

mmol, 8%) of **4**, mp 179–181°, ir (KBr) 1155 and 874 cm^{-1} . Removal of the ether yielded approximately 27 mg (0.15 mmol, 12%) of **2**, ir (CCl_4) 1667 cm^{-1} . Finally, elution with benzene gave 247 mg (0.95 mmol, 71%) of **3**, mp 158–160°.

In a final experiment a magnetically stirred mixture consisting of 13.1 g (0.16 mol) of freshly distilled 2,3-dimethylbutadiene,¹³ 4.87 g (0.01 mol + 10% excess) of LTA from which the acetic acid had previously been removed *in vacuo*, and 36 ml of methylene chloride was immersed in a Dry Ice–acetone bath and maintained under a nitrogen atmosphere. A solution of 2.75 g (0.01 mol) of **1** in 25 ml of methylene chloride was then admitted dropwise during a period of 30 min. The brown reaction mixture was stirred for 1 hr, at the end of which time the color had entirely discharged. Work-up of the reaction mixture in the usual aqueous fashion, followed by the removal of the solvent and excess 2,3-dimethylbutadiene *via* rotary evaporator, yielded as the major product 2.20 g (0.0043 mol, 85%) of a crystalline white solid, mp 179–183°. The white solid exhibited the same melting point behavior noted with authentic trityl peroxide,⁷ and, analogously, was also insoluble in either cold benzene or cold ether but readily soluble in cold concentrated sulfuric acid. In the latter solvent, an orange-red solution resulted. The spectral (ir, nmr) properties of the product were identical with those of authentic trityl peroxide.⁷ Recrystallization of the solid from benzene–chloroform gave the analytical sample.

Anal. Calcd for $\text{C}_{38}\text{H}_{30}\text{O}_2$: C, 88.00; H, 5.79. Found: C, 87.51; H, 6.02.

Registry No.—**1**, 31938-11-1; **2**, 119-61-9; **3**, 76-84-6; **4**, 596-30-5; LTA, 546-67-8.

(13) C. F. H. Allen and A. Bell, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 312.

Amine–Hydroperoxide Adducts. Use in Synthesis of Silyl Alkyl Peroxides

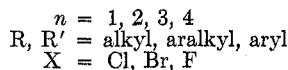
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Silyl alkyl peroxides (compounds containing one or more Si–O–O–C bonds) were first reported by Bunce and Davies in 1956.¹ Subsequently, a number of publications were released concerning the preparation and characterization.^{2–5}

The general method for the preparation of silyl alkyl peroxides involves reaction of an alkyl, aryl, or aralkyl hydroperoxide with a chlorosilane.



Such reactions are usually carried out in an inert solvent in the presence of an acid acceptor, pyridine for instance. Much lower yields result in the absence of acid acceptors.²

A less frequently used method involves the condensation of trimethylsilyl alkyl amines with *tert*-butyl hydroperoxide. A 20% yield of trimethyl(*tert*-butylperoxy)silane has been reported.⁵

Generally speaking, there are two drawbacks to these

methods: (1) the yields are fairly low, especially for silyl alkyl peroxides containing more than one peroxy group; (2) the silyl alkyl peroxides made must be purified by distillation or other suitable means subsequent to the preparation step.

Results and Discussion

Synthesis by the Amine–Hydroperoxide Adduct Method.—The amine–hydroperoxide adduct synthesis of silyl peroxides requires two steps: (1) preparation of the amine–hydroperoxide adduct; (2) reaction of the adduct with chlorosilane in an inert solvent. Preparation of the adduct is carried out by mixing stoichiometric amounts of a suitable amine and the hydroperoxide in an inert solvent.⁶ Assuming that the proper solvent has been selected, the crystalline adduct separates and can be collected by filtration.

Not all amines form adducts with hydroperoxides. For the majority of our work we have used 1,4-diazabicyclooctane (Dabco). The selection of Dabco resulted when other amines examined failed one or more of the following criteria: (1) the adduct must be a solid at the reaction temperature; (2) the solid adduct should be fairly insoluble in the solvent of choice; (3) the amine should not be oxidized by any of the reactants or products.

