## ENE REACTIONS OF ALLYLIC TIN COMPOUNDS WITH SINGLET OXYGEN

## Hai-Shan Dang and Alwyn G. Davies\* Chemistry Department, University College London, 20 Gordon Street, London WC1H OAJ

Abstract. Allyltin compounds react with singlet oxygen by metalloallylation to give stannyl peroxides, by hydroallylation to give hydroperoxides, and by rearrangement and cycloaddition to give 4-stannyldioxolanes.

The mechanisms of the ene reactions of singlet oxygen (equation 1, M = H) have been studied for many years,<sup>1</sup> but continue to be a very active field of investigation.<sup>2</sup>

$$\begin{bmatrix} M & 0 & \frac{1}{02} \\ 0 & \frac{1}{02}$$

The superficially attractive hypothesis that a pericyclic transition state 1 is involved, analogous to that which is accepted for the corresponding diene (Diels Alder) reaction, appears to be untenable: it is incompatible with the deuterium isotope effects which are observed with stereospecifically labelled enes (e.g. *cis*- and *trans*-but-2-ene and 2,3-dimethylbut-2-ene)<sup>3</sup> and the lack of stereospecificity with certain enes.<sup>4</sup> An intermediate is required, and most current argument centres around the correct representation of this intermediate. The diradical 2 and zwitterionic 3 structures are at variance with other evidence,<sup>1</sup> and present opinion tends to favour a perepoxide structure 4, or a charge transfer complex of similar geometry. Recent progress has been slow because of the difficulty of designing suitable definitive experiments.



In organic reactions, organometallic substituents often simulate the behaviour of hydrogen,<sup>5</sup> and it secured probable that with suitably ligated metals, allyimetallic eners should react with singlet oxygen by metalloallylation (equation 1; M = a metal or organometallic group) rather than by hydroallylation. We report here the first examples of these reactions and of the alternative reactions which can be observed. 1-Trimethylstannylprop-2-ene 5 and 1-triphenylstannylbut-2-ene (5) reacted with  ${}^{5}O_{2}$  (TFP, CH<sub>2</sub>(C)<sub>2</sub>, 4DD W Na Jamp, -2D °C, 2 h) to give the products shown in equations 2 and 3



Cyclohexene 7 gave the hydroperoxide 7b in 30% yield after 8 h, whereas under the same conditions 1-triethylsilylcyclohex-2-ene 8 gave the hydroperoxide 8b in 65% yield after 5 h. There was no evidence for the formation of any sityl peroxide, or dioxetane, or dioxolane; this is in accord with previous work on the reactions of allylsilanes.<sup>6</sup>



Under the same conditions 1-trimethylstannyl-, 1-tributylstannyl-, and 1-triphenylstannyl-cyclohex-2-ene, 9, 10, and 11 respectively, reacted relatively rapidly (2 h) to give the stannyl peroxides 9a, 10a, and 11a and the stannyldioxolanes 9c, 10c, and 11c respectively; yields are given in equation 5. The stannyl peroxides do not cyclise to the stannyldioxolanes under the reaction conditions. In methanol/benzene solvent, 10 gave the stannyl peroxide 10a in >95% yield, and <5% of the dioxolane 10c.



9 R = Me	<b>9a</b> 85%	<b>9c</b> 15%
10 R = Bu	10a 76%	10c 24%
11 R = Ph	11a 64%	11c 36%

Organometallic substituents therefore have a dramatic effect on the course and rate of the ene reactions of singlet oxygen. The stannylallylation which we expected has been identified, but this can be accompanied by hydroallylation and/or cycloaddition with migration of the organotin group to give a 4-stannyldioxolane.

The results can be accommodated by an extension of the model of a perepoxide intermediate 4. Our preliminary conclusions are as follows.

The allylic rearrangement which is observed with 6 confirms that an ene reaction is taking place, not merely an insertion of dioxygen into the carbon-metal bond. Nor could we find any evidence for a radical chain reaction involving an  $S_H^2$  or  $S_H^2$ ' step, which could in principle give the same products.

