Tetrahedron Letters,Vol.27,No.51,pp 6153-6156,1986
Printed in Great Britain

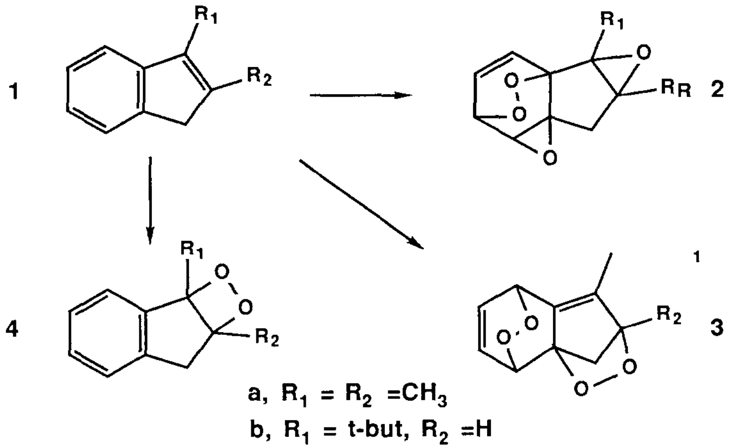
0040-4039/86 $3.00 + .00
Pergamon Journals Ltd.

PHOTOOXIDATION OF SUBSTITUTED INDENES AT LOW TEMPERATURE

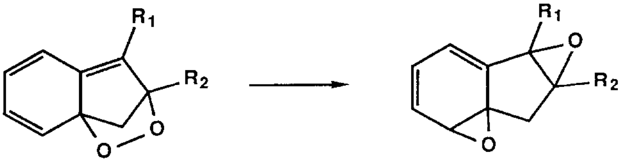
Zhang Jiancheng[1] and Christopher S. Foote[2]
Department of Chemistry and Biochemistry
University of California, Los Angeles
California 90024

Abstract: 1,2-, 1,4- and ene products were obtained on photooxidation of 2,3-dimethylindene and 3-*tert*-butylindene at low temperature. The product distribution depends on solvent.

Substituted indenes (**1**) can undergo ene, 1,2- and 1,4-addition reactions with singlet oxygen depending on the conditions.[3-11] In acetone containing Rose Bengal at -78°, diepoxyendoperoxide **2** is the major product.[6,7] However, with some sensitizers, the major product is diendoperoxide **3**.[9] Dioxetane **4** is the major product in methanol.[8]



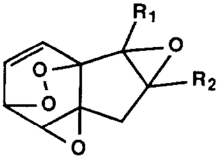
The formation of **2** and **3** was explained by the intermediacy of an unstable endoperoxide, **5**, which can either add a second molecule of singlet oxygen to give **3** or rearrange to diepoxide **6**. Addition of singlet oxygen to **6** would give **2**.[7,9] The reason for the effect of methanol is not yet certain. One possibility is that it causes rearrangement of **5** to **4**, as with some other endoperoxides.[12,13] An alternative is that a perepoxide or other intermediate is diverted in methanol to **4** instead of **5**.[8] The latter explanation would be consistent with the formation of methanol adducts under some conditions.[4,5,11]



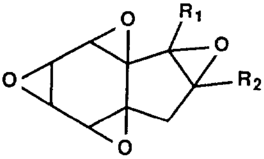
5 6

In order to establish the generality and mechanism of the environmental effects on reaction product, we investigated the photooxidation of 2,3-dimethylindene (**1a**) and 3-*tert*-butylindene (**1b**). 200 Mg of substituted indene was dissolved in 10 ml of solvent containing rose bengal (3 x 10^{-5} M) at -78°. The solution was irradiated with a 650 W tungsten-halogen lamp while O_2 was bubbled through the solution until the starting indene could not be detected by thin layer chromatography. The 1,4-addition product was isolated as a white solid, and the residue was purified by chromatography. Products[14] were identified by spectral comparison with known[6-9] compounds. Depending on the conditions, **2a**, **9a**, or **10** were formed from dimethylindene (**1a**), and **2b**, **7b**, **8b** (the latter two in traces) or **9b** from 3-tert-butylindene (**1b**). Product **2b** is unstable at room temperature in solution and slowly rearranges to **7b**. Traces of **8b** (also a rearrangement product of **2b**) are formed in acetone.

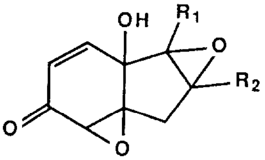
When **1a** was photooxidized in methanol at -78°, dioxetane **4a** was obtained only if $CuCl_2$-$CaCl_2$ solution was used to cut off light of wavelength ≤ 450 nm. **4a** is converted to **9a** at room or low temperature with unfiltered light.



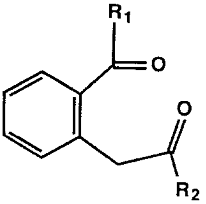
2



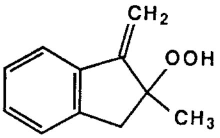
7



8



9



10

The results are given in Table 1.

