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247. The Reaction of Singlet Oxygen with Norbornene

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(9. VIII. 74)

In recent years there has been considerable speculation concerning the existence of perepoxide or peroxirane intermediates [1]. Two particular, but related instances are provided by the dye-sensitized photo-oxygenation of monoolefins to give hydro-

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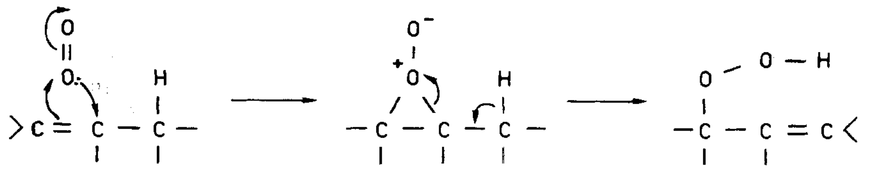
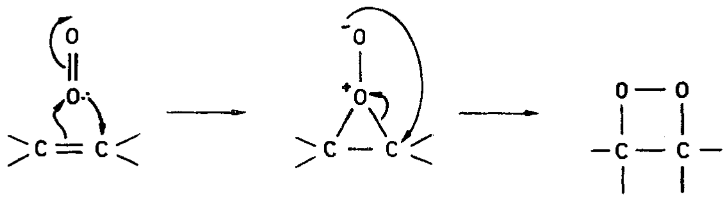
[1] Preliminary paper. A full account will appear in Helv.

peroxides and dioxetanes. For olefins possessing abstractable allylic hydrogen atoms, it has been postulated that singlet oxygen undergoes electrophilic addition to the double bond to give a fugitive perepoxide which subsequently captures a contiguous hydrogen atom thereby forming the hydroperoxide (*Scheme 1*) [2]. When allylic hydrogen atoms are not available and the double bond is sufficiently electron-rich, then dioxetanes may be isolated [3]. Although this would normally be considered the consequence of a simple [2 + 2]cycloaddition, it has been suggested that a perepoxide is first formed which then rearranges to dioxetane (*Scheme 2*). An interesting account of this last process has been offered to explain the behaviour of adamantylidene-adamantane towards singlet oxygen in the presence of pinacolone [4]. Steric strictures in the adamantane skeleton were thought to prevent the rearrangement course and therefore to preserve the life of the perepoxide to the extent of allowing it to react with pinacolone in *Baeyer-Villiger* fashion to give the epoxide and *t*-butyl acetate (*Scheme 3*).

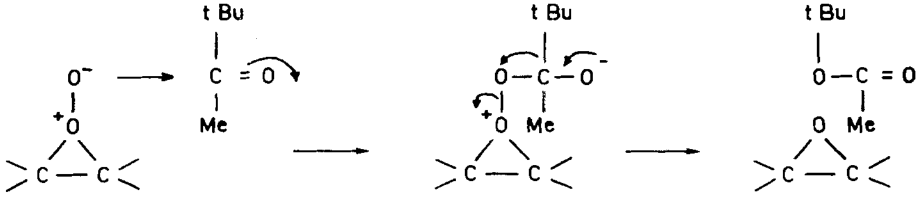
Scheme 1



Scheme 2



Scheme 3



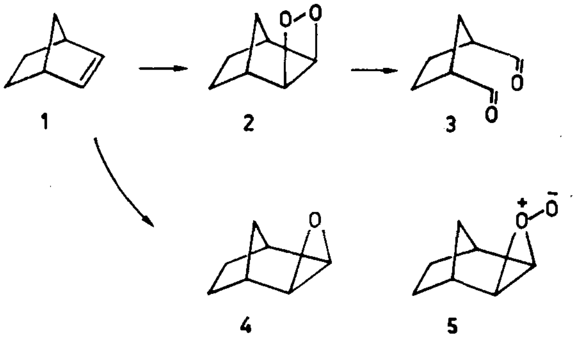
This is an intriguing mechanistic hypothesis, because it should lend itself to those cases where perepoxides are formed reversibly. Norbornene itself is supposed to be such an example. It has been reported that norbornene is inert towards singlet oxygen generated in methanol and pyridine using methylene blue or hematoporphyrin as sensitizer. Apparently, no depletion of olefin occurred even after a reaction time of a month [5]. Here it has been argued that as the allylic hydrogen atoms lie in the nodal plan of the double bond, no avenue to product is open and consequently olefin and oxygen are simply regenerated [6]. However, further reaction to dioxetane at least, if not to rearranged skeletal products, would have been expected. We now report our preliminary findings on the reaction of singlet oxygen with norbornene in a variety of solvents including pinacolone as a potential oxygen trapping agent.

Norbornene was photo-oxygenated in acetonitrile using methylene blue as sensitizer and two 500 W tungsten filament projector lamps (*Sylvania* FFX) as light source. For equimolar amounts of reactants, oxygen uptake occurred, albeit slowly, and some 15% absorption was observed over 10 hours. Norbornene (**1**) was oxidized and two major products, corresponding to more than 95% of the newly formed compounds, were detected and isolated by gas-liquid chromatography[2]. These products were identified by direct comparison with authentic samples as *cis*-cyclopentane-1,3-dicarboxaldehyde (**3**) and *exo*-norbornene epoxide (**4**) [8]. Careful re-examination of the crude reaction mixture confirmed that the chromatographic products were also those formed from the photo-oxygenation.

