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SYNTHESIS OF α-SILYLOXYHYDROPEROXIDES FROM THE REACTION OF SILYL ENOL ETHERS AND HYDROGEN PEROXIDE

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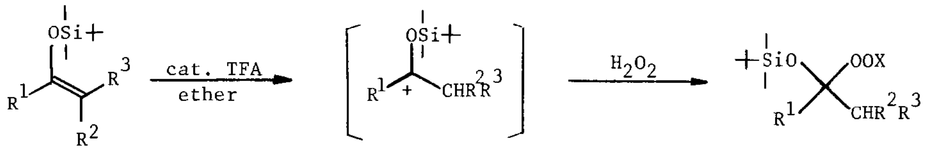
Summary: *t-Butyldimethylsilyl enol ethers derived from a wide range of ketones react with hydrogen peroxide in the presence of acid to give remarkably stable α-silyloxyhydroperoxides.*

α-Hydroxyhydroperoxides are an important class of compounds among the family of organic peroxides and their chemical reactions have been extensively studied for many years.[1] Generally, reaction of hydrogen peroxide with ketones in the presence of strong acid yields hardly isolable α-hydroxyhydroperoxides which in turn rapidly form complex mixtures of linear and cyclic dimeric, trimetic and tetrameric peroxides, possibly the most hazardous class of peroxides.[1] A notable exception is the formation of α-hydroxyhydroperoxide from 2-chlorocyclohexanone.[2] In our study directed toward the synthesis of dioxirane and carbonyl oxide, we required a silyl ether derivative of α-hydroxyalkyl peroxycarboxylate, such as **1**, a protected form of hypothetical "Criegee adduct".[3] We now wish to report herein a remarkably clean formation of stable α-silyloxyhydroperoxides (**2**) from the reaction of *t*-butyldimethylsilyl enol ethers with hydrogen peroxide in the presence of a catalytic amount of acid.[4] This method can be carried out on a gram scale without difficulties and leads to preparation of α-silyloxyhydroperoxides from a wide range of ketones in high yields. These α-silyloxyhydroperoxides possess reasonable thermal



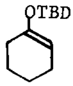
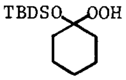
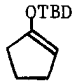
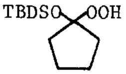
1: X = COR
2: X = H

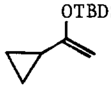
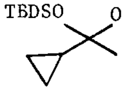
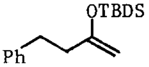
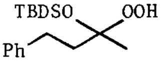
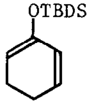
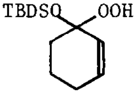
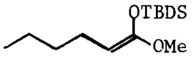
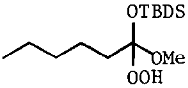
stability and high solubility in ordinary organic solvents, and hence can be easily purified by column chromatography at ambient temperature.[5]

Treatment of *t*-butyldimethylsilyl (TBDS)[6] enol ethers, prepared from the corresponding ketones (LDA/TBDSCl/THF-HMPA), with excess anhydrous H_2O_2[7] in dry ether in the presence of a catalytic amount of trifluoroacetic acid (TFA) gave high yields of α-*t*-butyldimethylsilyloxy-hydroperoxides (60 - 88%). Table I details the results. Addition of anhydrous $MgSO_4$ accelerated the reaction and hence improved the yields of hydroperoxides. Usually, a higher yield has been obtained when the reaction was stopped at *ca.* 60% conversion to prevent further reaction of the resulting α-silyloxyhydroperoxides. Reaction of O-silylated dienolate obtained from 2-cyclopenten-1-one (entry 5) and ester-derived silyl ketene acetal (entry 6) with anhydrous H_2O_2 gave the isolable hydroperoxides (8, 9) which are otherwise difficultly accessible. In the latter case acetic acid was used as acid catalyst, in place of TFA, in order to prevent decomposition of acid-sensitive hydroperoxide 9. It is worthwhile to mention here that the hydroperoxide 9 is regarded as a masked peracid, and a very few members of this class of compounds have been isolated and characterized.[8]

The following procedure is representative (entry 1). To a dry ether solution of *t*-butyldimethylsilyl enol ether 3 (3.0 g, 14.2 mmol) was added ether solution of anhydrous H_2O_2[7] (70 mmol) at room temperature. To this was added TFA (105 μℓ, 1.4 mmol) by syringe under stirring. The resulting mixture was stirred for 3 h at room temperature, then poured into a mixture of ice-cooled, saturated $NaHCO_3$ aqueous solution and *n*-hexane, and extracted with *n*-hexane. The combined hexane extracts were throughly washed with saturated NaCl aqueous solution to remove unreacted H_2O_2, dried over anhydrous $MgSO_4$ and evaporated under reduced prossure at 0 ∿ 8 °C. The residue was chromatographed on a silica gel column by using a 10 : 1 mixture of *n*-hexane and ethyl acetate to give unreacted 3 (1.15 g) and hydroperoxide 4 (1.90 g, 88% based on consumed 3), ^1H NMR ($CDCl_3$) δ 0.16 (s, 6 H), 0.86 (s, 9 H), 1.07-1.90 (m, 10 H), 7.28 (s, 1 H, OOH).

