A Convenient and General Preparation of Alkyl Hydroperoxides and Dialkyl Peroxides

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Summary Primary, secondary, and tertiary alkyl hydroperoxides and dialkyl peroxides can be prepared from the appropriate alkyl bromide or iodide and hydrogen peroxide or alkyl hydroperoxide in the presence of silver trifluoroacetate.

THE established syntheses of alkyl hydroperoxides and dialkyl peroxides are limited in their scope. We report here a new general preparative method which overcomes these limitations.

Organic peroxides are usually prepared by the nucleophilic substitution reaction of a peroxide reagent at a carbon centre (equation 1; $X = OH_2^+$, OSO_2OH, OSO_2OR, or OSO_2Me; $R^2 = H$ or alkyl).[1]

$$R^2OOH + R^1X \rightarrow R^2OOR^1 + HX \qquad (1)$$

When R^1 is a tertiary alkyl group, R^1X is normally an alcohol[2] or alkyl hydrogen sulphate,[3] the reaction being carried out in the presence of concentrated sulphuric acid and involving an S_N1 mechanism. Symmetrical t-butyl, t-pentyl, and t-hexyl peroxides can be prepared by this method, but the attempted synthesis of higher homologues leads to dehydration of the alcohol and the formation of rearranged products; $Et_2PrCOOCEt_2Pr$, and presumably also the higher homologues, cannot be obtained by this procedure.[4]

When R^1 is a secondary or primary alkyl group, R^1X is usually a sulphate[5] or methanesulphonate,[6] and the reaction is carried out under basic conditions to promote an S_N2 mechanism. However, the peroxides are sensitive to base-catalysed decomposition,[7] and yields (especially of the secondary derivatives) are generally low.[1]

We have found that primary, secondary, and tertiary alkyl hydroperoxides and dialkyl peroxides can readily be prepared by treating the appropriate alkyl bromide (tertiary and secondary derivatives) or iodide (primary derivatives) and hydrogen peroxide or alkyl hydroperoxide with silver trifluoroacetate (equation 2; $R^2 = H$ or alkyl; $X = Br$ or I).

$$R^2OOH + R^1X + AgOCOCF_3 \rightarrow R^2OOR^1 + AgX + HOCOCF^3 \qquad (2)$$

TABLE

Peroxide	Reactants	Yield (%)
Bu^nOOBu^t	$Bu^nI + Bu^tOOH$	50
$n\text{-}C_6H_{13}OOH$	$n\text{-}C_6H_{13}I + H_2O_2$	38
$n\text{-}C_6H_{13}OO\text{-}n\text{-}C_6H_{13}$	$n\text{-}C_6H_{13}I + n\text{-}C_6H_{13}OOH$	40
Bu^sOOBu^t	$Bu^sBr + Bu^tOOH$	38
Bu^sOOH	$Bu^sBr + H_2O_2$	42
Bu^sOOBu^s	$Bu^sBr + Bu^sOOH$	27
Bu^tOOBu^t	$Bu^tBr + Bu^tOOH$	48
$Me_2EtCOOH$	$Me_2EtCBr + H_2O_2$	39
$Me_2EtCOOCMe_2Et$	$Me_2EtCBr + Me_2EtCOOH$	93
$Me_2EtCOOCMe_2Et$	$2Me_2EtCBr + H_2O_2$	30
$Me_2EtCOOBu^t$	$Me_2EtCBr + Bu^tOOH$	66
Me_2Pr^iCOOH	$Me_2Pr^iCBr + H_2O_2$	40
$Me_2Pr^iCOOCMe_2Pr^i$ [b,c]	$Me_2Pr^iCBr + Me_2Pr^iCOOH$	60
Me_2Bu^tCOOH	$Me_2Bu^tCBr + H_2O_2$	45
$Me_2Bu^tCOOCMe_2Bu^t$ [b]	$Me_2Bu^tCBr + Me_2Bu^tCOOH$	58
Pr_3COOH	$Pr_3CBr + H_2O_2$	60
$Pr_3COOCPr_3$ [b]	$Pr_3CBr + Pr_3COOH$	54

[a] t-Alkyl bromides which were not commercially available were prepared by treating the appropriate alcohol with conc. aqueous HBr in the presence of conc. H_2SO_4 (*cf.* D. Bryce-Smith and K. E. Howlett, *J. Chem. Soc.*, 1951, 1141). [b] Compounds previously unreported. [c] An attempted synthesis of this compound from Me_2Pr^iCOH, sulphuric acid, and hydrogen peroxide at low temperature led to the formation of tetramethylethylene, none of the required product being isolated.

The compounds obtained by this method are shown in the Table. The hydroperoxides were prepared by adding silver trifluoroacetate[8] in small portions to an ice-cooled solution in ether of the appropriate alkyl halide and hydrogen peroxide in up to a one-fold excess. The reaction is virtually instantaneous; the silver halide was filtered off, the trifluoroacetic acid formed and the excess of hydrogen peroxide were removed by treatment with aqueous sodium hydrogen carbonate, and the solvent was removed to leave the crude hydroperoxide. The dialkyl peroxides were prepared similarly in pentane using only a slight excess of the crude hydroperoxide (the purity of which was determined iodometrically), were purified either by distillation, crystallisation, or chromatography on basic alumina, and were characterized by elemental analyses, i.r. and ^1H and ^{13}C n.m.r. spectroscopy, and mass spectrometry. Di-t-pentyl peroxide was also prepared (yield, 30%) from a one-step reaction of t-pentyl bromide and hydrogen peroxide (in ratio 2:1) and silver trifluoroacetate in ether.

The reaction is apparently safe and is very easily carried out on readily obtainable materials. In particular, it provides for the first time a general method for preparing primary, secondary, and tertiary alkyl peroxides.

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