

CYCLOPROPYL H-ABSTRACTION IN PHOTOOXYGENATION OF
DICYCLOPROPYLALKENES

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(Received in UK 14 September 1976; accepted for publication 19 November 1976)

Mono olefins bearing allylic hydrogens react smoothly with singlet oxygen by hydrogen abstraction and double bond migration to form allylic hydroperoxides (1).

In the present paper we describe the surprising regioselective addition of $^1\text{O}_2$ to 1-alkyl-(and 1,1-dialkyl) 2,2-dicyclopropyl-ethylenes derivatives (1-5) for which the difference in bond character of hydrogens in α -positions of the double bond (cyclopropyl- and alkyl-hydrogens) is well established (2).

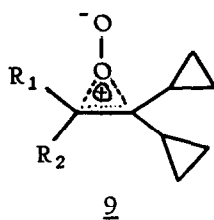
The olefins (1-5) were prepared, either by a Wittig reaction between the appropriate phosphoranes and dicyclopropylketone (1-3; yield 65%), or by coupling cycloalkylcarboxylic dilithium salts with dicyclopropylketone (3) followed by hydrolysis, lactonisation and CO_2 extrusion (4, 5; yield 65%). Spectroscopic data of 1-5 are in agreement with those already reported (1, 2) (4) and with the expected structures of the new ones (3, 4, 5).

Olefins (1-5) were submitted to photooxygenation in pure acetone (100 ml); t^0 range 3 - 5°C; sensitizer (eosin) = $2 \cdot 10^{-6} \text{ ml}^{-1}$; [substrate] = $8 \cdot 10^{-3} \text{ ml}^{-1}$; photolamp Sylvania DXX 800 W under 150 v. The hydroperoxides formed, stable at room temperature, were reduced with triphenylphosphine in benzene solution. The alcohols were isolated in pure state by liquid chromatography on silica gel column (total yield of isolated product 80%). No oxygen absorption was observed when dye-sensitizer was absent or when reaction was carried out in the presence of a $^1\text{O}_2$ quencher like 1,4 diaza [2.2.2]bicyclooctane.

For example olefin 2 (R = H, R' = CH_3) led to the hitherto unknown alcohols 2A arising from cyclopropyl H-abstraction (37%) [IR (CCl_4) (cm^{-1}) ν_{OH} : 3590, 3450 (free and bonded OH), $\nu_{\text{C}=\text{C}}$ 1750; NMR (CCl_4) δ (ppm) 0.52 and 0.68 (m, 4H); 0.95 (broad s, 4H); 1.4 (broad m, 1H); 1.38 (s, OH); 2.25 (s, 6H)] and 2B arising from alkyl H-abstraction (63%) [IR (CCl_4) (cm^{-1}) ν_{OH} 3600, 3500 (free and bonded OH); $\nu_{\text{C}=\text{C}}$ 1638; NMR (CCl_4) δ (ppm) 0.2 - 1.1 (m, 11H)].

Satisfactory MS and elemental analysis were obtained in all cases. No rearranged product were detected.

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Although the facts reported above and the conformational orientation of the tertiary cyclopropyl hydrogen in 1-5 (¹¹) are not opposed to the participation of a reactant-like ene-type process, we favour the polar perepoxide route in which the positive charge ought to be well delocalized over three centers particularly at the carbon alpha to the cyclopropane rings because of their strong electron releasing effect (⁶) a factor which would promote cyclopropyl H-abstraction.

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% photooxydation ~ 50 ; mass spectrometric isotope ratios were determined from olefins 2 and 2-D before and after partial photooxydation.

- 8) Relative rates of photooxygenation from ref. 10 ; a 2 : 2 : 1 mixture of 3, trimethylstyrene 10, tetradecane (internal reference) (980 mg) was photooxygenated at 3°C in 100 ml of various solvents (CH₃COCH₃, C₆H₆, CH₃OH, CH₂Cl₂, CS₂, ICH₂CH₃) ; degree of photooxydation $\sim 50\%$; ratios of residual olefins 3 and 10 were estimated from pic areas by G.C. Rate ratios found $0,21 < \frac{k_3}{k_{10}} < 0,26$.

Distribution of A/B compounds in those various solvents : photooxygenation and products ratio were obtained from olefin 2. Temperature effect : rate and ratio of A/B alcohol were determined at 0° and -50°C.

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