Preparation and Rearrangement of *O*-Sulphinyl Oximes

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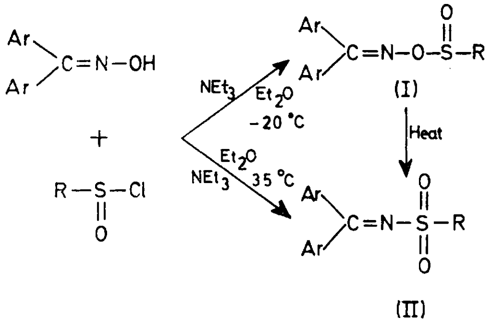
Summary Aldoximes and ketoximes react rapidly with sulphinyl chlorides to give derivatives which rearrange at low temperatures *via* radical pathways to the corresponding sulphonyl imines, and in the case of the aldoximes to imines, aldehydes, and sulphonyl imines.

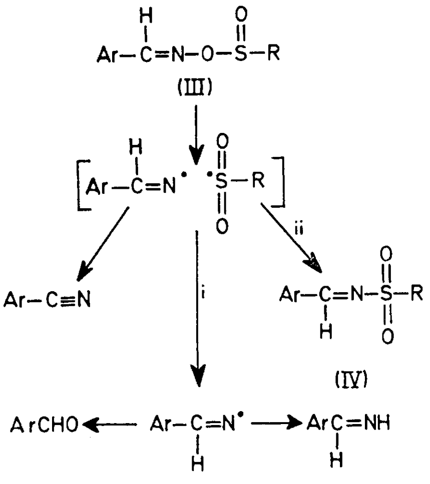
We report the synthesis and rearrangement of some *O*-sulphinylated derivatives of aryl ketoximes and aldoximes. The *O*-sulphinylated ketoximes (I) were prepared by the reaction of the ketoxime with a sulphinyl chloride in the presence of triethylamine in ether at −20 °C. The sulphonyl imine (II) may be obtained directly by carrying out the same reaction at room temperature. Heating solid (I) or a solution of (I) results in a quantitative formation of (II). Compound (IIb) was found to be identical to the product of the reaction of di-*p*-tolylmethanimine and benzenesulphonyl chloride.



(Ia), (IIa); Ar = R = Ph
(Ib), (IIb); Ar = C_6H_4Me-*p*, R = Ph
(Ic), (IIc); Ar = Ph, R = Me

Well resolved e.s.r. spectra of ketiminyl radicals[1] (g = 2·0033, a_N = 1·0 mT) and sulphonyl radicals[2] (g = 2·0043) were observed when solutions of (I) were placed in the probe of an e.s.r. spectrometer at 35 °C.

The progress of the rearrangement (Ic) → (IIc) was monitored by ^{1}H n.m.r. spectrometry by observing the disappearance of the methyl sulphinyl resonance at δ 2·8 and the simultaneous formation of the methyl sulphonyl resonance at δ 3·4. The rearrangement was complete within 5 min at 35 °C. No abnormal resonances were observed during the rearrangement.



(IIIa), (IVa); Ar = R = Ph
(IIIb), (IVb); Ar = Ph, R = C_6H_4Me-*p*
(IIIc), (IVc); Ar = Ph, R = Me
(IIId), (IVd); Ar = $C_6H_4NO_2$-*p*, R = Me
(IIIe), (IVe); Ar = $C_6H_4NO_2$-*p*, R = C_6H_4Me-*p*
i, Escape; ii, In-cage recombination

The corresponding sulphinyl derivatives (III) of benzaldoximes were similarly prepared, and these were shown to give rise to the sulphonyl imines (IV), aryl nitriles, and aryl aldehydes on heating. The sulphonyl imines may be obtained directly by reaction of the oxime and sulphinyl chloride at room temperature. Compounds (IIIa; R = Ar = Ph) and (IIIc; Ar = Ph, R = Me) are oils and all compounds (IIIa—e) decompose explosively at room temperature but are quite stable in solution or as solids below −30 °C.

Signals due to the phenyl methaniminyl radical ($g = 2{\cdot}0028$; $a_N = 1{\cdot}0$, $a_H = 7{\cdot}8$ mT) and toluene-*p*-sulphonyl radical[2] were observed when solutions of (IIIb) were placed in the probe of an e.s.r. spectrometer at 35 °C.

When a solution of (IIId; Ar = $C_6H_4NO_2$-*p*, R = Me) *in* chloroform was placed in a 60 MHz n.m.r. spectrometer at 35 °C, CIDNP effects were observed for the formation of (IVd), enhanced absorption at δ 9·8 corresponding to the proton resonance of the CH proton of (IVd), and emission signals for the CH protons of *p*-nitrobenzaldimine δ 9·3, and *p*-nitrobenzaldehyde δ 10·9. No CIDNP effect was observed in the methyl resonance of the sulphonyl group of (IVd) at δ 3·4. During the rearrangement, resonances at δ 9·0 and 3·0 [corresponding to the CH proton and Me group of (IIId) respectively] disappear.

We were unable to isolate pure sulphonyl aldimines from the rearrangement reactions, but they were prepared in a pure state from the room temperature reaction of the aldoxime with the sulphinyl chloride. These products had identical n.m.r. chemical shifts, to the products of the rearrangement as observed in the CIDNP experiments.

The sulphonyl aldimines (IV) are rapidly hydrolysed by atmospheric moisture to the corresponding benzaldehyde and sulphonamide but at this time the origin of the aromatic aldehyde which is derived from the sulphinylated aldoxime is unknown. The large CIDNP emission however shows that it originates from a radical precursor.

The above evidence suggests that the rearrangement of the sulphinylated oxime to the sulphonyl imine occurs *via* a free radical pathway. Kaptein's rules[3] (giving the sign of the CIDNP effect) predict that the sulphonyl imine is formed from an in-cage radical recombination of the iminyl and sulphonyl radicals, and that the benzaldehyde and benzaldimines are products from the escaped iminyl radicals.

This is the first rearrangement of an aldoxime derivative proceeding by a free radical mechanism although free radical pathways have recently been detected[4] for the decomposition of some other oxime derivatives.

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