TABLE I[a]

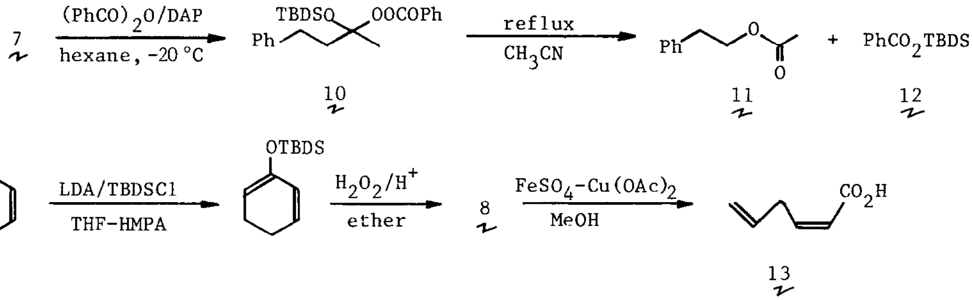
ENTRY	SILYL ENOL ETHER	ACID	PRODUCT	CONVERSION (%)	YIELD (%)[b]
1	 3	TFA	 4	62	88
2		TFA	 5	59	60

3		TFA[c]	 6	100	70
4		TFA[c]	 7	78	71
5		TFA	 8	43	76
6		CH_3CO_2H[d]	 9	100	72

[a] The reaction was conducted in dry ether using 5 ∿ 10 mol equiv. of anhydrous H_2O_2 and 5 mol% of TFA, unless otherwise noted. [b] All yields based on consumed silyl enol ethers represent isolated pure products after silica gel column chromatography. All new compounds gave consistent spectral data and elemental analyses. [c] 1 mol% TFA. [d] 5 mol% acetic acid.

A few examples of the use of α-silyloxyhydroperoxides in synthesis are illustrated in Scheme 1. Benzoylation (benzoic anhydride/4-dimethylaminopyridine/hexane/-20 °C) of the hydroperoxide 7 gave 10[9] (95%), a silyl protected compound proposed as an intermediate in Baeyer-Villiger oxidation of ketones with perbenzoic acid.[3a] Refluxing of the acetonitrile solution of 10 without any acid catalyst immediately produced 11 and 12 in almost quantitative yield. Addition of $FeSO_4$ to a solution of 8 in methanol saturated with $Cu(OAc)_2$ resulted in fragmentation of 8 to give (2Z)-2,5-hexadienoic acid[10] (13) (65%) in a regiospecific manner.[11]

Scheme 1



Further studies on the utility of α-silyloxyhydroperoxides are underway.

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(2) M. S. Kharash and G. N. Sosnovsky, *J. Org. Chem.*, **23**, 1322 (1958).

(3) (a) W. S. Trahanovsky Ed., "Oxidation in Organic Chemistry", Part C, Academic Press, 1978, p. 257. (b) J. d'Ans, K. M. Dossow, and J. Mattner, *Angew. Chem.*, **66**, 633 (1954).

(4) Alkenes with electron-donating groups are known to undergo acid-catalyzed reaction with hydrogen peroxide via carbenium ion intermediates.[1b]

(5) We had no experience of any small explosion throughout this work. However, these hydroperoxides should be handled with care.

(6) Trimethylsilyl enol ethers can not be used because of their acid-catalyzed solvolytic lability.

(7) The ether solution (2.5 M) of anhydrous H_2O_2 was prepared by extraction of 30% aqueous H_2O_2 solution with ether. The ether extracts were dried over anhydrous $MgSO_4$ and titrated iodometrically.

(8) (a) A. Riche, E. Schmitz, and E. Beyer, *Chem. Ber.*, **91**, 1942 (1958). (b) J. Rebek, Jr. and R. McCready, *J. Am. Chem. Soc.*, **102**, 5602 (1980), and references therein.

(9) ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 6 H), 0.93 (s, 9 H), 1.60 (s, 3 H), 1.93-2.40 (m, 2 H), 2.53-3.0 (m, 2 H), 7.23 (bs, 5 H), 7.30-7.67 (m, 3 H), 7.97 (dd, 2 H, J = 8, 2 Hz); IR (Nujol) 1765 cm^{-1}

(10) For a recent alternative approach to the synthesis of this compound, see P. F. Hudrlik, A. M. Hudrlik, G. Nagendrappa, T. Yimenu, E. T. Zellers, and E. Chin, *J. Am. Chem. Soc.*, **102**, 6896 (1980).

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