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STEREOCHEMICAL COURSE IN THE ADDITION OF SINGLET OXYGEN TO VINYLCYCLOPROPANE DERIVATIVES.

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We recently described the regioselective addition of singlet oxygen to 1,1-dialkyl 2,2-dicyclopropylethylenes and reported a remarkably easy cyclopropyl hydrogen abstraction (1). This result was rationalized in terms of a perepoxide intermediate.

In contrast, both regio- and stereoselective orientations are known in the addition of $^1O_2$ to olefins bearing α-hetero-substituents. For instance, the reaction of $^1O_2$ with the Z and E methyl enolethers of α-phenylpropanal led specifically to H-abstraction and to [4 + 2] cycloaddition respectively (2). This result was analysed by taking into account the polarity of the π-bond (regio-control) and the intermolecular non-bonding (HOMO-LUMO) attractive effect existing between the attacking oxygen atom and the methoxy group (stereo-control) (2).

We present in this paper a series of new results obtained with various cyclopropylethylene derivatives (see Schemes 1 and 2), with or without, a methoxy group in the α-position to the olefinic centre. α-Substituted vinylcyclopropanes (3) were prepared by Wittig reaction between various phosphoranes and the corresponding alkylcyclopropylketones, and were submitted, under standard conditions in benzene solution (4), to dye-sensitized photooxygenation.

As found for dicyclopropylmethylenecyclobutane (1) a clean regioselective cyclopropyl H-abstraction is obtained with 1 leading mainly to the cyclopropylidene hydroperoxide 1b (86%) (5), without formation of a cycloadduct involving the aromatic ring, in contrast to the known cases of mono- and diphenylmethylenecyclobutane (6). Enolether E of cyclopropylphenylethanal 2 (7) yielded the hydroperoxide 2a (5) by a process which involves a cyclopropyl H-abstraction, whereas the Z isomer 3 led, via a [4 + 2] cycloadduct, to the epoxide 3a (8). Our findings agree with those of Foote, cited by Fukui (2).

This result is clearly understandable on the grounds of intermolecular control of the approach of the two reactants induced by the methoxy group on the olefin centre.

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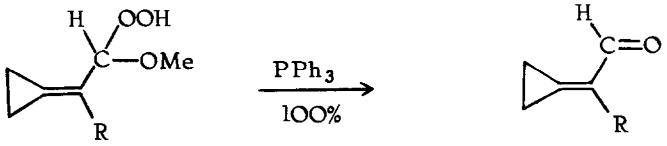
However, as in Fukui's example (2), the existence of two different pathways does not allow a clear conclusion concerning the possibility of a single (common) intermediate.

To overcome this difficulty we studied separately each isomer of the methyl enolether of α-cyclopropylpropanal 5 and 6 (7), in which H-abstraction is the only process expected, but with substrates having hydrogens of different mobility on the same side of the double bond (scheme 2). Enolether 5 stereospecifically adds $^1O_2$ giving rise unique by to the hydroperoxide 5a while the isomer 6 leads to a mixture of 28% of 5a and 72% of the thermodynamically less stable hydroperoxide 6a (5).

No such stereocontrol was observed when the methoxy substituent was replaced by a methyl group (4 in scheme 2) and H-abstraction occurred only on the methyl groups of the molecule.

Consequently the regioselective H-abstraction process in 5 and 6 must be attributed again to a stereoelectronic control of the reaction path by the methoxy group, not only in the approach of the two reactants but also at the level of the perepoxide intermediate ; in the case of 6 the pronounced reversibility[*] of perepoxide formation seems to constitute the main limiting factor in the conversion to 6a.

In this way, using triphenylphosphine as reducting agent we were able to synthesize three members, 7, 8 and 10, of the α-cyclopropylidene acetaldehyde series, a still unknown class of compounds (10).



