

ON THE POSSIBILITY OF DIOXIRANE FORMATION FROM CRIEGEE PEROXIDE ADDUCTS

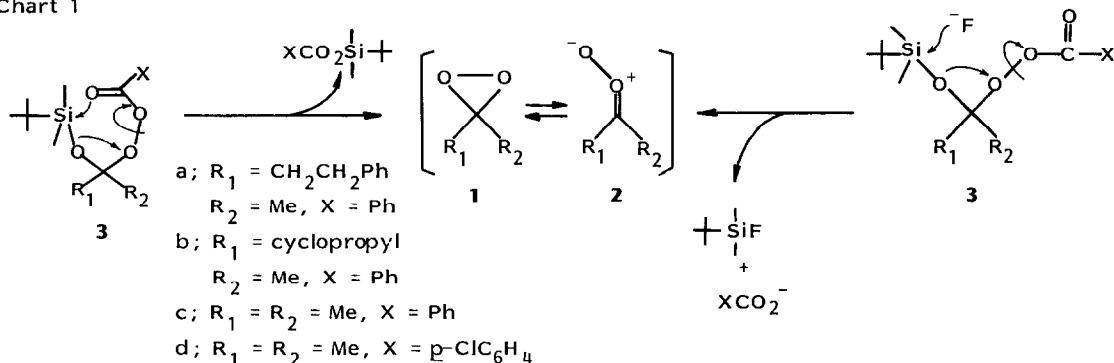
Isao Saito,* Ryu Nagata, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University,
 Kyoto 606, Japan

Summary: The possibility of dioxirane formation from thermal and cesium fluoride induced decomposition of α -t-butyl dimethylsilyloxyalkyl peroxybenzoates has been examined.

Much attention has been devoted to the structure and reactivity of dioxiranes (1) and its isomeric carbonyl oxides (2) of nonozonolytic origin¹ not only because of synthetic and mechanistic considerations^{2,3} but also as model oxenoids.⁴ Dioxirane, a hypothetical three-membered peroxide,⁵ has also been proposed as reactive species in epoxidation with many organic and inorganic peroxides.⁶ It has previously been reported that oxidation of simple acyclic ketones such as acetone with peroxomonosulfate⁷ or peracetic acid⁸ produces an epoxidizing species for which a dioxirane structure has been proposed. In these reactions an unstable Criegee peroxide adduct that is the intermediate produced in Baeyer-Villiger (BV) oxidation has been assumed to be the precursor of such epoxidizing species.^{7,8} It occurred to us that a silyl-protected derivative of such peroxide adducts, e.g., 3, would be stable enough to be isolated and might generate 1 or 2 by appropriate deprotection as illustrated in Chart I, where R₁ and R₂ should preferably be the alkyl groups of poor migratory aptitude in BV oxidation,

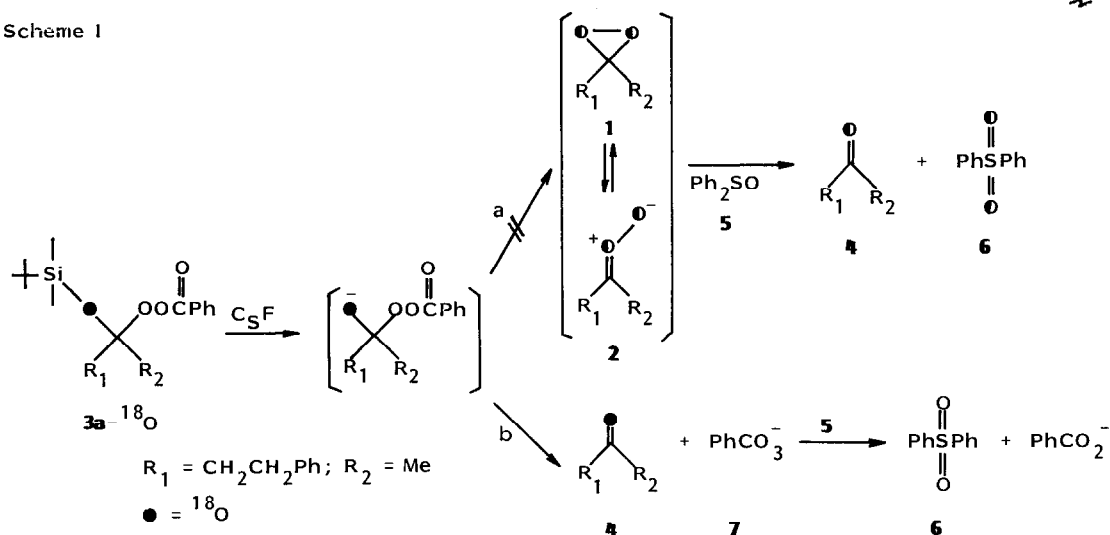
Chart 1



such as methyl, cyclopropyl or phenethyl groups.

