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AN INTRAMOLECULAR ALKOXYHYDROPEROXIDE FORMED DURING OZONOLYSIS IN INERT SOLVENT.

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Ozonolysis of olefins in hydroxylic solvents often leads to alkoxyhydroperoxides through the interaction of solvent with an intermediate believed to be the Criegee zwitterion (1). We wish to report an analogous intramolecular reaction which occurs during the ozonolysis in an aprotic solvent of the hydroxydiene diterpenoid cis abienol (I), to give the alkoxyhydroperoxide (II). An intramolecular reaction of this type does not appear to have been previously observed.

Ozonolysis of cis abienol (I) in ethyl acetate at -70° followed by oxidative hydrolysis with glacial acetic acid and hydrogen peroxide gave a crystalline product, m.p. 167-9° (with evolution of gas), in 50-70% yield. The same compound crystallized directly during ozonolysis when a more concentrated ethyl acetate solution was ozonized. The product, $C_{16}H_{28}O_3$, had hydroxyl but no carbonyl bands in the infrared. It liberated iodine from potassium iodide in acetic acid and was therefore a peroxide. Reduction with lithium aluminium hydride gave the known (2) diol (II), identified by physical comparison and by oxidation to (+)norambreinolide (III). This result suggests the peroxide had either structure (IV) or (V).

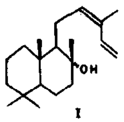
t-Butoxymethyl hydroperoxide and t-butylhydroxymethyl peroxide, simple analogues of (IV) and (V), can be differentiated by quantitative reactions with potassium iodide and with lead tetraacetate (3). The ozonolysis product liberated iodine quantitatively from potassium iodide within five minutes, and reaction with lead tetraacetate was complete within ten minutes, indicating that the compound had the alkoxyhydroperoxide structure (IV).

The ozonolysis product on treatment with sodium hydroxide in ethanol gave approximately equal amounts of the known hemiacetal (VI) and the known hydroxyacid (VII) (2)(4). While the acid (VII) might be expected from both structures (IV) or (V), the hemiacetal (VI) is unlikely to be formed from structure (V) by base hydrolysis.

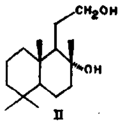
The infrared spectrum of the ozonolysis product provides support for structure (IV). Besides bonds in the region 1080-1082, 967, 890-896 cm^{-1}, all of which are also present in the hemiacetal (VI), and all of which are assigned to the ether group (4), a further strong bond occurs at 840 cm^{-1} very close to the position (839 cm^{-1}) assigned to a hydroperoxy group in the spectrum of α-hydroperoxyethyl ether (5).

The p.m.r. spectrum of the ozonolysis product (IV) also closely approximated that of the hemiacetal (VI); in particular the methyl signals in (IV) fell at 9.13, 9.13, 9.13 and 8.70τ, while in (VI) they occured at 9.13, 9.13, 9.13 and 8.69τ. The peroxide had a single proton triplet at 4.36τ (C_{12} proton) while the C_{12} proton of the hemiacetal occured as a broad band from 4.0 to 4.75τ.

While the alkoxyhydroperoxide may form by interaction of the C_8 hydroxyl group with a zwitterion formed at C_{12}, it seems very attractive to suggest that the product forms by attack of the hydroxyl group on the molozonide (VII).



I



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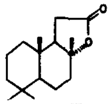

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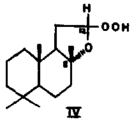

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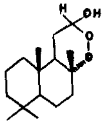

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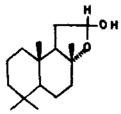

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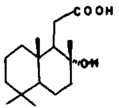

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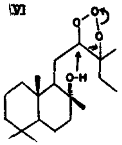

VIII

References

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