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GENERATION OF ALLYLOXY ANIONS OR RADICALS : SOME PRELIMINARY OBSERVATIONS

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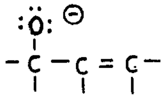
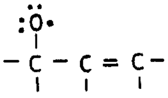
Allyloxy anions (I) or radicals (II) are isoelectronic with the corresponding epoxy carbanions and radicals represented by III and IV respectively.



I



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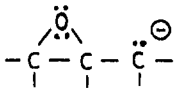
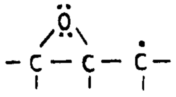


III



IV

Generation of III and IV would be expected to be followed by rapid rearrangement to I and II respectively,[*] because of a combination of two factors: a) relief of strain accompanying the opening of a three-membered epoxide ring, and (b) greater stability of electron/s localized on oxygen relative to carbon. What needs investigation is whether the process is so rapid that products derived from III and IV with an intact epoxide group cannot be obtained, or whether there is a partitioning between the pairs I and III or II and IV.

In this connection we wish to report some reactions of a 1:1 mixture of *cis-trans* 1-iodo-2,3-epoxy-3,7-dimethyl-oct-6-ene (VI).

1) A NEW REACTION RESEMBLING THE WHARTON REACTION

The allylic alcohol, linalool, VIII, was formed in quantitative yields when the iodide (5 g) in dry dimethyl sulphoxide (30 ml) was treated with tosyl hydrazine (3.3 g) in the presence of calcium carbonate (1.8 g) and the mixture

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[*] For simplicity fully developed carbanions are depicted and the word 'rearrangement' used. The partitioning may be depicted as competition between proton capture by an incipient carbanion and concerted opening of the epoxide.

left at 0°C for four days. At 70 to 80°C, the reaction was complete in ten minutes but TLC indicated slight contamination. Variable amounts of linalool were obtained by the action of the sodium or potassium salt of tosyl hydrazine, with or without added base, in solvents such as <u>tert</u>. butanol, tetrahydrofuran and dioxan*, but required refluxing for several hours.

The reaction is envisaged as going <u>via</u> the alkyl diimide VII shown in Scheme (Path a). Formation of a nitrogen-containing intermediate is inferred from the observation that if aniline is used in place of tosyl hydrazine, the epoxy halide appears to be converted to nitrogen-containing compounds. Reactions of similar epoxy halides with nucleophiles (1) make it safe to presume that displacement of the iodine on the primary carbon would be preferred to attack on the epoxide.

There remained a possibility that the diimide had isomerized to the corresponding hydrazone and that the <u>latter</u> was the source of linalool. Hence the above reaction was repeated using a deuterated derivative of tosyl hydrazine in which the three exchangeable hydrogens were replaced by deuterium. The linalool produced was found to be entirely free of non-exchangeable deuterium as judged from IR and NMR: this shows that the hydrazone could not have been formed to any extent. This establishes that the reaction bears no more than a superficial similarity to the Wharton reaction (1).

It would not be appropriate at this stage to comment on the exact mode of decomposition of the diimide - particularly as the reaction was also observed to proceed even if calcium carbonate was omitted. It is sufficient to recall that Cram (3) has shown that alkyl diimides lose nitrogen to generate carbanions under basic conditions, but that in the absence of bases a radical cage mechanism is operative.

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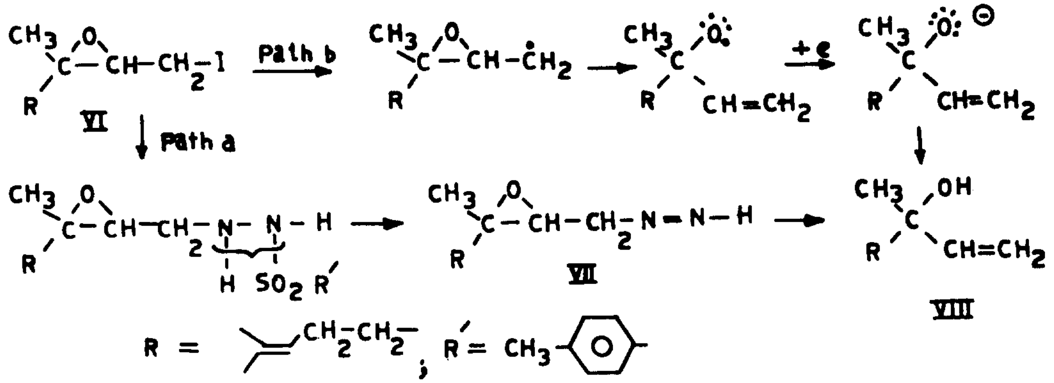
* In dioxan substantial amounts of dihydrolinalool were formed as a result of the reduction of the less substituted double bond by diimide generated from excess tosyl hydrazine.

SCHEME



2) REACTION WITH SODIUM NAPHTHALENIDE

Alkyl iodides have been reported to react with sodium naphthalenide to generate free radicals (4). Hence a solution of the naphthalenide in dimethoxyethane (1 molar) was run into the iodide dissolved in the same solvent (0.5 molar) at -8 to -10°C till the bluish-green colour persisted. Quantitative conversion to linalool occurred. This happened even though relatively concentrated solutions were being brought together. Under these conditions the dimerization of the carbon radical or its attack on the double bond should be favoured relative to its reduction to the carbanion (4). Failure to detect these products indicates that the rearrangement to the allyloxy radical must be faster. The overall conversion must then follow Scheme (Path b).

3) REDUCTIVE ELIMINATION WITH ZINC IN THE PRESENCE AND ABSENCE OF PROTON DONORS

Use of zinc and acetic acid for reductive conversion of epoxy halides to allyl alcohols has been reported before (5). The conditions described herein are much milder. Thus the iodide (0.7 g) in dry ether (50 ml) containing acetic acid (0.5 ml) was stirred with activated zinc dust (4 g) at room temperature for fifteen minutes. Total conversion to linalool occurred. Careful examination of the crude product by TLC failed to reveal any other products. Complete absence of 2,3-epoxy-3,7 dimethyl oct-6-ene is significant. Since one may be dealing with the protonated epoxy iodide, the reaction was repeated with water (0.5 ml) as the proton source. The same result was obtained except for a five-fold drop in rate. In the absence of acid the reaction can be formulated as involving the rearrangement of the alkyl zinc iodide initially-formed to the allyloxy anion.

To test this hypothesis use was made of acetic anhydride as a trapping agent (6). The iodide (8 g) in dry ether (60 ml) containing acetic anhydride (8 ml) was stirred with activated zinc dust (8 g) at room temp, for one hour. Linalool acetate was the major product but was accompanied by substantial amounts of linalool (45 and 40 per cent respectively by GLC). Formation of the acetate does not represent simply acetylation of linalool as it was shown that linalool fails to react under the same conditions. Its failure to acetylate also rules out any possibility that acylium ions are involved (7). The formation of linalool as a by-product probably involves the abstraction of a proton from acetic anhydride by the allyloxy anion.

The identity of dl-linalool and dl-linalool acetate obtained in this work was confirmed by comparison with authentic samples.

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