2a	: R = phenyl	7
6a	: R = CH_3	8
9	: R = cyclopropyl	10

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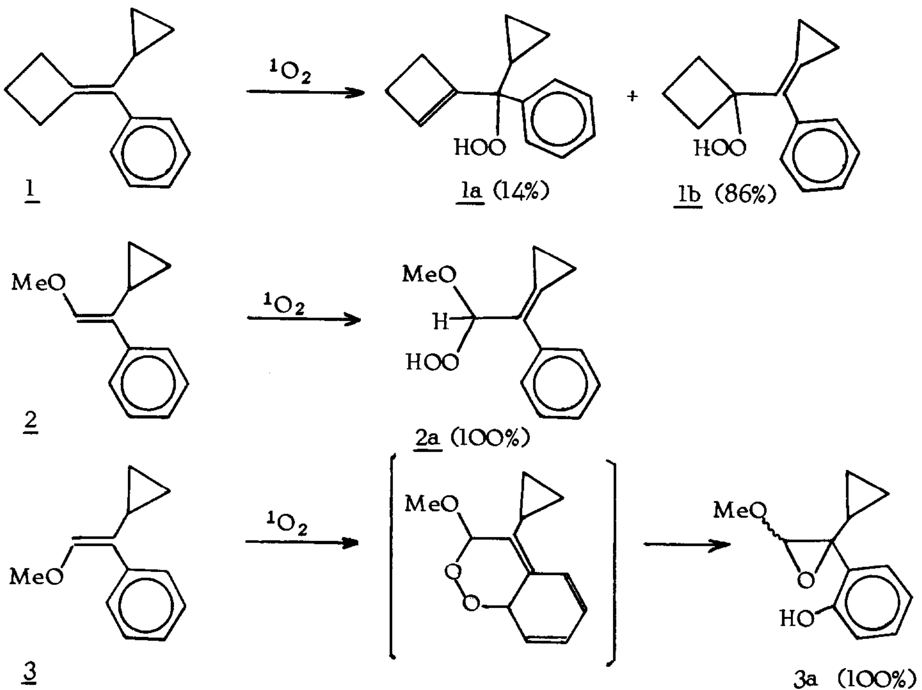
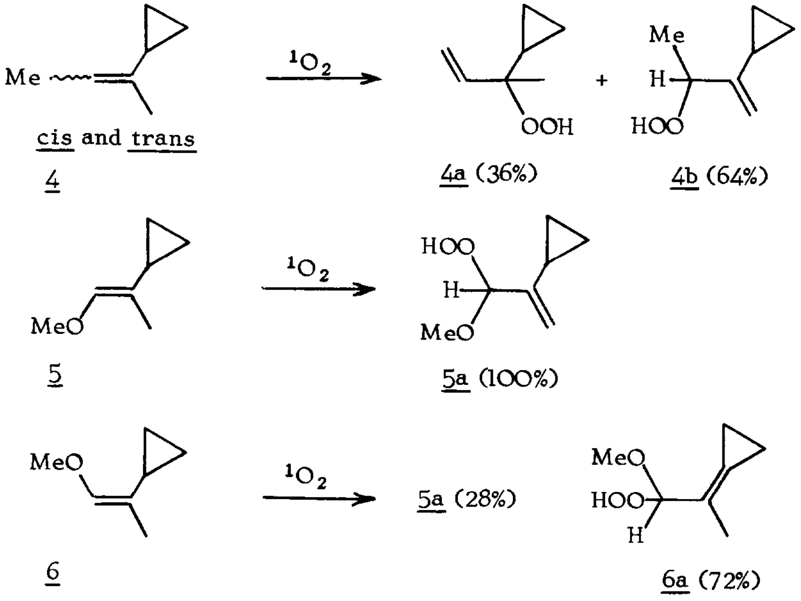
[*] Considering the high energy barrier calculated (9) for interconversion of the tricoordinate oxygen (~23 kcal mole^{-1}) in the perepoxide and the low activation energy for the perepoxide formation ($E_A < 4$ kcal/mole (11)) it is conceivable that a reversible process takes place in the singlet oxygen reaction with olefins.



