

## Evidence for a Radical Cage Mechanism in the Thermal Elimination of Benzaldoxime Thiocarbamates

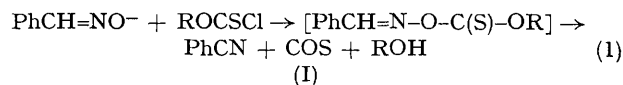
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*Summary* The sodium salt of benzaldoxime and phenyl isothiocyanate give the corresponding *O*-[(*p*-tolyl)thiocarbamoyl]oxime which spontaneously eliminates benzonitrile at least partly by a radical-cage mechanism.

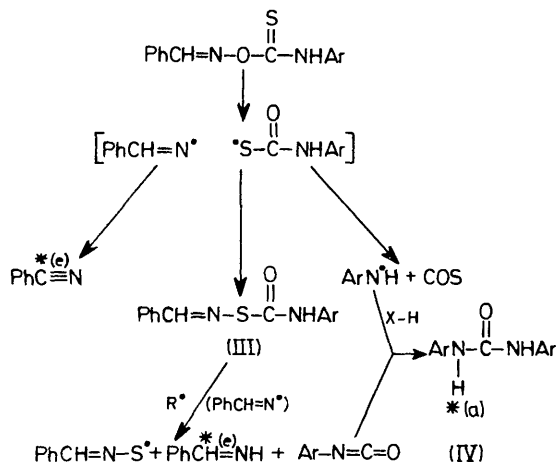
*via* the unstable oxime thiocarbonate (I), by analogy with the reaction of the corresponding ketoxime,<sup>2</sup> is particularly interesting since both *syn* and *anti* oximes give similar yields of nitrile (*ca.* 60%) (equation 1).

OF the various methods for the dehydration of oximes, one of the simplest is the treatment of the oxime with a thiochloroformate.<sup>1</sup> The reaction, which presumably proceeds



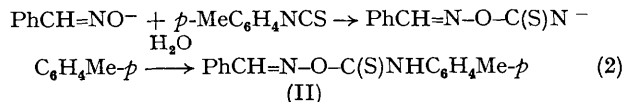
The intermediate (I) is too unstable for isolation, and we find that the corresponding carbamate prepared from *NN*-dimethylthiocarbamoyl chloride decomposes similarly.

Thiobenzoyl chloride and benzaldoxime give an intermediate which rapidly decomposes in chloroform, to give benzonitrile, carbonyl sulphide, biphenyl, and dibenzoyl disulphide.



SCHEME. (a) CIDNP absorption, (e) CIDNP emission, Ar = C<sub>6</sub>H<sub>4</sub>Me-*p*.

We have been able to isolate the *O*-[(*p*-tolyl)thiocarbamoyl]oxime (II) from the reaction of the sodium salt of benzaldoxime with *p*-tolyl isothiocyanate (equation 2).



This compound decomposed at room temperature in chloro-

† In order to apply Kaptein's rules, the *g* value of *p*-MeC<sub>6</sub>H<sub>4</sub>NHCOS• was assumed to be similar to that for Me<sub>2</sub>NCOS•, which is much greater than the value for the iminyl radical. The coupling constant (*a<sub>c</sub>*) was assumed to have the same sign (negative) as in the diphenyliminyl radical (C. Brown, R. F. Hudson, and A. J. Lawson, *J. Amer. Chem. Soc.*, 1973, 95, 6500), and it was also calculated by the INDO method.

<sup>1</sup> D. L. J. Clive, *Chem. Comm.*, 1970, 1014.

<sup>2</sup> D. Cross, R. J. G. Searle, and R. E. Woodall, *J. Chem. Soc. (C)*, 1971, 1833; R. F. Hudson, A. J. Lawson, and K. A. F. Record, *J.C.S. Perkin II*, 1974, 869.

<sup>3</sup> R. Kaptein, *J. Amer. Chem. Soc.*, 1972, 94, 6251.

form into a mixture of products including di-*p*-tolylurea, carbonyl sulphide, and sulphur in addition to benzonitrile which is the major product.

Evidence for radical pathways was obtained by carrying out the reaction in an n.m.r. tube, and observing strong CIDNP effects for the N-H proton of ditolylurea. Strong emission was observed in the <sup>13</sup>C n.m.r. spectrum associated with the nitrile group.

The application of Kaptein's rules<sup>3</sup> predicts emission for the nitrile carbon atom in a solvent cage process† as experimentally observed. Since the reaction is complex with appreciable escape of radicals from the cage, this correlation suggests that the elimination proceeds, at least in part, in a solvent cage. The sign of the CIDNP effects suggest in a similar manner that the imine and di-*p*-tolylurea are formed from escaped radicals. These observations can be explained as shown in the Scheme.

According to this explanation of these observations, the radical pair either disproportionates into the nitrile and *N*-phenylthiocarbamic acid, or recombines to give the carbamoylthio-oxime (III). The latter then undergoes a 1,2-elimination of *p*-tolyl isocyanate, promoted by the iminyl or toluidinyl radical. Strong CIDNP effects in the imine formed show that this radical reacts in an unusual way in abstracting a hydrogen atom from the rearranged product (III). Combination of the aminyl radical with the isocyanate gives the corresponding urea (IV).

No e.s.r. signals were observed in any of these reactions as the lifetime of the imine radical under these conditions is too short to be observed at room temperature. Photolysis of benzaldoxime *p*-tolylthiocarbamate at -30 °C in toluene in the cavity of an e.s.r. spectrometer gave a strong signal (*g* = 2.0028; *a<sub>N</sub>* = 11.3 and *a<sub>H</sub>* = 78 G) due to the phenyliminyl radical.

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