Primary and secondary amines were largely ruled out by **3**. The convenience of operating at ambient temperatures, or slightly above, eliminated those amines which gave insoluble adducts only at lower temperatures.

No compromises were required when Dabco was used as the adduct amine. Both nitrogens of Dabco are involved and the resulting adduct contains 2 mol of hydroperoxide/mol of Dabco. The same solvent used for adduct preparation may be used for the halosilane reaction. The reaction is exothermic and usually complete within minutes. Once the Dabco hydrochloride is removed by filtration, solvent evaporation produces very pure silyl alkyl peroxide.

Hexamethylenetetramine (Hexa) also formed solid *tert*-butyl or cumyl hydroperoxide adducts. Unlike Dabco, only one nitrogen was involved in the Hexa adduct. When treated with halosilanes, poor yields, typically below 50%, of silyl alkyl peroxides were obtained. Reasoning that the remaining nitrogens were involved, calcium chloride was introduced into the reaction medium prior to the addition of halosilane to complex and nitrogens not involved in adduct formation. Under these conditions, high yields of product were obtained. Other metal salts (Ba^{2+} , Mg^{2+}) capable of complexing nitrogen were used successfully. Metals which did not complex had no effect.

Tables I–IV list the silyl alkyl peroxides prepared using the amine–hydroperoxide adduct technique. For convenience they are grouped according to the number of alkylperoxy substituents on silicon. References are given, where available, to those compounds appearing in the literature previously along with their reported yields.^{7–9}

(1) E. Bunce and A. G. Davies, *Chem. Ind. (London)*, 1052 (1956).
 (2) A. G. Davies and E. Bunce, British Patent 827,366 (Feb 3, 1960).
 (3) H. Jenkner, U. S. Patent 2,997,497 (Aug 22, 1961).
 (4) G. Sosnovsky and J. H. Brown, *Chem. Rev.*, **66**, 529 (1966).
 (5) R. A. Pike and L. H. Shaffer, *Chem. Ind. (London)*, 1294 (1957).

(6) A. A. Oswald, U. S. Patent 3,236,850 (Feb 22, 1966).
 (7) A. K. Litkovets and T. I. Yurzenko, *Dokl. Akad. Nauk SSSR*, **142**, 1316 (1962).
 (8) T. I. Yurzenko and A. K. Litkovets, *ibid.*, **136**, 1361 (1961).
 (9) E. Bunce and A. G. Davies, *J. Chem. Soc.*, 1550 (1958).

