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Chemistry of Singlet Oxygen. Dye-Sensitized Photooxygenation of Arylallenes[1]

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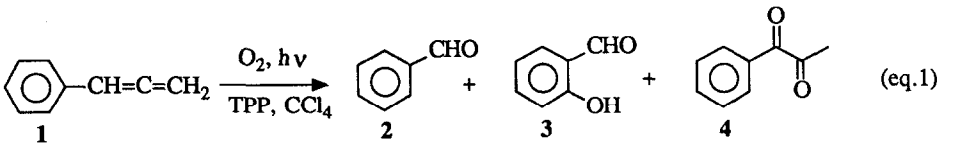
Abstract: 1-Arylallenes react with singlet oxygen via 1,2-and 1,4-cycloaddition modes giving rise to three types of carbonyl fragments. 1,1-Diphenyl- and 1-methyl-1-phenylallenes react predominantly by the 1,4-mode. Plausible mechanisms are discussed for the formation of the observed products.

In Greibrokk's initial report on the dye-sensitized photooxygenation of substituted acyclic allenes a bisdioxetane was postulated to account for the carbonyl cleavage products;[2] tetramethylallene was reported to give a cyclic peroxide believed to arise from initial photochemical isomerization to 2,4-dimethyl-1,3-pentadiene. On the other hand, Gollnick and Schnatterer[3] recently showed that tetramethylallene reacts with singlet oxygen to give products resulting from [2+2] cycloaddition and ene reactions. The same group reinvestigated[4] the photooxygenation of tetraphenylallene and again was not able to corroborate Greibrokk's results. In this communication we report our results from the photooxygenation of arylallenes.

Irradiation (sodium vapor lamp) of an oxygen-saturated solution of phenylallene (1-phenyl-1,2-propadiene, **1**) and tetraphenylporphyrin (TPP) in carbon tetrachloride at room temperature led to slow consumption of **1**. The ^{1}H NMR spectrum of the crude photolysate indicated the presence of three products.

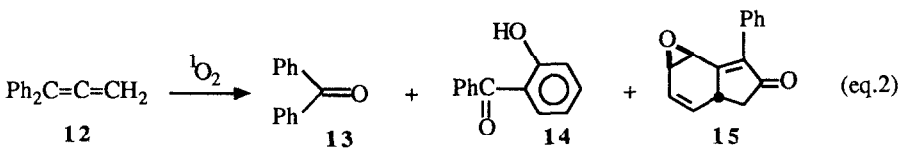


1 2 3 4 (eq.1)

They were separated by column chromatography on SiO_2 and identified as benzaldehyde **2**, salicylaldehyde **3** and 1-phenyl-1,2-propanedione **4** (eq.1). 3-Methyl (**5**) and 3,3-dimethyl (**8**) analogs of **1** gave similar product spectra except in these latter cases acetaldeyde and acetone, respectively were clearly discernible in the NMR spectra and further confirmed by gas chromatography. In the case of **8** a small amount of the acyloin **11**[5] was also formed. The results from the photooxygenation of 1-phenylallenes are summarized in Table 1.

1,1-Diphenylallene (**12**) reacted with $^1O_2$ under the same conditions to give a mixture of benzophenone, *o*-hydroxybenzophenone and a major product which according to its elemental analysis had the molecular composition $C_{15}H_{12}O_2$ (eq.2). Its ^{1}H NMR spectrum (300 MHz, C_6D_6) exhibits the following signals: δ 7.0-7.5 (m, 5H); 5.52 (ddd, A part of an ABXY system, J= 9.5, 3.26, 2.92 Hz, 1H); 5.37 (ddd, B part, J= 9.5, 1.8, 1.5 Hz, 1H)); 3.96 (d, J= 4.0 Hz, 1H); 3.16 (m, 1H); 3.05 (dddd, J= 4.0, 3.26, 2.12, 1.5 Hz, 1H); 2.30 (dd, J= 18.4, 7.36 Hz, 1H); 1.86 (dd, J= 18.4, 3.60 Hz, 1H). Its ^{13}C NMR spectrum (75 MHz, $CDCl_3$) contains signals at δ 208.2, 172.3, 141.2, 133.9, 133.2, 132.8, 132.5, 132.2, 127.6, 57.7, 57.4, 45.7, 42.1 ppm. Its IR spectrum displays a carbonyl absorption at 1701 cm^{-1}. Selective decoupling and 2D experiments allowed the assignment of its structure to that of **15**. The stereochemistry of the hydrogen at the ring junction is tentatively assigned based on the postulated mechanism of the formation of **15** (Scheme 1). Additional

