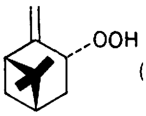
Tritylation, Methoxymethylation, and Silylation of Allylic Hydroperoxides *via* Stannyl Peroxide Intermediates. Allylic Rearrangement of a Stannyl Peroxide

Richard K. Haynes* and Simone C. Vonwiller

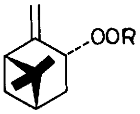
Department of Organic Chemistry, The University of Sydney, Sydney, N.S.W. 2006, Australia

Whereas primary and secondary allylic hydroperoxides are quantitatively converted by tributyltin methoxide into stannyl peroxides, whose treatment with trityl chloride, chloromethyl methyl ether, and t-butyldimethylsilyl trifluoromethane-sulphonate give the corresponding trityl, methoxymethyl, and silyl peroxides, a tertiary allylic hydroperoxide gives rearrangement products on stannylation and treatment with trityl chloride.

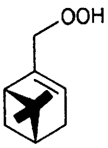
In continuing an examination of Lewis acid-catalysed oxygenation of alkenes,[1] we required allylic hydroperoxides containing hydroperoxy groups protected in such a way that intra- or inter-molecular oxygen transfer characteristic of the activity of such groups in the presence of Lewis acids is unable to take place. We required a simple general method for characterizing allylic hydroperoxides arising from catalysed oxygenation of steroids[2] and unsaturated fatty acids, particularly in those cases where the products are formed in small yields. Although base-catalysed silylation[3] and acid-catalysed alkylation[4] of secondary allylic hydroperoxides have been reported, such allylic hydroperoxides undergo competing decomposition to the corresponding ketones under the mildly acidic or basic conditions required for conventional protection.[5] We now describe a method which is free of such a side reaction and provides protected hydroperoxides in good yields.



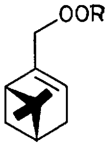
(1)



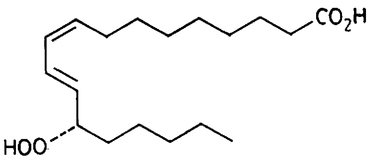
(2) R = $SnBu_3$
(3) R = COMe
(4) R = CPh_3
(5) R = CH_2OMe
(6) R = $SiMe_2Bu^t$



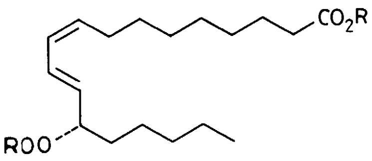
(7)



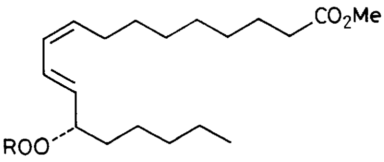
(8) R = $SnBu_3$
(9) R = CPh_3
(10) R = $SiMe_2Bu^t$



(11)

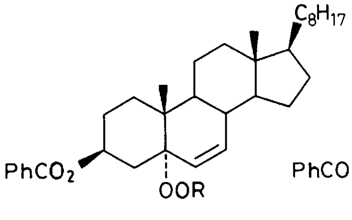


(12) R = $SnBu_3$
(13) R = CPh_3

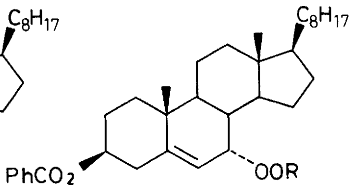


(14) R = $SnBu_3$
(15) R = CPh_3
(16) R = CH_2OMe

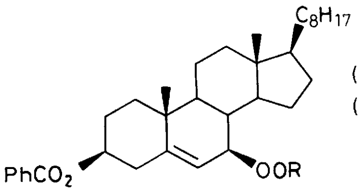
Treatment of the hydroperoxide (1)[6] (1 mmol) with tributyltin methoxide (1 equiv.) in ether during 4 h at room temperature[7] quantitatively converted it into the moisture-sensitive stannyl peroxide (2). Removal of the ether and the methanol produced in the reaction by evaporation under reduced pressure followed by treatment of the stannyl peroxide with acetyl chloride (1 equiv.) in dichloromethane at room temperature rapidly gave the acetyl peroxide (3) and tributyltin chloride in quantitative yields, as determined by ^{1}H NMR spectroscopy of the crude product mixture. The peroxide (3) is unstable, and decomposed cleanly to pin-2(10)-en-3-one during the silica gel-chromatography required to remove the tributyltin chloride. The stannyl peroxide (2) also reacted cleanly with each of 1 equiv. of trityl chloride during 20 h and chloromethyl methyl ether during 4 h under similar conditions to give the crystalline trityl peroxide (4) (67% after recrystallization) and the methoxymethyl peroxide (5) (80%). t-Butyldimethylsilyl triflate reacted in ether at −80 °C during 1 h to give the silyl peroxide (6) (82%). The primary allylic hydroperoxide (7)[6] similarly was converted by way of the



(17) R = H
(18) R = $SnBu_3$



(19) R = CPh_3
(21) R = $SnBu_3$



(20) R = CPh_3
(22) R = $SnBu_3$

stannyl peroxide (**8**) into the trityl peroxide (**9**) (85%) and the silyl peroxide (**10**) (57%). The protected hydroperoxides are stable on prolonged storage at 0 °C.