Table 1. Photooxidation Products at -78°.

Substrate	Solvent[a]	Product, %		
		1,4	1,2	Ene
1a	AC	79	9	12
	ACN[b]		91	9
	MeOH		91	9
	AC/ACN (95:5)	63	16	21
	AC/MeOH (95:5)		91	9
1b	AC	95	5	—
	ACN[b]	47	53	—
	MeOH		100	—
	AC/ACN (95:5)	96	4	—
	AC/MeOH (95:5)	56	44	—

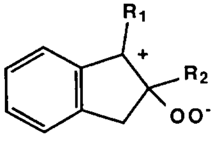
[a] AC: Acetone; ACN: Acetonitrile; MeOH: Methanol. [b] Reaction temperature was - 40 ± 5° in acetonitrile.

Table 1 shows that, in contrast to the room-temperature results,[4,5] photooxidation of **1a** at -78° gives very little ene product: 1,4 product **2a** predominates except in methanol, acetonitrile, and mixtures. Product **2a** is not observed at room temperature.[4,5] Also, methanol adducts, which form at room temperature,[4,5,11] are not formed to any significant extent at low temperature. These facts suggest that intermediates that would otherwise be diverted to ene product or trapped by methanol give rise to 1,4-addition at low temperature.

As in previous systems, methanol is the most favorable solvent for formation of dioxetane **4**. Small amounts of methanol added to acetone dramatically increase the amount of **4**. This suggests that the hydrogen-bonding ability of the solvent is more important than polarity for dioxetane formation. Although small amounts of acetonitrile in acetone do not affect the products much, pure acetonitrile favors 1,2-addition relative to acetone, suggesting polar intermediates. (Preferential formation of dioxetane relative to other products in polar solvents appears to be a general phenomenon).[15] Acetone is the best solvent for 1,4-addition under the conditions studied.

In the photooxidation of **1a**, only **10** was observed to the exclusion of the other two possible ene products. Fenical **et al.** also isolated only this ene product from the photooxidation of **1a** in methanol or CH_2Cl_2 at room temperature.[4,5] The ene product from **1b** was never found. Internal ene products do not seem to be formed from indenes.

Dioxetane and ene product, and perhaps the 1,4 product as well, are probably formed via zwitterion **11**, or from a perepoxide polarized in this direction. Because **11** should be more stable than the anti-Markovnikov isomer, only ene product **10** is formed. This conclusion is consistent with Hatsui's[11] view derived from the regiochemistry of methanol addition products during photooxidation where only the Markovnikov products are also formed.



11

References

1. Current address: Institute of Photographic Chemistry, Academia Sinica, Bei Sha Tan, Beijing, China.

2. Address correspondence to this author. Supported by NSF Grant No. CHE-83-11804. C. S. F. thanks the Alexander von Humboltstiftung for a Senior Scientist Award, and the Hahn-Meitner Institut, Berlin, for hospitality.

3. H.H. Wasserman and R.W. Murray, Eds. "Singlet Oxygen" Academic Press, New York, 1979, Chapters 6 and 8.

4. W. Fenical, D.R. Kearns and P. Radlick, *J. Amer. Chem. Soc.* **91**, 3396 (1969).

5. W. Fenical, D.R. Kearns and P. Radlick, *J. Amer. Chem. Soc.* **91**, 7771 (1969).

6. P.A. Burns, C.S. Foote and S. Mazur, *J. Org. Chem.* **41**, 899 (1976).

7. C.S. Foote, S. Mazur, P.A. Burns and D. Lerdal, *J. Amer. Chem. Soc.* **95**, 586 (1973).

8. P.A. Burns and C.S. Foote, *J. Amer. Chem. Soc.* **96**, 4339 (1974).

9. J.D. Boyd and C.S. Foote, *J. Amer. Chem. Soc.* **101**, 6758 (1979).

10. L.E. Manring, R.C. Kanner and C.S. Foote, *J. Amer. Chem. Soc.* **105**, 4707 (1983).

11. T. Hatsui and H. Takeshita, *Bull. Chem. Soc. Jap.* **53**, 2655 (1980).

12. J.-P. LeRoux and C. Goasdoue, *Tetrahedron* **31**, 2761 (1975).

13. J. Rigaudy, C. DeleTang, D. Sparfel, and N. K. Cuong, *Comptes Rends.* **267**, 1714 (1968).

14. Compound 2a (m. p. 109-109.5°) is stable in solution below 70°. Compound 4a, m. p. 40-41°, is yellow-green; NMR (d, CDCl3) 1.8 (6H), 3.4 (2H), 7.5 (4H). Compound 2b, m. p. 118-118.5°, is rapidly and completely converted to **7b**, m. p. 168-169°, above 70°. In acetone, a small amount of **8b**, m. p. 124-125°, is also formed.

15. P. D. Bartlett and M. Landis in Ref. 3.

(Received in USA 19 August 1986)