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CONCERNING AN UNIQUE INTERMEDIATE IN THE FORMATION OF HYDROPEROXIDES AND DIOXETANES FROM MONOOLEFINS AND SINGLET OXYGEN

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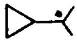
We recently described the regioselective addition of singlet oxygen ($^1O_2$) to various cyclopropylethylenes and reported easy cyclopropyl hydrogen abstractions (1a) ; moreover with methoxy-substituted olefins we found a stereoselective control of the methoxy group which leads to a strong preference for H-abstraction *cis* to that group (1b-c).

These results seemed compatible with a perepoxide intermediate stabilized by a nonbonded interaction of its tail oxygen and the methoxy oxygen lone pair (1), confirming Fukui's (2a) and Dewar's (2b) semi-empirical calculations (CNDO/2 and MINDO/3, respectively).

Another explanation has been more recently proposed by Goddard and Harding (3a) who, by *ab initio* calculations (GVB-CI), showed that the intermediate may be a biradical ($^\bullet CCOO^\bullet$) stabilized by an anomeric effect. Although Goddard's calculations (3) are more consistent than those of semi-empirical methods (2), and though we believe that an anomeric effect may be involved to explain stereoselective control (see also (4)) and that a ring-opened intermediate is more probable, we feel in our case this has an important zwitterionic character. Indeed it is known that inhibitors of free radicals do not influence the reaction of $^1O_2$ with monoolefins (5). In the particular case of vinylcyclopropanes (1a) such an intermediate would lead to a species () particularly suitable to the opening of the cyclopropyl ring, a reaction we have none the less never observed. Moreover, it seems that GVB calculations overestimate biradical structures (6) and in fact it is difficult to differentiate between zwitterionic and biradical character (7). Finally, presumption of a zwitterionic intermediate has been recently reported by Jefford and Rimbault (8) in the photooxygenation of olefins lacking allylic hydrogens. Scheme 1 shows the mechanism which best interprets our previously reported results on the formation of hydroperoxides (1) :

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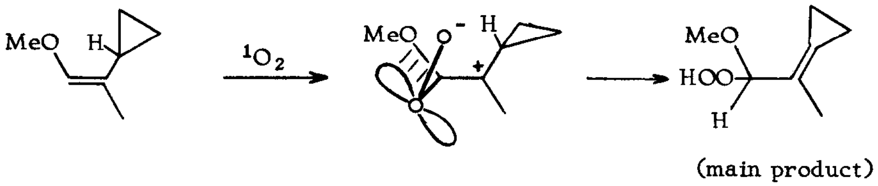
[*] Equipe de Recherche Associée au C.N.R.S.

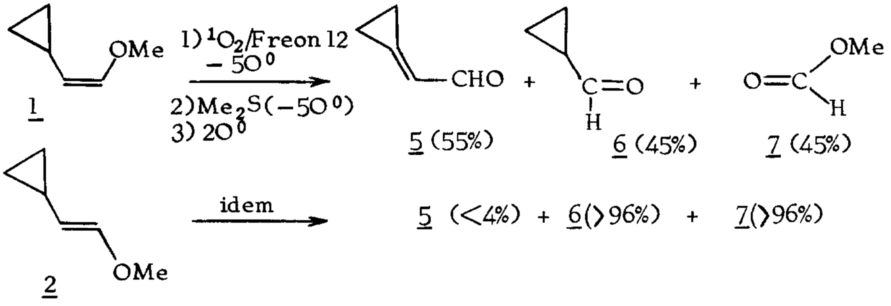


Scheme 1

The purpose of the present communication is also to report new results which are consistent with a recent hypothesis of Harding and Goddard who proposed that in the reaction of monoolefins with $^1O_2$, the formation of hydroperoxides (H-abstraction) and dioxetanes ([2 + 2] cycloaddition) would involve a common intermediate ([3]). In this connection we report the preparation of the first member of a new and interesting series, cyclopropylidene-acetaldehyde 5.

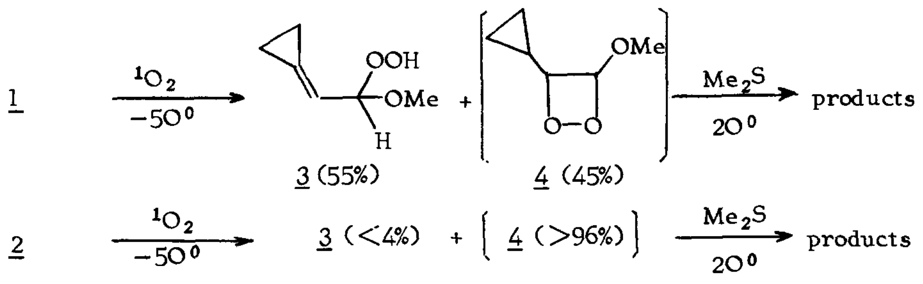
A mixture of 1-methoxy 2-cyclopropyl-ethylenes ([9]) Z (1) and E (2) (45 : 55 respectively) was prepared either by a Wittig reaction between methoxymethylenetriphenylphosphorane and cyclopropanecarbaldehyde by the Corey procedure ([10a]) (70% yield) or better by Warren's new procedure ([10b]) from the anion of methoxymethyldiphenylphosphine-oxide and cyclopropanecarbaldehyde and then treatment of the adduct obtained with sodium hydride in triglyme (88% yield).

