Conversion of an Oxime into the Corresponding Thio-oxime

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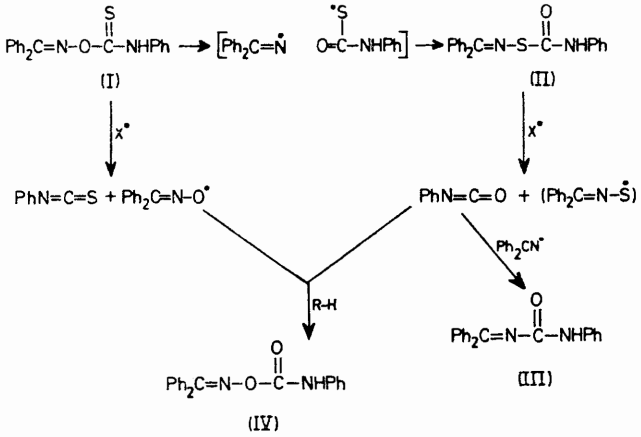
Summary The thio-oximate anion derived from benzophenone oxime is prepared in solution by the action of sodium t-butoxide on *N*-diphenylmethylene-*S*-phenylcarbamoylsulphimide, itself prepared by thermal rearrangement of the isomeric *N*-diphenylmethylene-*O*-phenylthiocarbamoylhydroxylamine.

The preparation of thio-oximes as unstable intermediates, and their alkylation have recently been described.[1a] We now report a different approach to the synthesis of these interesting compounds from the corresponding oxime. The method involves the rearrangement of the *S*-phenylcarbamoylsulphimide, prepared by addition of the oxime to phenyl isothiocyanate, to the corresponding *O*-phenylthiocarbamoylhydroxylamine,[2] followed by base-catalysed elimination of the thio-oximate anion.

The sodium salt of the oxime was added to 1 equiv. of phenyl isothiocyanate in dimethylformamide (DMF) at 0 °C, and the mixture was treated with water after the reaction had proceeded for 1·5 h. The oxime thiocarbamate (I), m.p. 64—66 °C, was obtained in 70% yield. The rearrangement of (I) to (II) had to be performed under special conditions.

In solution (CCl_4 or $CHCl_3$) the e.s.r. spectra of the iminyl and iminoxyl radicals persisted for *ca.* 1 min. The yield of rearranged product (II) was low (*ca.* 10%), and the major products formed under these conditions were the urea (III), m.p. 161—162 °C,[3] and the carbamate (IV), m.p. 174—176 °C.[4] These are probably formed in free-radical processes by the addition of iminyl and iminoxyl radicals to phenyl isocyanate, itself obtained by radical elimination from (II). Compound (II) is stable in solution, and in the presence of weak bases elimination is slow. The formation of the products (III) and (IV) is explained by the paths in the Scheme.

High yields (*ca.* 70%) of (II) were obtained by suspending (I) (3 g) in hexane (15 ml) and stirring the mixture for 24 h in the presence of sunlight. Similar yields [2·2 g of (II) from 3·0 g of (I)] were obtained by allowing the solid form of (I) to remain for 3 weeks at room temperature. The product, melting at 110—120 °C with decomposition to give a high yield of carbonyl sulphide and benzophenone azine was characterised by the carbonyl stretching frequency of 1668 cm^{-1} (replacing the C=S band at 1100 cm^{-1}) and by elemental analysis.



SCHEME

Treatment of (II) in DMF with sodium t-butoxide produced an intermediate red coloration attributed to the thio-oximate anion, reaction of which with 1 equiv. of 2,4-dinitrofluorobenzene for 2 h followed by treatment with dilute HCl and extraction with chloroform gave *N*-(2,4-dinitrophenylthio)diphenylmethyleneamine (yield 90%), m.p. 226—228 °C.[1b]

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