The absence of hydrogen transfer from  $CH_3$  or  $CH_2$  *cis* or *trans* to  $CH_2M$  in 6 or to CHM in 8-11 suggests that only one of the two possible isomeric pereposide intermediates is being formed, and that this is stabilised by association of the oxygen with the metal as shown in 12. This is in contrast to the effect of deuterium substituents, which have a negligible effect on the initial formation of the two possible pereposides, but then can exert an isotope effect on the subsequent transfer of hydrogen.



The reaction can then be completed by transfer of the metallic group or of geminal hydrogen (equation 6). It is interesting that when hydrogen is transferred to give **6b**, the product is predominantly *cis*, whereas nonmetallic acyclic enes (M = R) usually give *trans* products.<sup>7</sup>

The migration of the metal and formation of the 4-stannyldioxolanes was unexpected. We can find no example in the literature of the shift of hydrogen and formation of a dioxolane, but there is an analogy in the reaction of 1-trimethylsilylprop-2-ene with N-phenyltriazolinedione to give a 4-

trimethylsilylpyrazolidine;<sup>8</sup> this might be taken to imply that the zwitterionic form 3 makes a substantial contribution to the structure of the intermediate.

The discovery of these new reactions may be useful in synthesis, and help to elucidate the mechanism of the ene reaction; with a suitable metallic substituent, it may be possible to identify directly the intermediate 12.

Acknowledgements. This work was supported by the SERC.

## **References.**

- R.W. Denney and N. Nickon, Org. React. (N.Y.), 1973, 20, 133. K. Gollnick and H.J. Kuhn, Singlet Oxygen, ed. H.H. Wasserman and R.W. Murray, Academic Press, N.Y. 1979. A.A. Frimer, Chem. Rev., 1979, 79, 359. A.A. Frimer and L.M. Stephenson, Singlet Oxygen, Vol. II, Part I, ed. A.A. Frimer, C.R.C. Press, Boca Raton, Florida, 1985, Chap. 3.
- e.g. M. Orfanopoulos, I. Smonou, and C.S. Foote, J. Am. Chem. Soc., 1990, 112, 3607.
  E.L. Clennan, X. Chen, and J.J. Koola, *ibid.*, 1990, 112, 5193. E.L. Clennan, J.J.Koola, and K.A. Oolman, *Tetrahedron Lett.*, 1990, 31, 6759. M. Orfanopoulos, M. Stratakis, and Y. Elemes, J. Am. Chem. Soc., 1990, 112, 6417. Y.-Y. Chan, X. Li, C. Zhu, X. Liu, Y. Zhang, and H.-K. Leung, J. Org. Chem., 1990, 55, 5497.
- B. Grdina, M. Orfanopoulos, and L.M. Stephenson, J. Am. Chem. Soc., 1979, 101, 3111.
  W. Adam, Pure Appl. Chem. 1980, 52, 2591. L.M. Stephenson, M.J. Grdina, and M. Orfanopoulos, Acc. Chem. Res., 1980, 13, 419. G. Tonachini, H.B. Schlegel, F. Bernardi, and M.A. Robb, J. Am. Chem. Soc., 1990, 112, 483. M. Orfanopoulos, I. Smonou, and C.S. Foote, J. Am. Chem. Soc., 1990, 112, 3607.
- 4. E.W.H. Asveld and R.M. Kellog, J. Org. Chem., 1982, 47, 1250. H.-S. Dang and A.G. Davies, unpublished work.
- 5. A.G. Davies. J. Organomet. Chem., 1982, 239, 87.
- J. Dubac and A. Laporterie, Chem. Rev., 1987, 87, 319. N. Shimizu, F. Shibata, S. Imazu, and Y. Tsuno, Chem. Lett, 1987, 1071. W. Adam and M. Schwarm, J. Org. Chem., 1988, 53, 3129.
- 7. C.D. Snyder and H. Rapoport, J. Am. Chem. Soc., 1969, 91, 731.
- 8. S. Ohashi, W.E. Ruch, and G.B. Butler, J. Org. Chem., 1981, 46, 614.

(Received in UK 14 January 1991)