The (13*S*)-hydroperoxide (**11**) (0.2 mmol) derived from linoleic acid[9] in ether at room temperature with tributyltin methoxide (2 equiv.) gave the bis-stannylated derivative (**12**). Removal of solvent followed by addition of trityl chloride (2 equiv.) in dichloromethane resulted in quantitative formation of the bis-trityl product (**13**) after 2 h. Some hydrolysis of the trityl ester took place during chromatography of the product on neutral alumina or silica gel, although the trityl peroxide remained intact. The final yield of purified compound (**13**) obtained after chromatography was 54%. The stannyl peroxide ester (**14**) (0.2 mmol) obtained from (**11**) (diazomethane, ether, 0 °C, and then tributyltin methoxide) was also easily converted into the trityl peroxide (**15**) (80%) during 1 h and the methoxymethyl peroxide (**16**) (65%) during 20 h according to the foregoing conditions. The trityl peroxide (**15**) was easily handled, and did not undergo detectable decomposition during isolation and storage over a period of several months.

Stannylation of the tertiary allylic hydroperoxide (**17**) proceeded smoothly to give the stannyl peroxide (**18**) in quantitative yield. Remarkably, the reaction of the stannyl peroxide (0.2 mmol) as a 0.1 M solution in dichloromethane with trityl chloride during 24 h yielded solely a 3.3 : 1 mixture of the allylically-transposed α- and β-epimers (**19**) and (**20**) in an overall yield of 70%. It was noted that a 0.1 M solution of the stannyl peroxide (**18**) in $CDCl_3$ also underwent rearrangement, albeit during a period of four days under normal laboratory lighting, to give a mixture of the stannyl peroxides (**21**) and (**22**) in a similar ratio. Thus, the trityl chloride accelerates the rearrangement, presumably by irreversibly trapping the peroxides (**21**) and (**22**) which are otherwise generated in an equilibrium with peroxide (**18**). Obviously on steric grounds, the trityl chloride is unable to react with the tertiary stannyl peroxide. Although an examination of the rearrangement lies outside the scope of the present work, the reaction is of obvious importance in relation to the rearrangement of allylic hydroperoxides.[10]

Thus, the foregoing limitation aside, the method described herein for the characterisation and protection of allylic hydroperoxides is easily carried out and is in principle extensible to other reactive electrophiles. Deprotection of alkyl and silyl allylic peroxides related to those described herein has been described elsewhere.[4,11] The method is also clearly applicable to, and appears superior to other methods[12] for, the preparation of trityl esters.

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References

1 M. F. Arain, R. K. Haynes, S. C. Vonwiller, and T. W. Hambley, *J. Am. Chem. Soc.*, 1985, **107**, 4582; *Aust. J. Chem.*, 1988, **41**, 505, and references cited therein.

2 R. K. Haynes and A. E. Hilliker, *Tetrahedron Lett.*, 1986, **27**, 509.

3 A. J. Bloodworth and H. J. Eggelte, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1375.

4 P. Dussault and N. A. Porter, *J. Am. Chem. Soc.*, 1988, **110**, 6276.

5 G. O. Schenck, O.-A. Neumuller, and W. Eisfeld, *Annalen*, 1958, **618**, 202; E. D. Mihelich and D. J. Eickhoff, *J. Org. Chem.*, 1983, **48**, 4135.

6 G. O. Schenck, H. Eggert, and W. Denk, *Annalen*, 1953, **584**, 177.

7 *Cf.* A. Rieche and J. Dahlmann, *Annalen*, 1964, **675**, 19.

8 *Cf.* treatment of saturated stannyl peroxides with acetic anhydride: V. A. Dodonov, V. N. Chesnokov, and T. A. Yurchenko, *J. Gen. Chem. USSR*, 1976, **46**, 1293.

9 H. W. Gardner, *Lipids*, 1975, **10**, 248.

10 The rearrangement of the stannyl peroxides is unlikely to involve allyl-peroxy radicals which are the presumed intermediates in the allylic hydroperoxide rearrangement: A. L. J. Beckwith, A. G. Davies, I. G. E. Davison, A. Maccoll, and M. H. Mruzek, *J. Chem. Soc., Chem. Commun.*, 1988, 475; D. V. Avila, A. G. Davies, and I. G. E. Davison, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1847.

11 E. J. Corey, A. Marfat, J. R. Falck, and J. O. Albright, *J. Am. Chem. Soc.*, 1980, **102**, 1433.

12 S. Hashimoto, M. Hayashi, and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 1431.