

A NEW TRIGONAL N-OXIDE THERMAL ELIMINATION REACTION TO GIVE OXIMES

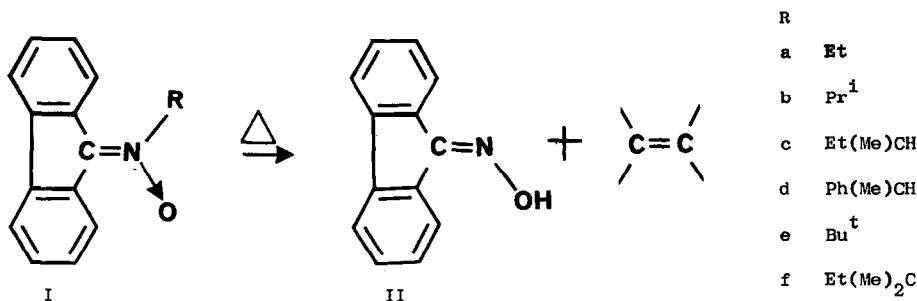
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While the Cope thermal elimination reaction of tetrahedral N-oxides (tertiary amine oxides) has been investigated in depth<sup>1</sup>, little information is available on the corresponding thermal reaction of trigonal N-oxides (nitrones).<sup>2,3</sup> The present report suggests that this type of elimination reaction may be general for those nitrones containing the necessary  $\beta$ -hydrogen atoms and where stereochemistry permits the formation of planar cyclic five membered transition state.

The nitrone elimination reaction to give oxime (II) and olefinic products was studied in the fluorenylidene series (I), where several members (I e and f) were found to undergo olefin elimination under mild experimental conditions ( $\sim 30^\circ\text{C}$  in  $\text{CDCl}_3$  solution). The results in the table were obtained when the nitrones (I) were heated without solvent under vacuum. The product olefins were collected and analysed by g.l.c. and m.s.



TABLE

Nitrone	Temperature ( $^\circ\text{C}$ ) <sup>f</sup>	Olefins
a	210	ethene
b	180	propene
c	180	but-1-ene (58%), but-2-ene (32% <u>E</u> , 10% <u>Z</u> )
d	155	styrene
e	80	2-methyl propene
f	80	2-methylbut-1-ene (80%), 2-methylbut-2-ene (20%)

<sup>f</sup> Lowest temperature at which an appreciable evolution of olefin was observed

The proportions of but-1-ene (58%) and but-2-ene (42%) or 2-methylbut-1-ene (80%) and 2-methylbut-2-ene (20%) detected from their precursors Ic and If suggest that the direction of elimination is mainly dependent on the availability of  $\beta$ -hydrogen atoms (statistical factor). The ratio of Z (10%) and E (32%) but-2-ene (formed by pyrolysis of Ic) is consistent with the steric influence to be expected in a cyclic five membered transition state which favours the E isomer. These results show a close similarity to those found in the Cope thermal elimination of tetrahydrai-N-oxides which proceeds via a concerted cis elimination mechanism.<sup>1</sup> The ease of elimination of olefin from nitrones Ie and f, compared with Ia, b, c and d, may be rationalized in terms of the relief in steric strain, concomitant gain in  $\pi$  delocalization associated with the oxime product, and conformational restrictions placed upon the R substituents by the proximate fluorenyl hydrogen atoms. This elimination reaction seems to be general for a range of N-alkyl aldo- and ketonitrones which are heated directly or pyrolysed after generation in situ.<sup>5</sup>

The present observations are pertinent since the thermal rearrangement of oxaziridines has become a standard synthetic route to nitrones and N-alkylhydroxylamines.

A more detailed mechanistic analysis of this nitron elimination reaction is in progress.

#### REFERENCES

1. A.C. Cope in "Organic Reactions", Vol. 11, Wiley, New York, 1960, p.317.
2. Suggestions have previously been made that nitron intermediates are involved in the formation of oxime and olefinic products in the pyrolysis of an oxaziridine<sup>3</sup> and from the reaction of aldehydes and N-(1-aryl-2-nitroethyl)hydroxylamines.<sup>4</sup>
3. W.D. Emmons, J. Amer. Chem. Soc. 1957, 79, 5739.
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