TABLE I

Registry no.	Compd	Yield, % (lit.)	MONOPEROXYSILANE		O-O frequency in the ir, cm ⁻¹	Characteristic nmr signals, ^f δ
			Dec temp, °C	Physical characteristics, lit.		
3985-63-7	Trimethyl(<i>tert</i> -butylperoxy)silane ^a	91 (54-89)	114 (boiling)	Colorless liquid, bp 41° (0.05 mm) ^g	906 (m)	0.1 (s, 9, trimethylsilyl), 1.15 (s, 9, <i>tert</i> -butyl)
18057-16-4	Trimethyl(α,α -dimethylbenzylperoxy)silane ^b	75 (53)	176	Colorless liquid, bp 43° (0.05 mm) ^g	905 (m)	0.13 (s, 9, trimethylsilyl), 1.55 (s, 6, isopropyl)
2097-21-4	Triethyl(<i>tert</i> -butylperoxy)silane	74	175	Colorless liquid, bp 39° (0.05 mm) ^h	903 (w)	0.92 (t, 9, methyl), 1.18 (s, 9, <i>tert</i> -butyl)
39809-93-3	Triethyl(α,α -dimethylbenzylperoxy)silane	80	167	Colorless liquid	909 (m)	0.88 (t, 9, methyl), 1.54 (s, 6, isopropyl)
39809-94-4	Tri- <i>n</i> -butyl(<i>tert</i> -butylperoxy)silane	95	170	Colorless liquid	903 (w)	0.90 (t, 9, methyl), 1.21 (s, 9, <i>tert</i> -butyl)
39809-95-5	Tri- <i>n</i> -butyl(α,α -dimethylbenzylperoxy)silane	95	157	Colorless liquid	902 (vw)	0.90 (t, 9, methyl), 1.56 (s, 6, isopropyl)
25836-01-5	Allyldimethyl(<i>tert</i> -butylperoxy)silane ^c	95	178	Colorless liquid	927 (w)	0.13 (s, 6, dimethylsilyl), 1.16 (s, 9, <i>tert</i> -butyl)
39809-97-7	Vinyldiphenyl(α,α -dimethylbenzylperoxy)silane	92	155	Colorless liquid	900 (w)	1.52 (s, 6, isopropyl), 6.2 (m, 3, vinyl), 7.36 (m, 5, phenyl), 7.65 (m, 10, phenylsilyl)
39809-98-8	Chloromethyldimethyl(α,α -dimethylbenzylperoxy)silane	95	172	Slightly yellowish liquid	903 (m)	0.27 (s, 6, dimethylsilyl), 1.56 (s, 6, isopropyl), 2.82 (s, 2, methylene)
39809-99-9	Dimethylphenyl(α,α -dimethylbenzylperoxy)silane ^d	93	215	Colorless liquid	902 (w)	0.42 (s, 6, dimethylsilyl), 1.47 (s, 6, isopropyl)
39810-00-9	Methyldiphenyl(α,α -dimethylbenzylperoxy)silane	93	177	Colorless liquid	902 (w)	0.70 (s, 3, methylsilyl), 1.50 (s, 6, isopropyl)
18751-58-1	Triphenyl(<i>tert</i> -butylperoxy)silane ^e	95 (80)	205	White crystal of mp 62°, 50° ^g	902-920 (vw)	1.13 (s, 9, <i>tert</i> -butyl), 7.45 (m, 15, triphenylsilyl)
31731-51-8	Triphenyl(α,α -dimethylbenzylperoxy)silane	70	220	White crystal of mp 72°	904 (vw)	1.51 (s, 6, isopropyl), 7.45 (m, 15, triphenylsilyl), 7.75 (m, 5, phenyl)

^a Calcd for C₇H₁₈O₂Si: C, 51.8; H, 11.2. Found: C, 52.03; H, 11.27. ^b Calcd for C₁₂H₂₀O₂Si: C, 64.25; H, 8.92. Found: C, 63.95; H, 8.88. ^c Calcd for C₉H₂₀O₂Si: C, 57.44; H, 10.64. Found: C, 57.16; H, 10.57. ^d Calcd for C₁₇H₂₂O₂Si: C, 69.23; H, 7.69. Found: C, 68.92; H, 7.87. ^e Calcd for C₂₂H₂₄O₂Si: C, 73.07; H, 7.69. Found: C, 72.79; H, 7.82. ^f m = multiple signals. ^g Reference 9. ^h Reference 4.