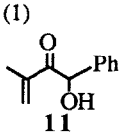
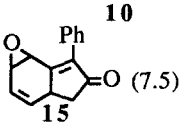
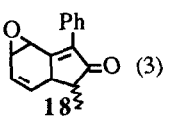
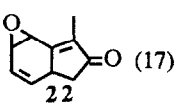
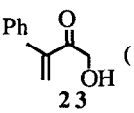
structural proof for **15** was obtained by a chemical transformation: when subjected to prolonged chromatography on SiO_2 or treated with a trace of trifluoroacetic acid in CH_2Cl_2 solution, **15** isomerizes quantitatively to 4-hydroxy-3-phenyl-2-indanone (**16**). The ^1H NMR spectrum (300 MHz, $CDCl_3$) of **16** exhibits signals at δ 7.15-7.4 (m, 6H); 7.0 (d, J= 7.48 Hz, 1H); 6.8 (d, J= 8.1 Hz, 1H); 4.90 (br. s, 1H); 4.68 (s, 1H); 3.7 (d, A part of an AB system, J=22.9 Hz, 1H); 3.6 (d, B part, J= 22.9 Hz, 1H). The IR spectrum contains absorptions at 3387 (ν_{OH}) and 1751 ($\nu_{C=O}$) cm^{-1}, consistent with the proposed structure.



The photooxygenation of 3-methyl-1,1-diphenyl-1,2-butadiene (**17**) and 3-phenyl-1,2-butadiene (**19**) gave the corresponding bicyclic epoxyketones **18**[6] and **22**[7] as major products (Table 1). In these latter cases *o*-hydroxybenzophenone (**14**) and *o*-hydroxyacetophenone (**21**) were formed in minute quantities, respectively.

In order to verify the involvement of singlet oxygen rather than free radical autoxidation control experiments were conducted. When the reactions were attempted in the absence of light or sensitizer (TPP) no reaction was observed. Irradiation of the phenylallenes in the absence of oxygen did not affect the substrates. Moreover, when the photooxygenations were performed in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO),[8] a singlet oxygen quencher, the disappearance of substrate was extremely slow.

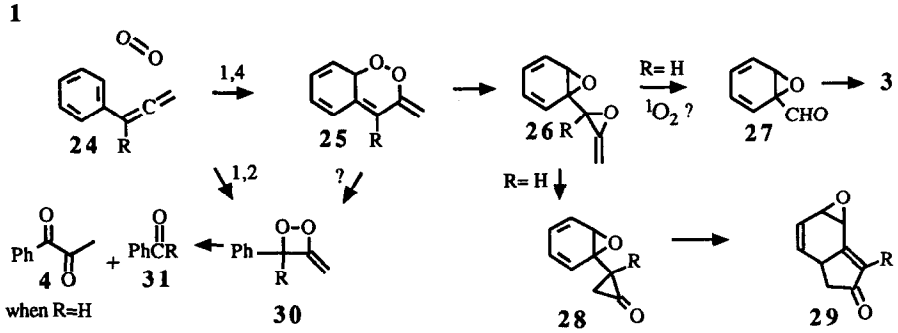
Table 1. Dye-Sensitized Photooxygenation of Phenylallenes[9]