In order to be sure that products **3** and **4** derive from singlet oxygen, a series of tests were carried out. Firstly, oxidation did not occur in the absence of sensitizer. Secondly, irradiation of the olefin in acetonitrile with methylene blue under nitrogen gave no reaction. Thirdly, when 1,4-diazabicyclo[2.2.2]octane (DABCO), an efficient singlet oxygen quencher [9], was added to the reaction mixture, then oxidation immediately stopped. Therefore it can be confidently concluded that singlet oxygen is indeed the reactive species.

Clearly, the first step or an early step in the photo-oxygenation is the cycloaddition of singlet oxygen to presumably the *exo* face of norbornene to give the dioxetane **2** which then suffers cleavage to the dialdehyde **3**. The origin of the epoxide **4** was not established and is more difficult to explain. Possible precursors are either the dioxetane **2** or possibly the pereopoxide intermediate **5**, both of which could lose an atom of oxygen in some way, perhaps to another molecule of norbornene. However, in contradistinction to the results reported for adamantylidene-adamantane, photo-oxygenation carried out in pinacolone, as opposed to acetonitrile or acetone,

Scheme 4



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[2] Separation was effected at 160° on a column of Apiezon L on Chromosorb W. Norbornene epoxide is stable under these conditions provided that traces of acid are absent, otherwise rearrangement to 4-formylcyclohexene occurs [7].

did not change significantly the proportion of norbornene epoxide (Table 1). Moreover, no trace of *t*-butyl acetate was found in the reaction mixture³).

Table 1. *Products from photosensitized oxidation of* **1** *at room temperature* ᵃ)

Solvent	% epoxide **4**	% dialdehyde **3**
Acetonitrile ᵇ)	39	61
Pinacolone ᵇ)	53	47
Acetone ᶜ)	65	35

ᵃ) Irradiation time 5 h, concentration of norbornene 2M/l. About 5% of olefin was oxidized in all cases.
ᵇ) Methylene blue as sensitizer.
ᶜ) Rose bengal as sensitizer.

These findings are a revelation in view of the general acceptance of the inertness of norbornene towards singlet oxygen and serve as a salutary reminder that longer reaction times and careful work-up are needed for recalcitrant substrates. Moreover, the absence of a special effect or reaction with pinacolone casts doubt on its purported property as a trapping agent for perepoxide, if indeed the latter is an intermediate⁴). In any event, the production of epoxide does not arise from a *Baeyer-Villiger* type reaction.

Similar results have been found for 7,7′-binorbornylidene where the corresponding product composition (dioxetane/epoxide) depends on and varies with solvent in exactly the same way as that seen for norbornene [11]. Lastly, it is worth remarking that norbornene is some four hundred times less reactive than 2-methylnorbornene, which incidentally gives only allylic hydroperoxides [12]. If the rate determining step for both norbornenes were the formation of a perepoxide then some convergence in rates and products would be expected, which is clearly not the case⁵). Evidence in favour of the existence of perepoxide intermediates is still wanting. In the meantime, investigations are under way to discover the provenance of norbornene and similar epoxides.

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[3] As a control, trace amounts of *t*-butyl acetate were independently added to the reaction mixture and easily detected by GLC.

[4] Pinacolone is not oxidized during the ozonolysis of ethylidenecyclohexane, consequently the intermediacy of the four-membered *Staudinger* molozonide has been discounted [10].

[5] Substitution of a methyl group on the double bond would be expected to increase the rate of oxidation some ten times [13].

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248. Selektive Synthesen mit Organometallen II[1]: Metallierung und Abwandlung funktionell substituierter Alkene

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Summary. 1,4-Dienes, vinyl ethers, allyl ethers, allyl thioethers and propene-thiolates are efficiently metalated by butyllithium in the presence of an activator such as potassium *t*-butoxide. Since the solvent, the counter-ion or the temperature may be varied before subsequent treatment with an electrophilic reagent, the critical ratio of direct *vs.* vinylogous attack (substitution at the α- or γ-position, respectively) can usually be adjusted within large limits. In many cases stereoselectivity is achieved as well.

In Gegenwart von Kalium-*t*-butylalkoholat vermag Butyllithium allylständige CH-Gruppen zu metallieren [1] [12] [13]. In der Reihe rein aliphatischer Alkene setzt sich das Anfangsglied, das Propen **1**, am leichtesten um: Allylkalium (63%) entsteht bereits im Bereich von −40°. Jeder hinzukommende Alkyl-Rest, insbesondere wenn in γ-Stellung oder – erst recht – wenn in α-Stellung gebunden, verzögert den Wasserstoff/Metall-Austausch. Deshalb kann man unter anderem Kalium in die allylständige Methyl-Gruppe des 2-Hexens einführen, ohne überhaupt die neben der Doppelbindung stehende Methylen-Gruppe anzugreifen [1].

Wie verhalten sich nun andere Liganden X in dieser Hinsicht? Wie beeinflussen sie Bildungstendenz und Beständigkeit der Allylkalium-Verbindung? Wie sehr hängt ihre Wirkung davon ab, ob sie bezüglich der zu metallierenden CH-Gruppe in Vinylogstellung untergebracht sind (**2**; *Z*- und *E*-Isomere), eine Nachbarposition einnehmen (**3**) oder unmittelbar angrenzen (**4**)? Besetzt das Metall den ihm zuge-

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[1] I. Mitt.: [1].

[2] Wesentliche Teile der hier behandelten Ergebnisse sind in der Dissertation *J. Hartmann* (Universität Heidelberg, Januar 1974) enthalten. Unabhängig und mit teilweise anderer Zielsetzung haben auch andere Laboratorien die Metallierbarkeit von Dienen [2], Vinyläthern [3], Allyläthern [4] [5], Allylthioäthern [6–9] und Allylmercaptiden [10] sowie Enaminen [11] untersucht.