TABLE II

Registry no.	Compd	Yield, % (lit.)	BISPEROXYSILANE		O-O frequency in the ir, cm ⁻¹	Characteristic nmr signals, δ
			Dec temp, °C	Physical characteristics, lit.		
10196-44-8	Dimethylbis(<i>tert</i> -butylperoxy)silane ^a	76	185	Colorless liquid	910 (m)	0.24 (s, 6, dimethylsilyl), 1.22 (s, 18, <i>tert</i> -butyl)
31602-49-0	Dimethylbis(α,α -dimethylbenzylperoxy)silane	85	142	Colorless liquid	913 (m)	0.23 (s, 6, dimethylsilyl), 1.58 (s, 12, isopropyl)
18027-26-4	Allylmethylbis(<i>tert</i> -butylperoxy)silane	90 (40) ^d	170	Colorless liquid, bp 31° (0.1 mm) ^e	900-930 (m)	0.26 (s, 3, methylsilyl), 1.25 (s, 18, <i>tert</i> -butyl), 1.81 (d, 2, methylene-silyl)
18002-70-5	Vinylmethylbis(<i>tert</i> -butylperoxy)silane ^b	92 (57) ^f	170	Colorless liquid, bp 90° (20 mm) ^g	910 (m)	0.24 (s, 3, methylsilyl), 1.25 (s, 18, <i>tert</i> -butyl)
39810-07-6	Vinylphenylbis(<i>tert</i> -butylperoxy)silane	95	137	Colorless liquid	905-925 (m)	1.25 (s, 18, <i>tert</i> -butyl), 6.23 (m, 3, vinyl), 7.57 (m, 5, phenyl)
15188-08-6	Diphenylbis(<i>tert</i> -butylperoxy)silane ^c	89	165	Colorless liquid, bp 110° (0.001 mm) ^d	905	1.21 (s, 18, <i>t</i> -butyl), 7.50 (m, 10, phenyl)

^a Calcd for C₁₀H₂₄O₄Si: C, 50.85; H, 10.17. Found: C, 51.09; H, 10.46. ^b Calcd for C₁₁H₂₄O₄Si: C, 53.23; H, 9.68. Found: C, 51.71; H, 9.39. ^c Calcd for C₂₀H₂₈O₄Si: C, 66.67; H, 7.78. Found: C, 64.97; H, 7.49. ^d Reference 9. ^e Reference 7. ^f Reference 10. ^g Reference 8.

Most of the silyl alkyl peroxides exhibit characteristic O-O absorption bands in the infrared.¹⁰ Monoperoxy-silanes usually show a weak band near 905 cm⁻¹. With increasing alkylperoxy substitution on silicon, both frequency and intensity are increased. Furthermore, two overlapping bands located between 900 and 940 cm⁻¹ have been observed for most of the multiply substituted alkylperoxy silanes. Along with the infrared data, nmr data are included in Tables I-IV.

As might be expected, increasing the number of alkylperoxy substituents decreases the thermal stability of the silyl alkyl peroxides. Using a qualitative test in which peroxides are examined for the temperature at which the onset of rapid gas evolution occurs, compounds of general formula (CH₃)_nSi(OO-cumyl)_{4-n} gave decomposition points of 176, 142, 100, <100° as *n* increased from 1 to 4. A similar trend was measured when *tert*-butyl was substituted for cumyl.

(10) A. Simon and H. Arnold, *J. Prakt. Chem.*, (4) **8** (5-6), 241 (1959).

Experimental Section

Dabco-*tert*-Butyl Hydroperoxide Adduct.—Syntheses of both the titled adduct and the Dabco-cumyl hydroperoxide adduct were carried out according to the literature procedures⁶ without modification.

Hexa-*tert*-Butyl Hydroperoxide Adduct.—To a solution containing 60 parts of *tert*-butyl hydroperoxide in 500 parts of hexane was added 43.5 parts of Hexa (Union Carbide Hexa, purity 99%). The slurry was stirred for 1 hr at room temperature. The white crystals were removed by filtration. Upon evaporating the filtrate an additional quantity was obtained. The total yield was 78 parts, corresponding to 100% theoretical. The salt decomposed without melting at 73° (lit. mp 74° dec).⁶ Spectroscopic data showed the product to be a Hexa-*tert*-butyl hydroperoxide (1:1) adduct rather than the 1:2 adduct reported previously:⁶ ir (KBr) 847 cm⁻¹ (weak, peroxide); nmr (CDCl₃) δ 1.25 (t, 9, *tert*-butyl), 4.70 (t, 12, methylene).

Anal. Calcd for C₁₀H₂₂O₂N₄: C, 52.17, H, 9.56. Found: C, 52.51; H, 9.72.