α -*t*-Butyldimethylsilyloxyalkyl peroxybenzoates (**3a~d**) were prepared in high yields (80 ~ 95%) by benzoylation (Bz₂O, DMAP, hexane, -20 °C) of α -silyloxy hydroperoxides obtained by acid-catalyzed addition of hydrogen peroxide to silyl enol ethers.^{9,10} These peroxyesters possess reasonable thermal stability in ordinary organic solvents. Treatment of **3a**⁹ with CsF (10 equiv) in dry acetonitrile in the presence of excess *trans*-stilbene gave after an aqueous workup ketone **4** (92%) and benzoic acid (90%) but no detectable amount of stilbene oxide. In contrast, the same reaction in the presence of diphenyl sulfoxide (**5**) (2 equiv) afforded sulfone **6** (55%). Similar results have been obtained in the reaction with **3b** and **3c**. It is known that certain carbonyl oxides effectively oxidize **5** to sulfone **6**,² whereas peroxy anions are also able to oxidize sulfoxides to sulfones. In order to discriminate these two possibilities we examined ¹⁸O-labelled experiment using **3a** possessing ¹⁸O-labelled silyloxy group (¹⁸O enrichment 38%).¹¹ If sulfone **6** arises from oxidation with carbonyl oxide **2** formed via **1**, the ¹⁸O should be incorporated into **6** to some extent (Scheme I). Mass spectral analysis of the products indicated that all of the ¹⁸O was retained only in ketone **4** (¹⁸O 38%) with no incorporation into **6**. The result indicates that the oxidizing species for **5** is the peroxy anion **7** (path b) rather than dioxirane **1** or carbonyl oxide **2** (path a), implicating that intramolecular nucleophilic attack of alkoxide ion to the polarized perester oxygen resulting in the formation of **1** with the elimination of benzoate anion is not feasible at least under our conditions. The only reaction being observed with CsF is the elimination of peroxy anion **7**.¹²

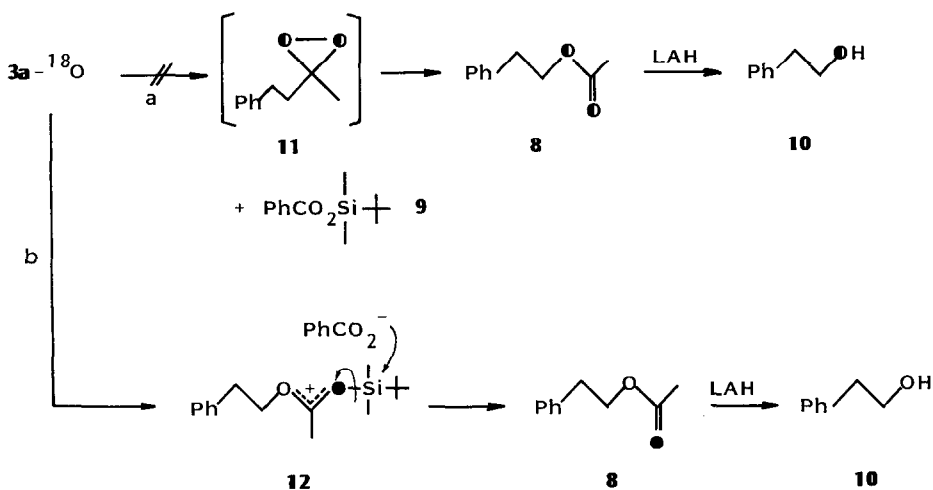
Scheme I



We then turned our attention to the possibility of dioxirane formation in thermal decomposition of **3**. Refluxing of **3a** in acetonitrile (80 °C, 40 min) in the presence of excess

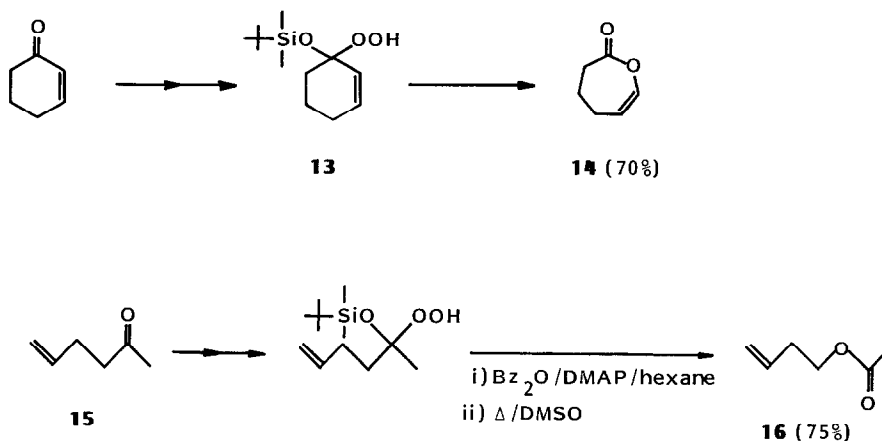
trans-stilbene resulted in an exclusive formation of phenethyl acetate **8** and silyl benzoate **9**.¹³ Neither stilbene oxide nor ketone **4** could be detected.¹⁴ Prolonged heating of **3c** in CD₃CN (90 °C, 12 h) slowly gave methyl acetate (68%) and **9** (73%) but no acetone as evidenced by ¹H NMR. A similar result was obtained with **3d** having a more good leaving group. Thermal decomposition of **3a** enriched with ¹⁸O gave **8** which was then reduced with LAH to **10**. Mass spectrum of **10** revealed no incorporation of ¹⁸O into **10**, implying no ¹⁸O scramble in the formation of **8** (Scheme II). Thus, the Criegee rearrangement of **3a** to **8** does not involve dioxirane intermediate **11** (path a) and may probably proceed via a dioxenium ion **12** as generally thought (path b).^{13,15} On the contrary to the earlier proposal,^{7,8} there has been no indication for dioxirane formation from peroxyesters **3** in our experiments. However, a metal-catalyzed decomposition of **3b** efficiently produces a powerful epoxidizing species as will be reported in an accompanying paper.

