

EREMOLACTONE

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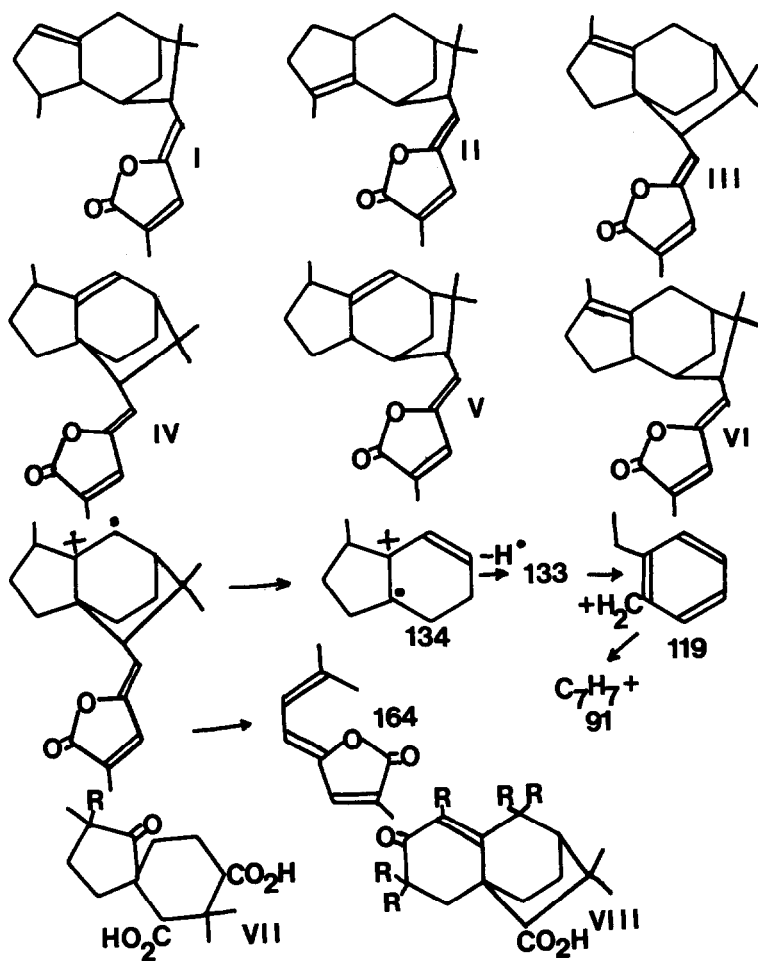
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Eremolactone, from Eremophila freelingii, is a new type of diterpene for which the formula (I) was put forward as a working hypothesis.¹ Isoeremolactone, suggested possible structure (II),¹ is readily obtained by bond isomerisation, and has recently² been assigned the structure (III) by X-ray analysis. We present some independent evidence to support (III) and suggest (IV) for eremolactone.

High resolution of the n.m.r. spectrum of eremolactone has shown that a band due to the proton on the nuclear double bond is clearly resolvable as a quartet at τ 4.15 ($J_2 = 7$; $J_2 = 2$ c/sec.) which immediately makes (I) untenable; an identical quartet is found in eremone,¹ lacking the lactone system.

Taking into account previous evidence,¹ the formula of eremolactone could be modified to (IV) or (V), with (III) or (VI) for isoeremolactone. Owing to the small quantities available, further work was confined largely to the use of mass-spectra.

Eremolactone (molecular ion 298) has a base peak at 134 and significant peaks at 165, 164, 135, 119, 92 and 91; the 134 peak at high resolution corresponds to $C_{10}H_{14}$ and that at 164 to $C_{10}H_{12}O_2$. Eremone (molecular ion 246) has peaks at 147, 135, 134 (base peak), 119, 105, 92 and 91, and tetrahydroeremolactone (lactone system hydrogenated) gives peaks at 302, 175, 173, 133 (base), 132, 131, 119, 105 and 91. Cleavage is therefore largely due to the nuclear double bond and the main fragments are explicable by the scheme below.



Isoeremolactone shows a more complex breakdown at higher mass-numbers with a base peak at m/e 173 instead of 134, suggesting that the double bond has moved away from the doubly allylic position found in (IV) where it facilitates complete cleavage of the bridge carrying the lactone.

This evidence, while strongly in agreement with (IV), does not copclusively prove the termination of the bridge. Neutral permanganate on eremolactone gives a ketodicarboxylic acid (VII) m/e 282 (2,4-dinitrophenylhydrazone dimethyl ester, $C_{23}H_{30}N_4O_8$, m. p. 165-168^o). Deuteration with NaOD in refluxing dioxan introduces only one D (m/e 283) agreeing with cleavage of the double bond in (IV), to give a cyclopentanone with one replaceable H; (V) would permit introduction of two D into the corresponding ketone.

Furthermore, oxidation of isoeremolactone gives a diketocarboxylic acid, ¹ (m/e 266), converted by alkali into (VIII; R = H), m/e 248, λ_{max} . 242 $m\mu$, ν_{max} . 1670 and 1623 cm^{-1} . Deuteration gives (VIII; R = D) (m/e 253) with tetradeutero- (m/e 252.1367); the n. m. r. spectrum of (VIII; R = D) shows the lack of a peak due to =CH compared with a peak at τ 4.13 in (VIII; R = H). The alternative from (VI) should permit introduction of a maximum of six D; this is excluded from the mass-spectral evidence. The position of the bridge at the ring-junction is also supported by failure ¹ to convert (VIII; R = H) into a phenol.

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References

1. A. J. Birch, J. Grimshaw, and J. P. Turnbull, J. Chem. Soc., 2412 (1963).
2. Yow-Lam Oh and E. N. Maslen, Tetrahedron Lett., **28**, 3291 (1966).