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(7) See, for example, the phase transfer modification described by L. Skattebol, G. A. Abskharoun, and T. Greibrokk, *Tetrahedron Lett.*, 1367 (1973).
(8) We thank Professor James A. Moore for calling to our attention the portion of the Ph.D. thesis of Thomas Newton (University of Delaware, 1973) wherein it is reported that *carbon monoxide* could be identified mass spectrometrically as a side product from the reaction of KO-*t*-Bu with bromoform. This finding was rationalized by a scheme similar to reaction sequence 3-6 (*vide infra*) followed by decomposition of the formyl bromide to CO and HBr.
(9) With the exception of one terse mention of its preparation by hydroboration [G. Zwerfel, A. Horng, and J. T. Snow, *J. Amer. Chem. Soc.*, **92**, 1427 (1970)], we have found no reports of the synthesis or properties of **1**.
(10) Even at −50°, evolution occurred at a rate of 7 ml/min.
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A Facile One-Step Synthesis of 5-Silaspiro[4.4]nona-2,7-diene

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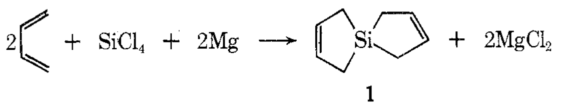
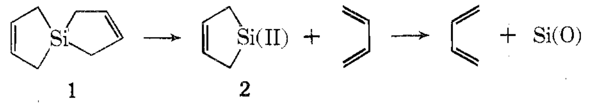
We wish to report a facile one step multiple annelation synthesis of the novel unsaturated heterocycle, 5-silaspiro[4.4]nona-2,7-diene (1) from silicon tetrachloride and 1,3-butadiene. We find that a mildly exothermic reaction ensues upon stirring a suspension of "active magnesium"[1] in tetrahydrofuran under an atmosphere of butadiene. The resulting mixture reacts vigorously with silicon tetrachloride to give the title compound in preparatively useful yield.[2] The assignment of the structure is based on elemental analysis: nmr (CCl_4) δ 1.46 (8 H) and 5.86 (4 H), ir (neat) 839, 942, 1100, 1170, 1205, 1395, 1600, 2900, and 3040 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 53 (52), 54 (49), 55 (61), 67 (49), 81 (56), 82 (99), 83 (47), 108 (44), 136 (100), 137 (46).



1

The major fragmentation involves extrusion of a silylene 2 (*m/e* 82). Related thermal reductive cycloeliminations of dimethylsilylene from 1,1-dimethyl-1-silacyclo-3-pentene derivatives are well known.[3] Interestingly, in the case of **2**, atomic silicon would result from a second extrusion.



1 2

One feature of the present synthesis is especially noteworthy. This is the great reactivity of "active magnesium" toward 1,3-butadiene which allows the reductive silylation to be performed under unprecedentedly mild conditions. The reaction of butadiene, dichlorodimethylsilane, and ordinary magnesium powder in hexamethylphosphoric triamide requires several days at elevated temperatures.[4] The reaction must be conducted in an autoclave, and the yield for this single annelation giving 1,1-dimethyl-1-silacyclo-3-pentene is about the same as we obtain in our *double annelation.*

Experimental Section

5-Silaspiro[4.4]nona-2,7-diene. The reaction is conducted in a 2-l. three-neck flask equipped with a Dry Ice–acetone condenser which is topped by a head of nitrogen. One neck is stoppered and another is fitted with a rubber serum cap. Butadiene is introduced through the serum cap with a hypodermic needle and the reaction is stirred magnetically.

A suspension of "active magnesium" (0.25 mol) in tetrahydrofuran (500 ml) is stirred under an atmosphere of butadiene (32 g) until the exothermicity subsides. Then $SiCl_4$ (0.09 mol) is added dropwise with a hypodermic syringe. After stirring overnight at room temperature, cold 10% HCl (250 ml) is cautiously added (vigorous evolution of excess butadiene) followed by water (250 ml) and pentane (150 ml). The aqueous phase is extracted with pentane (200 ml) and the combined pentane extracts are washed with water (200 ml), saturated aqueous Na_2CO_3 (200 ml), and saturated aqueous NaCl (200 ml), and dried (Na_2SO_4). If greater quantities of aqueous washes are employed, voluminous sticky precipitates and emulsions result. Distillation gives **1**, bp 65–68° (13 mm), 21% based on $SiCl_4$. *Anal.* Calcd for $C_8H_{12}Si$: C, 70.51; H, 8.88. Found: C, 69.97; H, 8.86.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—1, 52856-32-3; 1,3-butadiene, 106-99-0; magnesium, 7439-95-4; silicon tetrachloride, 10026-04-7.

