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Preliminary communication

THE 1,4-DIAZA[2.2.2]BICYCLOOCTANE—HYDROGEN PEROXIDE COMPLEX AS A SOURCE OF ANHYDROUS HYDROGEN PEROXIDE: THE PREPARATION OF BIS(TRIALKYLSILYL) PEROXIDES

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Summary

The hazard and inconvenience of storing and handling concentrated hydrogen peroxide can be avoided by using instead the solid 1/2 complex which 1,4-diazabicyclo[2.2.2]octane forms with hydrogen peroxide, it reacts with trialkylchlorosilanes to give bis(trialkylsilyl) peroxides in good yield.

The use of hydrogen peroxide as a reagent has been exploited less than it warrants because the anhydrous material is not readily available, and is inconvenient and hazardous to handle. We wish to report that these disadvantages can be overcome by the use of the 1/2 complex which 1,4-diaza-[2.2.2]bicyclooctane [DABCO, $N(CH_2CH_2)_3N$] forms with hydrogen peroxide [1]. The use of this reagent is illustrated in the preparation of bis(trialkylsilyl) peroxides.

The DABCO,$2H_2O_2$ complex was prepared from aqueous hydrogen peroxide (⩾ 30%) and the diamine in ether at about 0°, according to Oswald and Guertin's method [1]. It separates as a granular rather hygroscopic solid which can be kept at room temperature for at least some months, but is reported to decompose above 60°.

Bis(trialkylsilyl) peroxides were prepared by adding the appropriate chlorosilane (5-10 g) to a slurry of DABCO,$2H_2O_2$ (1.1 mol) and DABCO (1 mol) in dichloromethane, with ice cooling, when the amine hydrochloride was immediately precipitated**. The mixture was stirred for 2 h at room temperature, and then filtered. The filtrate was concentrated, and the peroxide extracted into pentane. When the pentane was removed, the peroxide was

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[**] Fan and Shaw [2] have reported the preparation of alkylperoxysilanes from the corresponding chlorosilanes and DABCO—alkyl hydroperoxide complexes.

generally obtained in high yield, the only contaminant being a small amount of the silanol or disiloxane

$$4R_3SiCl + N(CH_2CH_2)_3N{,}2H_2O_2 + N(CH_2CH_2)_3N \rightarrow 2R_3SiOOSiR_3 + 2[N(CH_2CH_2)_3N{,}2HCl]$$

Some examples of disilyl peroxides prepared by this method are given in Table 1.

TABLE 1

THE PREPARATION OF BIS(TRIALKYLSILYL) PEROXIDES

Peroxide	Yield (%)		B.p. (°C/mmHg)
	Undistilled	Distilled	
$Me_3SiOOSiMe_3$	62 [a]	35	42/30 [b]
$Et_3SiOOSiEt_3$	100	71	61/0.03 [c]
$Pr_3SiOOSiPr_3$	100	60	95/0.01
$Me_2PrSiOOSiPrMe_2$	96	72	81-83/10
$Me_2(PhCH_2)SiOOSi(CH_2Ph)Me_2$		45	m.p. 58 [d]
$Me_2(EtO)SiOOSi(OEt)Me_2$	95		82-84/20
$Et_3GeOOGeEt_3$ [e]	84		47/0.005 [f]

[a] Some peroxide was lost because of its volatility. [b] Lit. [3] 38°/30 mmHg. [c] Lit. [4] 62°/0.02 mmHg. [d] Recrystallised from hexane. [e] From triethylchlorogermane in acetonitrile. [f] Lit. [5] 56-57°/0.05 mmHg.

The reagent has the advantage that it can readily be prepared from aqueous hydrogen peroxide, and provides a convenient and apparently safe form in which anhydrous hydrogen peroxide can be isolated, stored, and handled. Appropriate safety precautions should of course be taken until its properties are better understood. Its use should make available new types of symmetrical peroxides (and thence the corresponding oxyl radicals), and it should also find more general application as a reagent in organic synthesis.

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