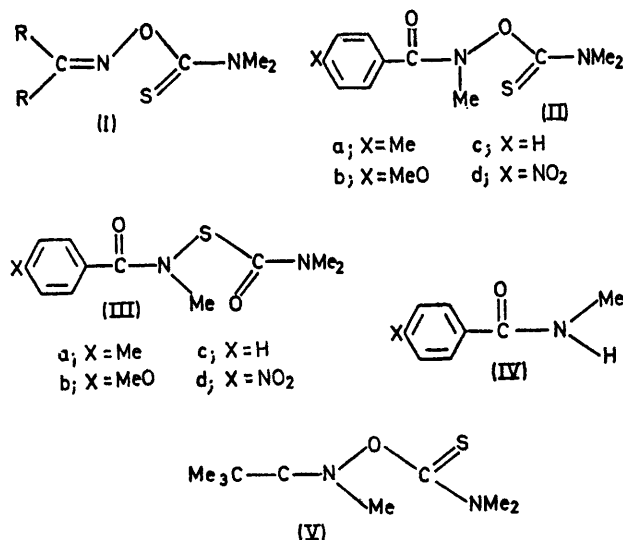
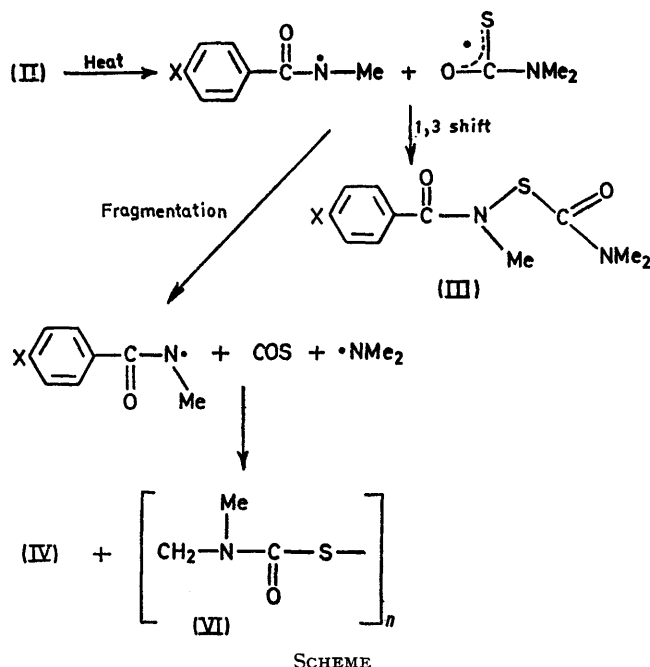


FIGURE. CIDNP effects in the products from (IIa): *N*-Methyl resonances of (IIIa) at A and of (IVa) at B; (—) after 1.5 min; (---) after 15 min.

ment of oxime thionocarbamates (I). As the intermediate imino radical is not appreciably stabilised by conjugation, hydroxylamine derivatives in general should rearrange in a similar manner. In agreement with this prediction, we find that *N*-acyl-*N*-methyl-*O*-thiocarbamoylhydroxylamines

(II) rearrange at low temperatures (25–80°) in a wide range of solvents to give high yields of the isomeric hydroxylamine derivatives (III).

Maximum yields of (IIIa–c) (ca. 95% by n.m.r.) were obtained by allowing a 5% solution of (II) in CHCl₃ to rearrange at room temperature for ca. 120 h. Recrystallisa-



hydroxamic acids, *e.g.* (V), at comparable rates. Moreover added DPPH is decolorised at a rate comparable to that of the rearrangement as followed by changes in the u.v. spectra of the reactants. The reaction rates are relatively insensitive to solvent changes (Table). These observations are very similar to those recorded¹ for the rearrangement of the oxime derivatives (I), indicating a common reaction mechanism for the two processes.

Further evidence for a radical cage mechanism for this 1,3 rearrangement is provided by the observed strong chemically induced dynamic nuclear polarisation² in the reaction products. Solutions of (IIa) in deuteriochloroform were placed in the preheated (120°) probe of a 14092 gauss n.m.r. spectrometer. After 1.5 min the spectra of the products only were observed with the following features: (a) the *N*-methyl resonance of (IIIa) at δ 3.30 is initially more intense than predicted and (b) the *N*-methyl resonance of *N*-methyltoluamide at δ 2.97 appears in *emission*. Both the enhanced absorption[†] and emission decay with time (Figure). Similar results were obtained for (IIa–d).

These results clearly indicate the intervention of radical species in the formation of both (III) and (IV), for which we suggest the reaction shown in the Scheme.

Fragmentation to (IV) is the major pathway at 110–120°, the temperature necessary for the satisfactory observation

Rearrangement of (II) \rightarrow (III) at 60.5°

Reactant	Solvent	$10^3 k(\text{min}^{-1})$	Reactant	Solvent	$10^3 k(\text{min}^{-1})$
(IIa)	Hexane	0.510	(IIa)	Chloroform	1.407
(IIb)	Hexane	0.707	(IIa)	CCl ₄	1.895
(IIa)	Ethanol	0.500	(IIc)	Hexane	0.460
(IIa)	Acetonitrile	0.292	(IIId)	Hexane	0.580
(IIa)	Benzene	0.294	(V)	Hexane	0.978

tion from benzene-petroleum ether gave pure samples[†] of (IIIa) m.p. 99–100°, (IIIb) m.p. 104–106°, and (IIIc) m.p. 79–80°. (IIId) was not isolated in a pure state as extensive decomposition to (IV; X = NO₂) occurred. In all cases the ratio of (IV) to (III) increased with increasing temperature [*e.g.* 35:65 at 60° and 70:30 at 120° for (IIa)].

Kinetic measurements showed that the rate of reaction is insensitive to substitution in the benzene ring (Table), and the rearrangement also occurs with derivatives of aliphatic

of a CIDNP effect. Quantitative conversion into (III) and (IV) is observed, but the fate of the Me₂NCOS radical has not been completely established. Polymeric material is obtained from the reaction, and the n.m.r. spectra of the products indicate structure (VI) for this side product.

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[†] Satisfactory analytical and spectroscopic data were obtained for these new compounds.

[‡] $V_{\text{expt}} = 15$ (see ref. 3).

¹ R. F. Hudson, A. J. Lawson, and E. A. C. Lucken, *Chem. Comm.*, 1971, 807.

² H. R. Ward, *Accounts Chem. Res.*, 1972, 5, 18.

³ H. Fischer and J. Bargon, *Accounts Chem. Res.*, 1969, 2, 110.