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# AEROBIC OXIDATION OF 8β(H),1β-METHYL-CIS-TRICYCLO(6.2.2.$0^{5,12}$)DODEC-5-EN-7-ONE : FACILE FORMATION OF AN ALLYLIC HYDROPEROXIDE

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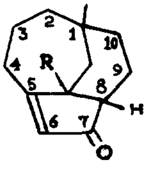
The susceptibility of βγ-unsaturated ketones to undergo oxygenation at the γ-position with simultaneous reconjugation is well recorded[1]. We report here the facile oxygenation of an αβ-unsaturated ketone at the γ-position with the formation of a hydroperoxide. In connection with a project operative in these laboratories for the synthesis of Isoclovene, the unsaturated ketone (I)[2] [UV 242 nm[3] ($\epsilon$= 10,480), IR($CHCl_3$) 1700, 1620 $cm^{-1}$, NMR($CCl_4$) $\delta$ 5.82 (d,J= 2Hz, 1H,C=CH), 0.91(s,3H,C-$CH_3$), red 2,4 DNPH m.p.150°] was prepared as an intermediate[4]. It was found that when this liquid unsaturated ketone was left for a few days at room temperature, it slowly underwent aerobic oxidation transforming into a crystalline solid. The rate of formation of this solid was enhanced when the liquid was evenly distributed as a film in a plate and kept under oxygen. The compound was found to be the hydroperoxide (II) and the structure has been arrived at as follows. Elemental analyses corresponded to a molecular formula $C_{13}H_{18}O_3$. A molecular weight of 222 was revealed from CI mass spectrum[5]. Under electron impact 189 was the base peak and the peaks at 206 and 222 were extremely weak : UV 235 nm ($\epsilon$=10,200); IR 1700, 1620 $cm^{-1}$; NMR($CDCl_3$) $\delta$ 6.15(s,1H,C=CH), 1.73(s,2H,bridge methylene protons),



I. R= H

II. R= O-OH

III. 5,6 dihydro, R= H

1.03(s,3H,C-$CH_3$); positive potassium iodide test. The assignment of the position of the hydroperoxide linkage follows from the UV and NMR data. The sharp fall in the UV absorption maximum in (II) is consistent with those encountered for $\alpha\beta$-unsaturated ketones with a negative group at the $\gamma$-position[6]. In the NMR, the olefinic signal which was a doublet in the ketone (I) is a singlet at a lower field on account of substitution at the allylic position and consequent anisotropic deshielding. The two proton singlet at $\delta$1.73 is assigned to the bridge-methylene group with no adjacent protons. It appears from molecular models that the anisotropic effect of the oxygen atom or atoms may equally affect both the hydrogens. The hydroperoxide (II) or the unsaturated ketone (I), when subjected to reduction with lithium in liquid ammonia furnished the saturated ketone (III).

It appears likely that the facile functionalisation of the bridge-head position is a consequence of the strained nature of the molecule, and hence may offer a procedure for bridge-head utilisation, usually of restricted accessibility.

The scope and synthetic utility of this observation in other strained $\alpha\beta$-unsaturated carbonyl systems is currently being investigated in these laboratories.

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