References and Notes

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(2) Many "diene-magnesium compounds" have been reported previously. Experimental details are generally lacking. (a) H. E. Ramsden, J. E. Engelhart, and W. Naegele, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967 Abstract No. 9-41; (b) M. Yang, K. Yamamoto, N. Otake, M. Ando, and K. Takase, *Tetrahedron Lett.*, 3843 (1970); (c) M. Yang, M. Ando, and K. Takase, *Tetrahedron Lett.*, 3529 (1971).
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Reaction of *tert*-Butyl Hydroperoxide and α-Cumyl Hydroperoxide with Acetic Acid[1]

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Following the chance observation that the hydroperoxide titer of a dilute solution of *tert*-butyl hydroperoxide in acetic acid decreased significantly on standing for several hours at room temperature, we investigated the system and found that direct esterification of the hydroperoxide occurred.[2,3] The reaction was strongly catalyzed by sulfuric acid. Equilibrium and kinetic data were obtained.

An investigation of the system, α-cumyl hydroperoxide–acetic acid, indicated that esterification probably occurred, but that the peroxy ester decomposed, as formed, *via* a

Table I
Apparent Equilibrium Constants, *K*, and Pseudo First-Order Rate Constants, *k*, for the Reaction of *tert*-Butyl Hydroperoxide with Acetic Acid at 30 ± 0.1°

	Initial concentrations, *M*				Final concentrations, *M*			Constants	
Expt	Peroxide	CH_3COOH	H_2O	H_2SO_4	$(CH_3)_3COOH$	$CH_3COOOC(CH_3)_3$	Hr[a]	*K*	*k*, sec^{-1}
1	1.037[b]	15.6	0.00	0.00	0.368	0.617	870	0.075 ± 0.005[c]	$6 \pm 1 \times 10^{-7}$
2	0.916[b]	15.7	0.00	0.01	0.121	0.795	90	0.35 ± 0.03	$6.2 \pm 0.5 \times 10^{-5}$
3	0.936[b]	15.7	0.00	0.005	0.131	0.805	120	0.33 ± 0.03	$3.2 \pm 0.3 \times 10^{-5}$
4	0.486[b]	16.5	0.00	0.01	0.036	0.450	50	0.35 ± 0.03	$6.6 \pm 0.5 \times 10^{-5}$
5	0.326[b]	15.9	3.67	0.008	0.135	0.191	140	0.35 ± 0.03	
6	0.313[d]	15.6	4.00	0.008	0.123	0.190	90	0.38 ± 0.03	

[a] Approximate time to reach equilibrium. [b] *tert*-Butyl hydroperoxide. [c] System probably not at equilibrium. [d] *tert*-Butyl peroxyacetate.

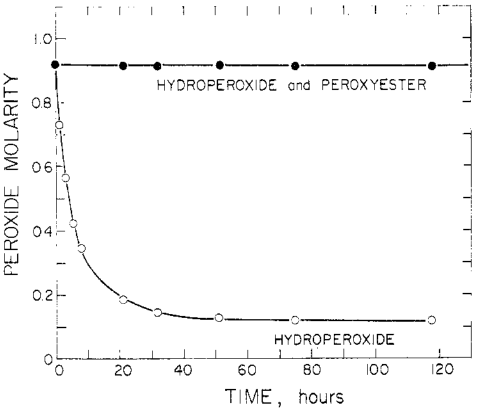

Figure 1. Reaction of *tert*-butyl hydroperoxide with acetic acid in the presence of H_2SO_4 at 30 ± 0.1° (expt 2, Table I).

rapid heterolysis to the acylal, $C_6H_5OC(CH_3)_2OCOCH_3$, a reaction previously reported by Yablokov and coworkers.[4]

Results and Discussion

tert-**Butyl Hydroperoxide.** Results of several experiments are summarized in Table I and data from expt 2 are presented graphically in Figure 1. Concentrations of hydroperoxide and peroxyacetate were determined by a differential iodometric titration (see Experimental Section). Concentrations of acetic acid and water, used in calculation of equilibrium constants, were determined from the formulation of reaction mixtures and the stoichiometry of the reaction. Pseudo first-order initial rate constants for the disappearance of the hydroperoxide were calculated from titration data at 10–20% reaction.