Silyl Alkyl Peroxide via the Dabco-Hydroperoxide Adduct Method. **General.**—To a slurry of Dabco-hydroperoxide adduct and an inert medium was added with vigorous stirring a stoichiometric amount of a halosilane. A rapid, exothermic reac-

TABLE III
TRISPEROXYSILANE

Registry no.	Compd	Yield, % (lit.)	Dec temp, °C	Physical characteristics, lit.	O-O frequency in the ir, cm ⁻¹	Characteristic nmr signals, δ
5797-01-3	Tris(<i>tert</i> -butylperoxy)silane	55	120	Colorless liquid	940 (s), 940 (s)	1.28 (s, 27, <i>tert</i> -butyl), ca. 1.35 (s, 1, silane)
10196-45-9	Methyltris(<i>tert</i> -butylperoxy)silane ^a	78 (49) ^a	150	Colorless liquid, bp 50° (0.1 mm) ^b	913 (s), 927 (s)	0.45 (s, 3, methyl), 1.28 (s, 27, <i>tert</i> -butyl)
31602-50-3	Methyltris(α,α -dimethylbenzylperoxy)-silane	57	100	Colorless liquid	923 (s)	0.45 (s, 3, methyl), 1.57 (s, 18, isopropyl), 7.35 (m, 15, phenyl)
31218-59-4	<i>n</i> -Hexyltris(<i>tert</i> -butylperoxy)silane	76	164	Colorless liquid	912 (s), 927 (m)	0.91 (t, 3, methyl), 1.27 (s, 27, <i>tert</i> -butyl)
39810-12-3	<i>n</i> -Hexyltris(α,α -dimethylbenzylperoxy)-silane	95	154	Colorless liquid	912 (s)	0.91 (t, 3, methyl), 1.57 (s, 18, isopropyl), 7.35 (m, 15, phenyl)
31218-60-7	<i>n</i> -Dodecyltris(<i>tert</i> -butylperoxy)silane	90	155	Colorless liquid	912 (m), 927 (w)	Ca. 0.95 (t, 3, methyl), 1.27 (s, 27, <i>tert</i> -butyl)
39810-14-5	<i>n</i> -Dodecyltris(α,α -dimethylbenzylperoxy)-silane	95	152	Colorless liquid	905 (m), 917 (m)	Ca. 0.95 (t, 3, methyl), 1.57 (s, 18, isopropyl), 7.30 (m, 15, phenyl)
15188-09-7	Vinyltris(<i>tert</i> -butylperoxy)silane ^b	86 (40) ^c	154	Colorless liquid, bp 78° (1 mm) ^d	913 (s), 930 (m)	1.27 (s, 27, <i>tert</i> -butyl), ca. 6.22 (m, 3, vinyl)
24685-79-8	Vinyltris(α,α -dimethylbenzylperoxy)silane	93	140	Slightly yellowish liquid	917 (s)	1.57 (s, 18, isopropyl), ca. 6.18 (m, 3, vinyl), 7.30 (m, 15, phenyl)
27612-79-9	Allyltris(<i>tert</i> -butylperoxy)silane ^e	80	174	Colorless liquid	917 (s), 927 (s)	1.27 (s, 27, <i>tert</i> -butyl), 2.05 (m, 2, methylenesilyl)
39810-18-9	Phenyltris(α,α -dimethylbenzylperoxy)silane	61	<i>f</i>	Colorless liquid	910-920 (m)	1.57 (s, 18, isopropyl)
39810-19-0	3,3,3-Trifluoropropyltris(<i>tert</i> -butylperoxy)-silane	80	177	Colorless liquid	913-926 (s)	1.25 (s, 27, <i>tert</i> -butyl)
27714-68-7	γ -Methacryloxypropyltris(<i>tert</i> -butylperoxy)-silane ^d	70	193	Colorless liquid	910 (m), 930 (m)	1.29 (s, 27, <i>tert</i> -butyl), 1.95 (s, 3, methyl), 4.17 (t, 2, ether methylene)
27612-88-0	Isocyanatopropyltris(<i>tert</i> -butylperoxy)-silane ^e	88	140	Colorless liquid	908-920 (s)	