The olefins 1 and 2 were separated by g.l.c (column XF 1150-20% at 85°) and separately submitted to dye photooxygenation at $-50°$ in Freon 12-$CDCl_3$ mixture (90 - 10) in the presence of Zn^{II} mesotetraphenylporphine as sensitizer, followed by reduction with dimethylsulfide and warming at room temperature. Enol ether E 2 led nearly exclusively to cyclopropanecarbaldehyde and methyl formate (>96% in the ratio 1/1), but enol ether Z 1 gave a mixture of these two products (in the same ratio) (45%) and of a new one, cyclopropylidene-acetaldehyde 5 (55%) ([11]) (scheme 2). The overall-yield was about 90%.



Scheme 2

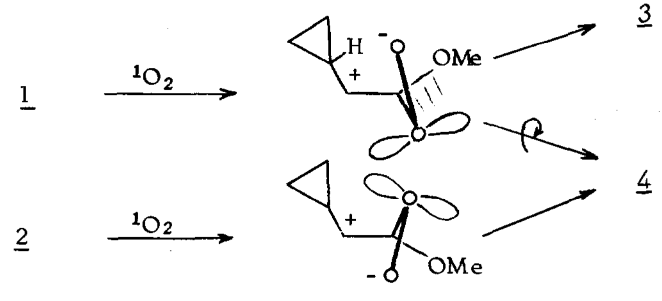
When the reduction step was omitted, hydroperoxide intermediate 3 could be isolated from 1, but very little intermediate 3 (<4%) was obtained from 2. Since it is well known that dioxetanes are easily cleaved into two carbonyl compounds (12), we may conclude that 4 was formed, giving rise to methyl formate and cyclopropanecarbaldehyde



Scheme 3

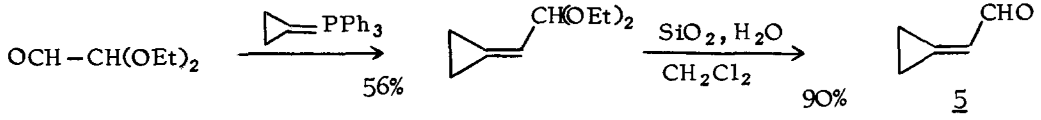
Consequently with $^1O_2$ the enol ether 2 is initially converted into dioxetane 4, and its isomer 1 into a mixture of hydroperoxide 3 and dioxetane 4 (scheme 3).

These results show that the methoxy group has a cis directing effect which can be interpreted by the stabilization of an intermediate by an anomeric effect (3a). The formation of 4, in addition to 3, observed from the enol ether 1, is probably due to the difficulty in accomplishing cyclopropyl hydrogen abstraction (1a). Finally, our results are in agreement with Goddard and Harding's hypothesis (3) which invokes an unique intermediate in the formation of hydroperoxide and dioxetane. This may have a zwitterionic structure (scheme 4).



Scheme 4

The claim of the formation of cyclopropylidene-acetaldehyde 5, a still unknown aldehyde, necessitated an unequivocal synthesis. This was carried out from a cyclopropylidene-ketal (obtained by a Wittig reaction between diethoxyethanal (13) and cyclopropylidene-triphenylphosphorane ([14]) which was treated by wet silicagel (an excellent deketalisation reagent ([15])). We obtained the desired aldehyde, whose spectra were identical to those of the aldehyde 5 isolated in the photooxygenation (scheme 5)



Scheme 5

Cyclopropylidene-acetaldehyde was sufficiently stable to be purified by g.l.c. (column Carbowax 20M at 80°). Its odor was pungent, reminiscent of acrolein. M$^+$ 82.05 ; calculated for C_5H_6O : 82.04. NMR (CCl_4) δ ppm : 9.66 (d, J = 8 Hz, 1H) ; 6.40 (m, 1H) ; 1.42 (m, 4H). IR (film) 3060 (ν ▷–H) ; 2820 - 2730 (νOC – H) ; 1695 (ν C=O). UV (cyclohexane) λmax 220 nm (ε : 9100) and 328 nm (ε : 24).

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