Allene	Products (ratios)
$PhCH=C=CH_2$ **1**	PhCHO (4) **2** o-HO-PhCHO (1) **3** $PhCOCOCH_3$ (6) **4**
$PhCH=C=CHCH_3$ **5**	**2** (5.3) **3** (3.7) CH_3CHO (3) **6** $PhCOCOCH_2CH_3$ (1) **7**
$PhCH=C=C(CH_3)_2$ **8**	**2** (4.4) **3** (4) $(CH_3)_2CO$ (3) **9** $PhCOCOCH(CH_3)_2$ (1) **10**  (1.3) **11**
$Ph_2C=C=CH_2$ **12**	Ph_2CO (5) **13** o-HO-PhCOPh (1) **14**  (7.5) **15**
$Ph_2C=C=CHCH_3$ **17**	**13** (1) **14** (trace)  (3) **18**
$Ph(CH_3)C=C=CH_2$ **19**	$PhCOCH_3$ (10) **20** o-OH-$PhCOCH_3$ (1) **21**  (17) **22**  (15) **23**

Benzaldehyde, benzophenone and acetophenone obviously arise from a 1,2-addition[10] of $^1O_2$ to the phenyl substituted π bond of the allene followed by a typical 1,2-dioxetane cleavage. The ketene fragments would be expected to undergo mostly polymerization by the action of O_2 as previous studies have shown.[11] 1,2-Dioxetanes derived from monophenyl substituted allenes probably serve as the precusors of the 1,2-diones as well, via an unusual dioxetane cleavage: after O-O homolysis a rare 1,3-hydrogen transfer[12] would account for their formation. Whether this hydrogen shift is inter- or intramolecular must await labeling studies which are in progress. A base catalyzed isomerization of the dioxetanes to the respective 1,2-diones cannot be excluded.

Salicylaldehyde formation suggests an initial 1,4 cycloaddition[13] to give endoperoxide **25** (see Scheme 1). One possible pathway involves an endoperoxide-bisepoxide isomerization.[14] It is difficult to unequivocally establish by which oxidative pathway the allene oxide moiety in **26** is cleaved to the formyl group. One possibility is isomerization to a cyclopropanone[15] followed by reaction with oxygen and decomposition of the resulting 1,2-dioxolan-4-one.[16] On the other hand, Chan's studies on allene oxide isomerizations indicate that 1-monoalkyl allene oxides are reluctant to isomerize to cylopropanones at room temperature.[17] It is therefore conceivable that the allene oxide **26** is directly cleaved by further photooxygenation to the formyl group and the respective carbonyl fragments formaldeyde, acetaldehyde or acetone. By whichever mechanism it may have been formed, 1-formyl benzene oxide (**27**) is the most likely source of salicylaldehyde.[18]

Scheme 1



According to Chan's studies 1-monoaryl or 1,1-dialkyl substituted allene oxides readily isomerize to the corresponding cyclopropanones, presumably via oxyallyl intermediates,[15] and exhibit the typical reactions of cyclopropanones generated by other methods,[19] including [4+2] and [3+2] cycloadditions with dienes and C=O or C=C π systems. It might therefore be due to the presence of the additional phenyl and methyl group in **26** that a similar rapid isomerization to the corresponding cyclopropanone takes place.This then could undergo intramolecular [3+2] cycloaddition to the benzene oxide moiety with concomitant 1,2-oxygen walk[20] leading to the bicyclic compounds **15**, **18** and **22**, respectively.

Finally, the hydroxy enones **11** and **23**[21] are to be considered as secondary products from an initial "ene reaction" and subsequent rearrangement of the unstable vinyl hydroperoxides, analogous to the ene-products from tetramethylallene.[3]

Studies on photooxygenations of cyclic allenes are in progress and will be reported in due course.