^a Calcd for C₁₃H₃₀O₆Si: C, 50.32; H, 9.68. Found: C, 50.00; H, 9.29. ^b Calcd for C₁₄H₃₀O₆Si: C, 52.46; H, 9.43. Found: C, 50.15; H, 9.22. ^c Calcd for C₁₅H₃₂O₆Si: C, 53.53; H, 9.58. Found: C, 51.20; H, 9.25. ^d Calcd for C₁₉H₃₈O₆Si: C, 54.02; H, 9.00. Found: C, 53.79; H, 8.78. ^e Calcd for C₁₆H₃₃NO₆Si: C, 50.66; H, 8.71. Found: C, 50.01; H, 8.41. ^f Decomposed gradually upon standing at room temperature. ^a Reference 11. ^b Reference 9. ^c Reference 10. ^d Reference 8.

TABLE IV
TETRAKISPEROXYSILANE

Registry no.	Compd	Yield, %	Dec temp, °C	Physical characteristics, lit.	O-O frequency in the ir, cm ⁻¹	Characteristic nmr signals, δ
10196-46-0	Tetrakis(<i>tert</i> -butylperoxy)silane ^a	64	135	White crystal of mp 53°, 35-40° ^c	922 (m), 940 (s)	1.28 (s, 36, <i>tert</i> -butyl)
39810-23-6	Tetrakis(α,α -dimethylbenzylperoxy)silane ^b	64	<100	Viscous liquid	920-940 (s)	1.55 (s, 24, isopropyl), 7.35 (m, 20, phenyl)

^a Calcd for C₁₆H₃₆O₈Si: C, 50.00; H, 9.37. Found: C, 49.69; H, 9.06. ^b Calcd for C₃₆H₄₄O₈Si: C, 68.35; H, 6.96. Found: C, 67.15; H, 6.59. ^c Reference 9.

tion usually occurred and the reaction temperature was kept below 35°, preferably below 15°, by adjusting the addition rate of halosilane and by using an outside cooling bath. The reaction was practically completed upon finishing addition of halosilane, although an additional 30 min of stirring was normally employed. The insoluble Dabco-HX salt was removed by filtration and used for regenerating the Dabco. The silyl alkyl peroxide was collected from the filtrate by evaporating the solvent under vacuum. The yield was usually greater than 70%. Occasionally, the product may be slightly colored. The color can be removed by a treatment with charcoal.

Silyl Alkyl Peroxides via the Hexa-Hydroperoxide Adduct Method. General.—To a slurry of Hexa-hydroperoxide adduct, anhydrous calcium chloride (excess amount) and an inert medium was added, while, under cooling, a stoichiometric amount of halosilane. The reaction was usually rapid and exothermic. Upon completion of reaction, the insoluble Hexa-HX and calcium chloride salts were removed by filtration and discarded. The silyl alkyl peroxide was recovered from the filtrate by evaporating the solvent. The yield and product purity are usually comparable but not quite as good as those of the Dabco-hydroperoxide salt method.

Instrumental.—The Varian Model A-60 and HA-100 instruments were used for the nmr measurements. Tetramethylsilane and CDCl₃ were employed as the internal standard and solvent, respectively. For infrared spectra, a Perkin-Elmer Model 221 was used with either KBr pellets or liquid film on NaCl plates. Thermal decomposition temperatures were taken with a Thomas-Hoover capillary apparatus.

Registry No.—Hexa-*tert*-butyl hydroperoxide adduct, 39810-24-7; Dabco-hydroperoxide adduct, 39810-25-8.

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Reactions of *N*-Nitrosamines with Grignard and Lithium Reagents

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In the course of studies on nitrogen-centered radicals we had the occasion to examine the reaction of *N*-nitrosamines with organometallic reagents. It is the purpose of this note to report the results of this study.