Esterification was slow in the absence of sulfuric acid (expt 1). After 870 hours, an apparent equilibrium was reached and an "equilibrium constant" of 0.075 ± 0.005 was calculated from the data. Analysis of the data from this experiment was complicated by the fact that the total peroxide concentration decreased to 95% of the initial value during the reaction. *tert*-Butyl peroxyacetate was isolated from the reaction mixture.

Experiments 2, 3, and 4 illustrate the catalytic effect of sulfuric acid. Kinetic results, indicating approximately first-order dependence on hydroperoxide and sulfuric acid concentrations, are consistent with the $A_{AC}2$ esterification mechanism. Equilibrium constants were reasonably consistent in the presence of added water (expt 5) and in a reaction starting with *tert*-butyl peroxyacetate (expt 6).

α-**Cumyl Hydroperoxide.** We were unable to isolate *α*-cumyl peroxyacetate from the reaction of the hydroperoxide with acetic acid. The pseudo first-order rate constant for the disappearance of the hydroperoxide in acetic acid at 30° was approximately the same as that for *tert*-butyl hydroperoxide under similar conditions, but differential iodometric titration indicated the absence of peroxyacetate. On the basis of the kinetic data, we believe that *α*-cumyl hydroperoxide was in fact esterified by acetic acid, but that the resulting peroxy ester, as formed, underwent a rapid heterolytic decomposition in acetic acid.[4] The first-order rate constant at 30° for the heterolysis is about 70 times the pseudo-first-order rate constant for the reaction of *α*-cumyl hydroperoxide with acetic acid at 30°.

Acetylation of *tert*-butyl and *α*-cumyl hydroperoxides by acetic anhydride, catalyzed by acetate ion, was found to be a convenient method for preparation of the peroxy esters.

Experimental Section

Nmr data were obtained with a Varian A-60A spectrometer.

Hydroperoxides. Commercial 90% *tert*-butyl hydroperoxide was distilled under reduced pressure through an unpacked insulated column (1.5 × 55 cm). The main fraction (~60% recovery) was collected at 36–38° (16 mm). Iodometric assay was 97.7%.

Commercial *α*-cumyl hydroperoxide (~80% assay) was distilled under reduced pressure through an unpacked insulated column (1.5 × 20 cm). The main fraction (~50% recovery) was collected at 49.5–51° (0.02 mm); iodometric assay 94.6%; nmr (CCl_4, concentrated solution) δ 1.48 (s, 6, $(CH_3)_2$), 7.25 (m, 5, C_6H_5), 8.32 (s, 1, OOH). Values for methyl and hydroperoxide protons were shifted somewhat from literature values,[5] 1.55 and 7.87, respectively, taken in 1.0 *M* solution.

Iodometric Titrations. A differential titration analysis was developed, based on the discovery of Silbert and Swern[6] that the oxidation of iodide ion by peroxy esters in acetic acid was strongly catalyzed by traces of ferric ion. Thus, titration in the presence of ferric ion gave total active oxygen concentration (hydroperoxide plus peroxy ester), whereas titration in the absence of added ferric ion gave hydroperoxide concentration, plus a small fraction of the peroxy ester concentration, for which correction was made (see below).

In the procedure for "non-Fe" titration, 25 ml of glacial acetic acid was added to a 250-ml iodine flask, small pieces of Dry Ice (2–4 g) were added, and the mixture was swirled for about 10 sec to displace oxygen. Two ml of a saturated solution of NaI and an aliquot of peroxide solution (2 ml or 5 ml, depending on peroxide concentration) were added. The flask was lightly stoppered, again swirled, and allowed to stand in diffuse light for 5 min. At the end of this time, 25 ml of water was added and the solution was titrated with $Na_2S_2O_3$ solution (0.1–0.15 *N*) to the disappearance of yellow color. Samples were run in duplicate and a blank determination without peroxide was run concurrently. The blank was subtracted from the volume required by the sample. The procedure for "Fe" titration was similar, except that the reaction medium was acetic acid containing 0.002% of $FeCl_3 \cdot 6H_2O$ and reaction time was 10 min. Analyses of neat hydroperoxides and peroxy esters were conducted on weighed samples.