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References and Notes

1. This paper was presented at the Pacific Conference on Chemistry and Spectroscopy on October 27, **1988**.
2. Greibrokk, T. *Tetrahedron Lett.* **1973**, 1663.
3. Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1985**, 5029.
4. Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1985**, 173.
5. **11**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2-7.4 (m, 5H); 5.95 (s, 1H); 5.8 (m, 1H); 5.68 (d, J= 6.0 Hz, 1H); 4.40 (d, J= 6.0 Hz, 1H); 1.86 (m, 3H): IR (neat): 3457 (ν_{OH}): 1675.6 ($\nu_{C=O}$) cm^{-1}.
6. **18**, initially a 3:1 mixture of stereoisomers, isomerizes to a single isomer after standing at 0 ° C in $CHCl_3$ for 3 months. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8 (m, 2H); 4.3 (d, J= 3.9 Hz, 1H); 3.68 (m, 1H); 3.25 (d, J=3.8 Hz, 1H); 2.32 (m, 1H); 1.32 (d, J= 7.34 Hz, 3H); IR (neat): 3083, 3035, 2972, 2932, 1706, 1643, 1599,1484, 1241, 812, 699 cm^{-1}.
7. **22**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.9 (m, 2H); 4.17 (d, J= 4.2 Hz, 1H); 3.72 (m, 1H); 3.53 (m, 1H); 2.77 (dd, J= 18.44, 7.12 Hz, 1H); 2.16 (dd, J= 18.44, 3.60 Hz, 1H); 1.89 (d, J= 2.4 Hz, 3H); IR (neat): 3080, 3029, 2970, 1701, 1653, 1496, 1045, 702 cm^{-1}.
8. Ouannes, C.; Wilson, T. *J. Am. Chem. Soc.* **1986**, *90*, 6527.
9. Crude yields, based on starting allene, ranged between 78-85% (after separation from polymeric material). Product ratios are determined from NMR integration. Compounds **11**, **15**, **16**, **18**, **22**, and **23** gave satisfactory elemental analyses.
10. Schaap, A.; Zaklika, K. A. in Singlet Oxygen; Wasserman, H. A.; Murray, R. N., Eds.; Academic: New York, **1979**, p 173.
11. (a) Wheland R., Ph. D. Dissertation, Harvard University, **1970**, p 261; (b) Staudinger, H; Dycherhoff, K.; Klever, H. W.; Ruzeka, L. *Chem. Ber.* **1925**, *58*, 1079; (c) Turro, N. J.; Ito, Y.; Chow, M.-F.; Adam, W.; Rodriguez, O.; Yany, F. *J. Am. Chem. Soc.* **1977**, *99*, 5836.
12. For similar 1,2-dioxetane cleavages in which a 1,3-hydrogen transfer has been invoked, see Frimer, A. A. in "The Reaction of Singlet Oxygen With Olefins: The Question of Mechanism", *Chem. Rev.* **1979**, *79*, 359-61.
13. (a) Foote, C. S.; Mazur, S.; Burns, P. A.; Lerdal, D. *J.Am. Chem. Soc.* **1973**, *95*, 586; (b) Steinchen, D. S.; Foote, C. S. *Tetrahedron Lett.* **1979**, 4363; (c) Steinchen, D. S.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1855; (d) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1979**, 1607; (e) Gollnick, K.; Schenk, G. O. in "1,4-Cycloaddition Reactions"; Hamer, J. Ed.; Academic: New York, **1967**, p 255; (f) Bloodworth, A. J.; Eggelte, H. J. in "Singlet Oxygen. Reaction Modes and Products"; Frimer, A. A. Ed.; CRC Press: Boca Raton, FL, **1985**; Vol. II, Part 1, p 93.
14. For a similar isomerization, see Griffin, G. W.; Kirschenheuter, G. P.; Vaz, C.; Umrigar, P. P.; Lankin, D. C.; Christensen, S. *Tetrahedron*, **1985**, *11*, 2069.
15. For a review, see Chan, T. H.; Ong, B. S. *Tetrahedron Report No. 91*; *Tetrahedron* **1980**, *36*, 2269.
16. Turro, N. J.; Leermakers, P. A.; Wilson, H. R.; Neckers, D. C.; Byers, G. W.; Vesley, G. F. *J. Am. Chem. Soc.* **1965**, *87*, 2613.
17. Chan, T. H.; Ong, B. S. *J. Org. Chem.* **1978**, *43*, 2994.
18. Review: Daly, J. W.; Jerina, D. M.; Witkop, B. *Experientia*, **1972**, *28*, 1129.
19. Turro, N. J. *Acc. Chem. Res.* **1969**, 25.
20. Bruice, P. Y.; Kasperek, G. J.; Bruice, T. C.; Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.***1973**, *95*, 6041.
21. **23**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3-7.45 (m, 5H); 6.17 (s, 1H); 6.0 (s, 1H); 4.6 (s, 2H); 3.35 (br s, 1H); IR (neat): 3438 (ν_{OH}); 1654 ($\nu_{C=O}$) cm^{-1}.

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