Scheme 1



Scheme 2

Dye-sensitized photooxygenation of vinylcyclopropanes 1 - 6 in benzene solution at 3°C.

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1) G. Rousseau, P. Le Perchec and J.M. Conia, *Tetrahedron Letters*, 45 (1977).

2) S. Inagaki, H. Fujimoto and K. Fukui, *Chem. Letters*, 749 (1976).

3) Compounds 1 - 6 were prepared by Wittig reaction between the corresponding carbonyl compounds and cyclobutylidenetriphenylphosphorane (1 : yield : 70%), methoxymethylenetriphenylphosphorane (2 - 3 and 5 - 6 ; yields : 80%) and ethylidenetriphenylphosphorane (4 ; yield : 80%).

4) For the conditions of photooxygenation see ref (1).

5) The yields were determined by NMR spectra after reduction by PPh_3.

6) G. Rio, D. Bricout and M.L. Lacombe, *Tetrahedron*, 29, 3553 (1973) ; J. Rigaudy, M. Maumy, P. Capdevielle and L. Breton, *Tetrahedron*, 38, 53 (1977).

7) The two isomers 2 and 3 (and 5 and 6) were separated by g.l.c. For assigment of the structure of such compounds see A.D. Ketley, A.J. Berlin and L.P. Fisher, *J. Org. Chem.*, 31, 2648 (1966) ; V.G. Benndorf, H.G. Hauthal, R. Holm and W. Höbold, *J. für prakt. Chemie*, 311, 587 (1969) and the references in these papers.

8) The structure of this compound 3a was established by NMR spectroscopic data (CCl_4) : 2 isomers : δ ppm : 7,10 (m, 4H) ; 5,58 and 5,40 (two s, 1H) ; 4,20 and 4,38 (two s, 1H) ; 3,15 and 4,90 (two s, 3H) ; 1,40 to 0,80 (m, 1H) ; 0,70 to 0,20 (m, 4H) ; IR (CCl_4) ν_{OH} : 3600 cm^{-1}.

9) M.J.S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, 97, 3978 (1975).

10) Cyclopropylidenephenylethanal 7 : NMR (CCl_4) : δ ppm : 9,92 (s, 1H) ; 7,25 (m, 5H) ; 1,55 (s, 4H) ; IR (CCl_4) $\nu_{C=O}$ 1695 cm^{-1}.
2-Cyclopropylidenepropanal 8 : NMR (CCl_4) : δ ppm : 9,68 (s, 1H) ; 1,86 (q, J = 1,50 Hz, 3H) ; 1,32 (m, 4H) ; IR (film) $\nu_{C=C}$ 1755 cm^{-1}, $\nu_{C=O}$ 1680 cm^{-1}.
2-Cyclopropylcyclopropylideneethanal 10 : NMR (CCl_4) : δ ppm : 9,68 (s, 1H) ; 2,10 to 1,60 (m, 1H) ; 1,30 (s, 4H) ; 1,10 to 0,60 (m, 4H) ; IR (film) $\nu_{C=C}$ 1755 cm^{-1}, $\nu_{C=O}$ 1700 cm^{-1} ; UV (cyclohexane) λ_{max} : 242 nm. (Z. Goldschmidt and S. Mauda, *Tetrahedron Letters*, 4183 (1976) recently reported the formation of cyclopropylideneacetone by photolysis of 2-acetyl methylenecyclopropane. For a new synthesis of α-cyclopropylidene-ketones and -aldehyde see F. Huet, A. Lechevallier and J.M. Conia : paper submitted for publication in this journal.

(11) R.D. Ashford and E.A. Ogryzlo, *J. Amer. Chem. Soc.*, 97, 3604, 1975.