

A Free-radical Intermediate in the Thermal Rearrangement of Oxime Thionocarbamates

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Summary A transient free-radical species has been detected by e.s.r. measurements in the thermal rearrangement of oxime thionocarbamates to thioxime carbamates, and evidence is presented which is consistent with this radical being an intermediate in the rearrangement.

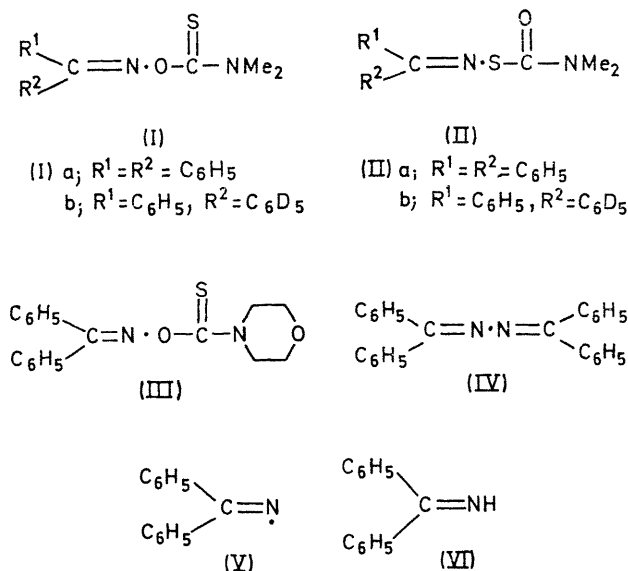
CERTAIN oxime thionocarbamates (I) rearrange in high yield to the corresponding thioxime carbamates (II) on heating for a short while in carbon tetrachloride or benzene.¹

Recent investigations² of the related thermal rearrangement of *O*-aryl thionocarbamates have demonstrated that reaction proceeds *via* the path outlined in Figure 1.

Our results, however, suggest that the rearrangement of oxime thionocarbamates involves an entirely different mechanism involving free-radical intermediates. In the rearrangement of the benzophenone oxime derivative (Ia) in a variety of solvents, a free-radical species was detected by e.s.r. experiments and by the decolorization of diphenylpicrylhydrazyl radical (D.P.P.H.).

Using equimolar quantities of (Ia) and D.P.P.H., 35%

of D.P.P.H. was decolourized in the process of rearrangement of (Ia). The rate of decolourization was closely parallel to that of rearrangement of (Ia) in the absence of D.P.P.H.



E.s.r. measurements taken before, during, and after the rearrangement of (Ia) in solution showed the appearance and subsequent disappearance of a paramagnetic species. Rearrangement of (III) was shown to produce an identical transient spectrum.

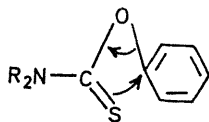


FIGURE 1.

The spectrum obtained in both cases is shown in Figure 2, each component of a triplet of splitting *ca.* 10.3 gauss showing evidence of hyperfine splitting into seven peaks equally spaced by *ca.* 0.35 gauss. The magnitude of the nitrogen splitting constant is consistent with a radical of the structure (V).³ It is assumed that three protons on each of the phenyl substituents, probably those in the *ortho*- and *para*-positions, have approximately equal splitting constants while those of the two remaining protons are undetectably small.

First-order rate coefficients for the rearrangement of p-X-C₆H₄·CMe=N·O·CS·NMe₂ at 54.0°

X	10 ² k (min ⁻¹)	Solvent
H	6.0	Hexane
NO ₂	3.06	Hexane
MeO	4.64	Hexane
H	11.5	Ethanol

Further evidence has been obtained from the nature of the reaction products. When the rearrangement of (Ia) was

carried out by melting the crystalline material at 105°, in the absence of solvent, the azine (IV) was formed in *ca.* 30% yield, with copious evolution of carbonyl sulphide.

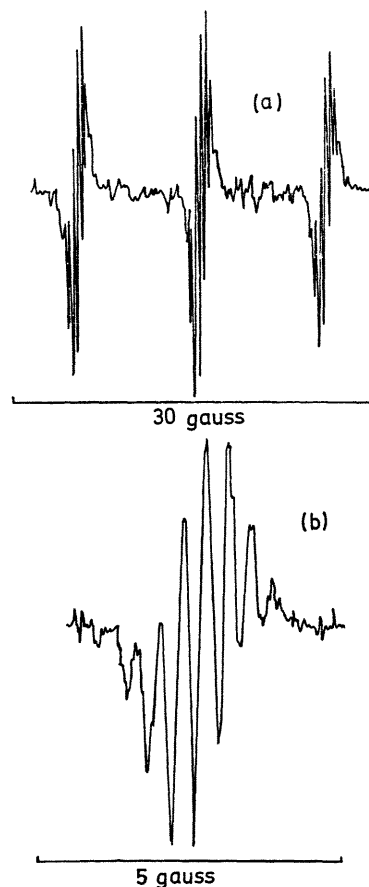


FIGURE 2.

The expected thioxime product (IIa) was also formed in approximately equal quantity. The azine (IV) was identified by mass spectral analysis and by chromatographic comparison with an authentic sample. Furthermore, rearrangement of the deuteriated substrate (Ib) in the presence of an excess of non-isotopically labelled diphenylmethyleimine (VI) produced a mixture (IIb) and (IIa), (in the ratio of 6:1), while (IIb) was shown independently to undergo no isotopic exchange with (VI) under identical experimental conditions.

The lack of appreciable solvent effects on the rate of rearrangement, and the insensitivity of the reaction rate to substitution in the benzene ring in a series of *para*-substituted acetophenone oxime thionocarbamates (Table), are likewise consistent with the formation of a free-radical intermediate in this rearrangement.

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² K. Miyazaki, *Tetrahedron Letters*, 1968, 2793.

³ J. A. Brivati, K. D. J. Root, M. C. R. Symons, and D. J. A. Tmling, *J. Chem. Soc. (A)*, 1969, 1942.