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THERMOLYSIS OF OXIME O-ALLYL ETHERS

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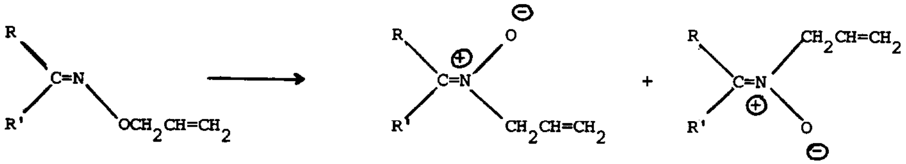
In the course of work designed to explore the synthetic potential of O-allyl oxime and N-allyl hydrazone derivatives, we have studied the thermolyses[1] of the oxime O-allyl ethers 1.



1. 2. 3.

a) $R = C_6H_5$; $R' = H$: b) $R = R' = CH_3$: c) $R,R' = -(CH_2)_5-$

The thermal interconversions of the oxime O-allyl ether (1a) and the nitrones (2a and 3a) have been categorised[2] as [2,3]-sigmatropic rearrangements. We present here evidence which suggests that their transformations proceed, at least in part, by an homolysis - recombination mechanism[3].

When heated to 210°C in the probe of an e.s.r. spectrometer, either neat, or in solution in o-dichlorobenzene(cf. 2), the oxime O-ethers (1a and 1b)[4] gave rise to signals which after one or two minutes assumed the forms shown in the Figure. These signals persisted for ~ 20-40 minutes after which they became severely distorted and eventually disappeared under an intense singlet, apparently associated with the production of carbon. Examination of the sample at this stage revealed significant darkening, and NMR analysis suggested the presence of ~ 5% nitrone.

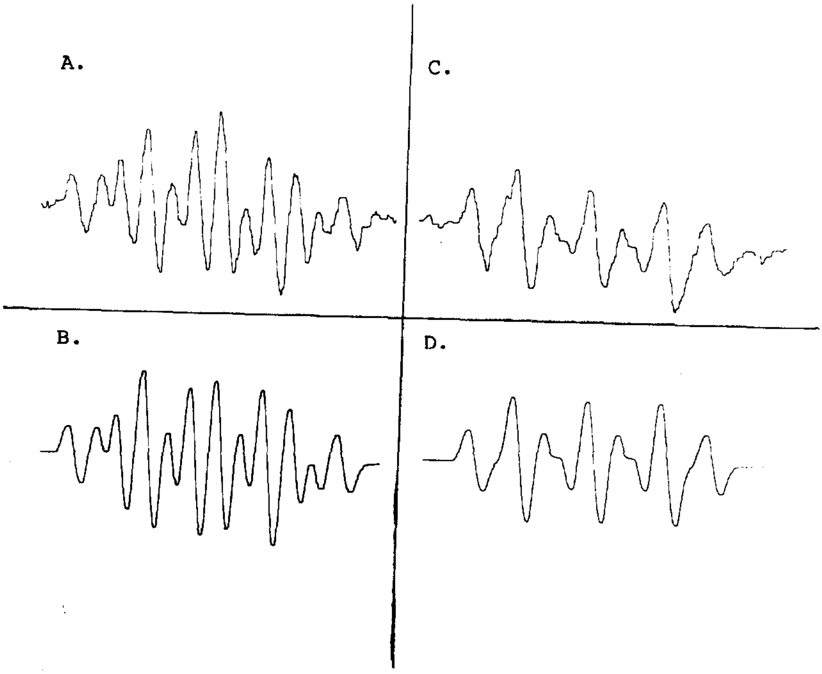
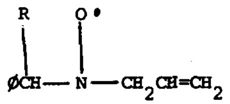


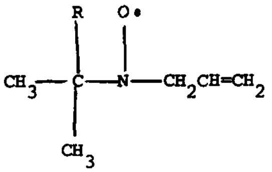
FIGURE. A: e.s.r. spectrum from 1a.; B: computer simulated spectrum; a_N = 14.8, $a_H(2)$ = 9.8, a_H = 5.9, line width = 1.5 mT; C: e.s.r. spectrum from 1b; D: computer simulated spectrum; a_N = 15.1, $a_H(2)$ = 9.2, line width = 1.5 mT.

The signal associated with 1a was interpreted in terms of the coupling arising from one nitrogen, two equivalent protons and one other proton. The abnormal line width can be associated with the high modulation amplitude necessary to obtain an acceptable signal to noise ratio. The signal associated with 1b was similarly interpreted in terms of the coupling arising from one nitrogen and two equivalent protons. Computer simulated spectra, and the parameters used in their construction, are shown in the Figure.

These signals suggest the presence of the nitroxide radicals 4 (from 1a) and 5 (from 1b) where R is either allyl or iminoxy.



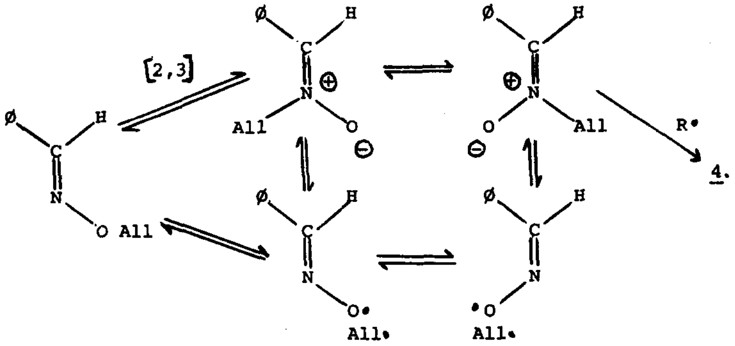
4.



5.

The hyperfine splitting constants are in accord with the suggested structures[5], and the well-known stability of such radicals means that their detection in the reaction mixture need not imply significant yields of products derived from them. The simplest, although not the only possible, mode of formation involves homolysis of the C-O bond of the oxime O-ether followed by the addition of a radical to the double-bond of the nitrone (see Scheme). Such a reaction pathway has been invoked to account for the formation of nitroxide radicals during the thermolysis of benzophenone oxime O-benzhydryl ether[5a].

Scheme.



In summary, while published work on 1a and closely related systems suggests that the conversion $1 \rightleftharpoons 2$ is a [2,3]-sigmatropic rearrangement, our results imply that, at least in part, it is a reversible Martynoff rearrangement[6], proceeding via a radical pair, escape from which may lead to other, observable paramagnetic species. It would appear that the thermolysis of oxime O-allyl ethers can be included among the growing number of reactions which proceed by competitive concerted and homolysis-recombination pathways(cf. 7).

We are continuing our studies of these and related systems.

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