Pure *tert*-butyl peroxyacetate reacted slowly with iodide ion in the absence of added ferric ion, possibly because of traces of transition metal ions in CP acetic acid. In a series of "non-Fe" titrations, 3 to 4% of the peroxy ester reacted in 5 min. On this basis, concentrations of hydroperoxide and peroxy ester were corrected as follows. The approximate peroxy ester concentration obtained from the difference in titers for "non-Fe" and "Fe" titrations, was multiplied by 1.03 to give the corrected peroxy ester concentration. This value was then subtracted from the total peroxide concentration (based on "Fe" titration) to give the corrected hydroperoxide concentration. Corrected values are listed in Table I.[7]

Reaction of *tert*-Butyl Hydroperoxide with Acetic Acid. Reaction mixtures were formulated by weight into volumetric flasks and were conducted in half-filled[8] glass-stoppered flasks maintained at 30 ± 0.1° in a thermostat. Except for expt 1, total peroxide concentration remained constant during the course of reaction. In Experiments 2–6, sulfuric acid catalyst, diluted 50:50 with acetic acid, was added just prior to or just after the initial titration.

tert-Butyl peroxyacetate was isolated from final reaction mixtures of expt 1 and 2 as follows. Water (400 ml) was added to a 100-ml aliquot and the solution was extracted with 70 ml of diethyl ether and then with 30 ml of 30–60° petroleum ether. Combined extracts were washed sequentially with 50 ml of 10% Na_2CO_3 solution, 25 ml of 10% Na_2CO_3 solution, and 50 ml of water. After drying with $MgSO_4$, solvents were removed and the residue was distilled under reduced pressure, peroxy ester being collected at 29–30° (5 mm), $n^{25}\text{D}$ 1.4030 (lit.[5] 1.4035), peroxide assay 96.8%. Recovery was about 60% of the theoretical amount of peroxy ester in the aliquots.

Preparation of *tert*-Butyl Peroxyacetate. A catalytic amount (0.4 g) of postassium acetate was added to a water-cooled stirred solution of *tert*-butyl hydroperoxide (14.1 g, 96% assay, 0.15 mol) and acetic anhydride (20 g, 0.196 mol, 30% excess) in 20 ml of 30–60° petroleum ether. Reaction was mildly exothermic. After standing overnight at room temperature, the reaction mixture was diluted with 80 ml of 30–60° petroleum ether, washed successively with 100 ml of water, 50 ml of 10% Na_2CO_3 solution, and 50 ml of water, dried with $MgSO_4$, and distilled under reduced pressure. Peroxy ester was collected at 30–30.5° (5 mm), yield 14.6 g (73%), peroxide assay 98.4%. The nmr spectrum agreed with literature data.[5]

Reaction of α-Cumyl Hydroperoxide with Acetic Acid. When a 0.984 *M* solution of α-cumyl hydroperoxide in glacial acetic acid was maintained at 30. ± 0.1°, the hydroperoxide concentration slowly decreased. "Non-Fe" and "Fe" titers were identical, indicating the absence of peroxy ester. Pseudo-first-order kinetics were observed at least up to 30% reaction. The rate constant, obtained graphically, was $6.3 \pm 0.3 \times 10^{-7}$ sec^{-1}. As the reaction proceeded, the solution became yellow in color and finally yellowish brown and the odor of phenol was apparent during titrations. A similar reaction mixture, but 0.035 *M* in potassium acetate (in an attempt to reduce solution acidity), gave similar results. We assume the development of color was the result of oxidation of phenol to quinoidal products by the hydroperoxide. (Similar colors were observed when a solution of phenol and *tert*-butyl hydroperoxide in acetic acid was let stand at room temperature.) The presence of phenol in the reaction mixture was established by making an aliquot basic with sodium hydroxide, extracting several times with ether to remove α-cumyl hydroperoxide, acidifying with acetic acid, and treating with bromine followed by sodium bisulfite in the usual manner. The product, 2,4,6-tribromophenol (mp 95.5°), was obtained in 58% yield, based on hydroperoxide reacted.

Preparation of α-Cumyl Peroxyacetate. A catalytic amount (0.2 g) of potassium acetate was added to a cooled stirred solution of α-cumyl hydroperoxide (16.0 g, 95% assay, 0.1 mol) and acetic anhydride (12.8 g, 0.125 mol) in 40 ml of 38–50° petroleum ether. The reaction was stirred at room temperature until the potassium acetate dissolved and then let stand at room temperature for 1 hr. (Reaction time was limited to minimize decomposition of the peroxy ester in the presence of acetic acid.) Product work-up was similar to that described for *tert*-butyl peroxyacetate. Peroxy ester was collected at 54–57° (0.1 mm), yield 15.5 g (80%), peroxide assay 92%. Redistillation at 56–57° (0.1 mm) or at 48–49° (0.05 mm) gave a somewhat purer product (peroxide assay 94%), nmr (CCl_4) δ 1.58 [s, 6, $(CH_3)_2$], 1.75 (s, 3, CH_3CO), 7.3 (m, 5, C_6H_5).[9]