Scheme II



Finally, we disclose a few examples of the utility of silyl-protected peroxyesters in a synthesis of enol lactone and ester. Benzoylation (Bz₂O, DMAP, hexane, -20 °C) of α -silyloxyhydroperoxide **13**, readily available from cyclohexenone,⁹ followed by column chromatography over silica gel afforded enol lactone **14** (70%) which usually suffers further oxidation under the conditions for BV oxidation using peracids. Unsaturated acyclic ketones typically exemplified by **15** were converted to the corresponding esters by the sequence depicted in Chart 2 with the carbon-carbon double bond being left intact.¹⁶

Chart 2



REFERENCES AND NOTES

- (1) (a) D. P. Higley and R. W. Murray, *J. Am. Chem. Soc.*, **96**, 3330 (1974). (b) T. A. Hinrichs, V. Ramachandran, and R. W. Murray, *ibid.*, **101**, 1282 (1979). (c) W. Ando, H. Miyazaki and S. Kohmoto, *Tetrahedron Lett.*, 1317 (1979). (d) W. Adam and A. Rodriguez, *J. Am. Chem. Soc.*, **102**, 404 (1980). (e) I. Saito, A. Nakata and T. Matsuura, *Tetrahedron Lett.*, 1697 (1981).
- (2) Y. Ogata, H. Kato and Y. Sawaki, *J. Am. Chem. Soc.*, **103**, 3832 (1981).
- (3) L. B. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, **100**, 7180 (1978).
- (4) G. A. Hamilton and J. R. Giacini, *J. Am. Chem. Soc.*, **88**, 1584 (1966).
- (5) Recently, formation of dioxirane has been observed in a gas phase reaction. R. D. Suenran and F. J. Lovas, *J. Am. Chem. Soc.*, **100**, 5117 (1978).
- (6) H. Mimoun, *Angew. Chem. Int. Ed. Engl.*, **21**, 734 (1982).
- (7) (a) J. O. Edward, R. H. Pater, R. Curci, and F. DiFuria, *Photochem. Photobiol.*, **30**, 63 (1979). (b) R. Curci, M. Fiorentino, L. Trosi, J. O. Edward and R. H. Pater, *J. Org. Chem.*, **45**, 4758 (1980). (c) G. Cicala, R. Curci, M. Fiorentino, and O. Laricchiuta, *ibid.*, **47**, 2670 (1982).
- (8) R. W. Murray and V. Ramachandran, *Photochem. Photobiol.*, **30**, 187 (1979).
- (9) I. Saito, R. Nagata, K. Yuba and T. Matsuura, *Tetrahedron Lett.*, **24**, 1737 (1983).
- (10) I. Saito, R. Nagata, K. Yuba and T. Matsuura, *Tetrahedron Lett.*, **24**, 4439 (1983).
- (11) Prepared from ^{18}O -enriched benzylacetone by the following sequence: a) LDA/TBDMSCl/THF-HMPA, (b) H_2O_2 /cat. TFA/ether, (c) Bz_2O /DMPA/hexane.
- (12) Attempts to isolate perbenzoic acid were unsuccessful probably because of the further reaction of **7** with **3a**.
- (13) An analogous reaction, see: S. L. Schreiber and W-F., Liew, *Tetrahedron Lett.*, **24**, 2363 (1983).
- (14) Sulfoxide **5** was not oxidized under the conditions.
- (15) N. Beaulieu and P. Deslongchamps, *Can. J. Chem.*, **58**, 164 (1980).
- (16) A similar BV-type oxidation of unsaturated ketones using bis(trimethylsilyl) peroxide has been reported. M. Suzuki, H. Takada and R. Noyori, *J. Org. Chem.*, **47**, 902 (1982).

(Received in Japan 16 March 1984)