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THE PYROLYTIC REARRANGEMENT OF A GERMOCRENE OXIDE

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The recent report[1] of the rearrangement on pyrolysis of a cyclodecene oxide prompts us to describe a similar rearrangement. Pyrolysis of the oxide[2] (1) in a sealed evacuated tube at 155°C for 24 hr. or in refluxing tetralin for 1 hr. yielded a crystalline alcohol believed to be (2) (30%), $C_{15}H_{24}O$, $\nu_{max.}^{Nujol}$ 3350cm^{-1}. τ(CDCl$_3$) 5.20 (1Hm), 8.33 (9Hs), 8.85(3Hs) and a liquid ketone(3) (41%), $C_{15}H_{24}O$, ν max. (film), 1710cm^{-1}. τ(CCl$_4$) 9.60 (2Hm); 8.95 (3Hs); 8.42(6Hs); 7.87 (3Hs). Dehydrogenation with 10% Pd/C in an evacuated tube at 325° yielded the liquid ketone (4), the structure of which was established by synthesis from the acid[3] (5) (reaction with methyl lithium). With the proviso that no rearrangement has taken place during dehydrogenation this leads to two possible structures for (3), since the n.m.r. spectrum indicates the presence of an isopropylidene group and two protons in a cyclopropane ring, one terminus of which must be the carbon (a) bearing the ring methyl group. Junction of (a) and (b) leads to (3) while (a) - (c) bond formation gives an isomer in which the double bond is conjugated to the cyclopropane ring. Ozonolysis of (3) gave a diketone, ε_{215nm} 220, excluding the alternative structure in which the newly generated carbonyl would have been conjugated with the cyclopropane ring (ε of at least 4000 expected).[4]

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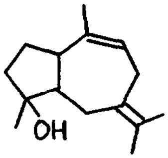

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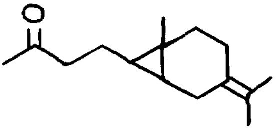

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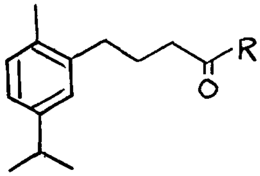
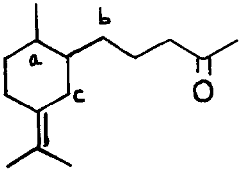


4 (R=CH$_3$)
5 (R=OH)



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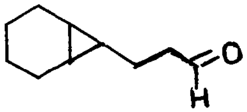

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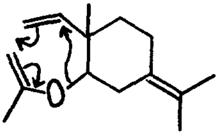
The generality of the reaction was tested by pyrolysis of the mono-oxides of 2,5-dimethylhexa-1,5-diene, 1,5-cyclooctadiene, and cis, trans-cyclodeca-1,5-diene.[5] Only in the latter case could any cyclopropyl carbonyl compounds be detected, there the aldehyde (7) ν max. 2700, 1700cm.$^{-1}$ τ(CCl$_4$) 0.17 (1Ht J=2Hz), 9.2 (3Hm) was formed in 27% yield at 250°C.

A radical mechanism has been proposed for the transformation[1]. However it is possible that an electrocyclic[6] rearrangement of (1) to (8) followed by a second electrocyclic transformation could generate (3).



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1. K. Wada, Y. Enomoto, and K. Munakata, Tetrahedron Letters, 1969, 3357
2. E. D. Brown and J. K. Sutherland, Chem.Comm., 1968, 1060
3. S. Dev and P. G. Guha, J.Ind.Chem.Soc., 1948, 25, 13
4. W. G. Dauben and G. H. Berezin, J.Amer.Chem.Soc., 1967, 89, 3449
5. W. Dittman and F. Sturzenhofecker, Ann., 1965, 688, 57
6. R. Hoffmann and R. B. Woodward, Accounts Chem.Res., 1968, 1, 17