

PHOTOOXYGENATION OF ALLENES

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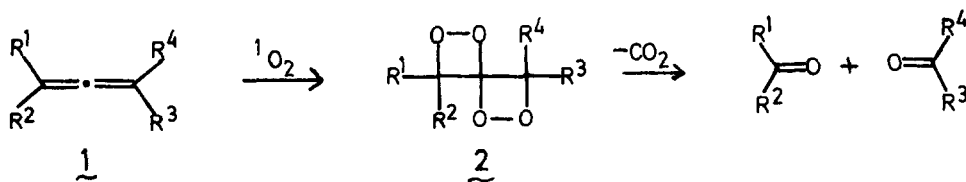
Reactions of singlet oxygen with reactive double bonds mainly result in the formation of carbonyl compounds, via 1,2-dioxetanes as unstable intermediates¹. Olefins with allylic hydrogen give hydroperoxides while cis-1,3-dienes and fused aromatic compounds give cyclic peroxides¹. Crandall et al.² attempted to react tetramethylallene with singlet oxygen generated by the hypochlorite/peroxide method, with no success. As a part of our investigations on electrophilic reactions with allenes³, we have studied reactions with singlet oxygen.

Tetramethylallene (1a), phenylallene (1b) and 1,3-diphenylallene (1c) were treated with the triphenylphosphite/ozone reagent⁴ at -78° and at -15°. In all cases unreacted starting material was recovered. When phenylallene was treated with singlet oxygen from decomposition of aqueous potassium perchromate⁵, small amounts of benzoic acid were isolated in addition to unreacted starting material.

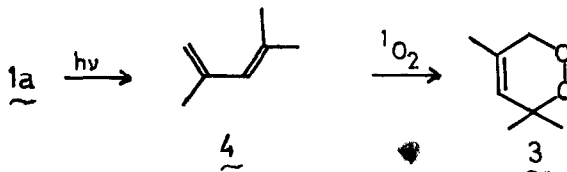
The photosensitization method¹ was then examined on triphenylallene (1d) and tetraphenylallene (1e) in addition to the allenes 1a, 1b, and 1c. Carbon disulfide was chosen as solvent because of its good properties for this kind of reactions¹ and eosin was used as sensitizer. The irradiation was effected by a 125 W Hanovia immersion lamp in Pyrex glass. One mole of oxygen was absorbed after 2-4 days. In the case of the allenes 1b, 1c, 1d and 1e about half the starting material was consumed, while the reaction for tetramethylallene (1a) had gone almost to completion. In addition to some polymeric material, benzaldehyde (from 1b, 1c, and 1d) and benzophenon (from 1d and 1e) were isolated in 30-70% yield. Carbon dioxide was evolved in all reactions except in that of 1a.

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Mechanistically the formation of these products may be explained by decomposition of the unstable tetraoxaspirocycloheptane 2. Although no such compound was isolated, the existence of 1,2-dioxetanes and dioxaspirocycloheptanes¹ makes this intermediate quite plausible.



- a: $R^1=R^2=R^3=R^4=CH_3$
 b: $R^1=Ph, R^2=R^3=R^4=H$
 c: $R^1=R^3=Ph, R^2=R^4=H$
 d: $R^1=R^2=R^3=Ph, R^4=H$
 e: $R^1=R^2=R^3=R^4=Ph$



Tetramethylallene (1a) gave only small amounts of acetone. The main product (3), which contained active oxygen, was not stable at room temperature. The absence of hydroperoxide absorption in the infrared, the nmr spectrum (O-CH₂ at δ 4,3, CH at δ 5,1, CH₃ at δ 1,3 and δ 1,7) and the M (^m/e 128), M-H, M-O₂, M-HO₂ fragments in the mass spectrum are consistent with the peroxide structure (3). This compound is probably formed by an initial light induced isomerisation^{6,7} of the allene 1a to the diene 4, followed by 1,4-addition of oxygen.

The phenylallenes 1d and 1e gave small amounts of compounds which contained active oxygen, had vinyl protons in the nmr and showed the M (^m/e 300, ^m/e 376), M-H, M-O₂, M-HO₂ mass spectral fragments. These preliminary results indicate that 1,4-addition of oxygen to one of the benzene rings has taken place, leaving the allenic linkage intact.

References

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