A 0.195 *M* solution of α-cumyl peroxyacetate in acetic acid at 30 ± 0.1° decomposed smoothly, following first-order kinetics up to at least 50% reaction. The rate constant was $4.5 \pm 0.05 \times 10^{-5}$ sec^{-1}, confirming results of Yablokov and coworkers.[4]

Registry No.—*tert*-Butyl hydroperoxide, 75-91-2; acetic acid, 64-19-7; *tert*-butyl peroxyacetate, 107-71-1; α-cumyl hydroperoxide, 80-15-9; 2,4,6-tribromophenol, 118-79-6; α-cumyl peroxyacetate, 34236-39-0.

References and Notes

(1) From the M.S. thesis of A.K.B., Northeastern University, 1969.

(2) C. Ruchardt and R. Hecht, *Chem. Ber.*, **97**, 2716 (1964) prepared *tert*-butyl peroxyformate from *tert*-butyl hydroperoxide and formic acid, noting that the reaction was applicable to other hydroperoxides but not to other carboxylic acids for preparative purposes.

(3) Since the completion of our work, patents have issued on the acid-catalyzed esterification of certain hydroperoxides with carboxylic acids: (a) R. J. Harvey and C. N. Winnick, U. S. Patent 3595898 (1971); (b) V. L. Antonovskii and O. K. Lyashenko, Ger. Offen. 1937037 (1971); *Chem. Abstr.*, **74**, 140973 (1971).

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(5) D. Swern, A. H. Clements, and T. M. Luong, *Anal. Chem.*, **41**, 412 (1969).

(6) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(7) Use of the correction gave more consistent equilibrium constants. Without the correction, *K* values were 0.28, 0.26, 0.24, 0.33, and 0.36 for Experiments 2 through 6, respectively; cf., Table I.

(8) It was felt that the presence of oxygen would minimize possible induced chain decomposition reactions of the peroxides.

(9) α-Cumyl peroxyacetate has previously been prepared by the reaction of the hydroperoxide with ketene[10] and with acetyl chloride–pyridine.[4] In both cases, the product was not distilled, possibly because of thermal decomposition, which was reported to be rapid at 90°.[4] We found that the peroxy ester could be distilled, provided the bath temperature was kept below 70° during distillation. At bath temperatures of 80–90°, exothermic thermolysis occurred during attempted distillations.

(10) D. Harman, U. S. Patent 2,608,570 (1952).

Preparation and Thermal Reactivity of α-(*p*-*tert*-Butylphenoxy)ethyl Hydroperoxide[1]

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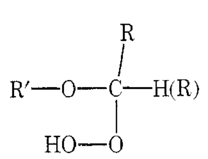
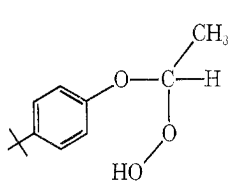
Compounds of type **1** where R′ is alkyl are well known and routes to their synthesis are established,[2] but compounds where R′ is aryl are unreported. An α-phenoxyalkyl hydroperoxide has been proposed[3] as a possible intermediate in various enzyme-catalyzed hydroxylations of phenols. The synthesis and study of the thermal reactivity of a model compound **2** [α-(*p*-*tert*-butylphenoxyl)ethyl hydroperoxide] was undertaken to test the plausibility of such an intermediate.



$$R'{-}O{-}\underset{\displaystyle HO{-}O}{\overset{\displaystyle R}{C}}{-}H(R)$$

1



2

Synthetic attempts, employing the *in situ* trapping by *p*-*tert*-butylphenol[4] of carbonyl oxides formed during the ozonolysis of various alkenes (2,3-dimethyl-2-butene, 2-ethyl-1-butene, 1,1-diphenylethylene, α-methylstyrene, and methylenecyclohexane), yield little or no peroxidic material which can be attributed to a compound such as **2**. Similar attempts to trap the carbonyl oxides from *trans*-1,4-dibenzoylethylene and 2-ethylidenecyclohexanone are unproductive in yielding in these cases α-keto-α-phenoxyalkyl hydroperoxides. The results indicate that phenols (dissolved in inert solvents) unlike alcohols (normally employed as solvents) do not efficiently trap carbonyl oxides.[5]

The acid-catalyzed addition of 98% hydrogen peroxide to *p*-*tert*-butylphenyl vinyl ether did produce compound 2 in