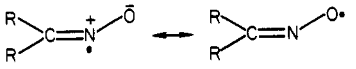
considering the small and apparently similar viscosities of these solvents at our relatively high (144 °C) working temperature.[12] Although the data used to obtain the kinetic parameters in *tert*-butyl alcohol are admittedly limited, there is an indication that the ratio of rates of collapse of the caged radicals at nitrogen compared with oxygen (k_{-1}/k_c) is significantly greater in *tert*-butyl alcohol than in diethylcarbitol. Alcohols are known to hydrogen bond to nitrones.[14] And iminoxy radicals possess nearly equal spin density at nitrogen and oxygen.[15] Thus hydrogen bonding which may persist with the iminoxy radical following initial homolysis (vide supra) may alter recombination rate ratios, k_{-1}/k_c, when compared with these competitive processes in aprotic solvents. Qualitatively this would be expected to increase k_{-1}/k_c in *tert*-butyl alcohol.



In recent years considerable interest has been expressed in effects of viscosity (and other solvent parameters[16]) on cage recombination processes. An examination of the range of yields of cage combinations to form *O*-benzhydryloxime in the three solvents (Table II) suggests only small variations in these solvent properties at our elevated working temperatures (144 °C). However, in one experiment, a mixture of 1 and 1-d_4 was decomposed at 173 °C in the absence of solvent. The melt, consisting primarily of nitrone and *O*-benzhydryloxime, is highly viscous at this temperature. The degree of intramolecularity (α = 0.51) for the *O*-oxime product was considerably higher than that obtained in any of the solution decompositions (cf. Table II). An 86% yield of *O*-ether was isolated from this decomposition. Thus the yield of *O*-benzhydryloxime formed via cage recombination was 44%. This compares with yields of 16–21% for solution decompositions at lower temperature. This suggests that diffusion of the geminate radical pair has been more severely limited in the melt.[17]

Experimental Section

Approximately equimolar amounts of deuterated and undeuterated nitrones (cf. Table I) were weighed into Pyrex tubes. The appropriate dry solvent (freshly distilled) was added with a pipet. The solutions were degassed and the tubes sealed under vacuum. The tubes were heated in a constant temperature bath at 144 ± 0.1 °C. In one experiment the decomposition was performed at 173 ± 0.1 °C. After a time required for 99.9% reaction, the *O*-benzhydryloxime and tetraphenylethane products were isolated quantitatively by chromatography on alumina. Hexane–benzene (49:1) eluted the tetraphenylethane. Hexane–benzene (4:1) eluted the *O*-oxime. After the decompositions corresponding to 10, 20, 30, and 50% reaction, it was necessary to first chromatograph the decomposition mixture on Florisil in order to isolate the undecomposed nitrone which was unstable on alumina. The fractions eluted prior to elution of nitrone were combined and chromatographed on alumina to isolate the *O*-benzhydryloxime.

The mass spectra of *O*-benzhydryloxime samples were obtained with scans under ionizing voltages of 12.5–20.5 eV at chamber temperatures of 60–95 °C. For the nitrones the corresponding conditions were 12.5–19 eV and 80–115 °C. Fragmentation due to loss of hydrogen was negligible under these conditions. Distributions of deuterated species obtained from the decompositions of mixtures of 1 and 1-d_4 are given in Tables V and VI.

Acknowledgment. We express appreciation to Professor G. Spiteller and Göttingen University for numerous mass spectral measurements. We also thank Professor Cheves Walling for reading the manuscript and making useful suggestions regarding the presentation of the data and kinetic analyses. This investigation was supported in part by the National Cancer Institute, National Institute of Health, and U.S. Public Health Service (Grant No. CA-10741-04).

Registry No. 1, 5076-57-3; 1-d_4, 65311-50-4; *O*-benzhydrylbenzophenone oxime, 65311-52-6; 1,1,2,2-tetraphenylethane, 632-50-8.

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[12] The viscosities of these solvents are very low at 144 °C. The value for DMA at 144 °C is approximately 4.3 × 10^{-3} P.[13] Those for *tert*-butyl alcohol and diethylcarbitol, based upon extrapolations, appear to be somewhat smaller.

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[17] It is possible that induced decomposition becomes important in the condensed phase. The nitrone does appear to trap free benzhydryl radicals to form nitroxides.[3c] And nitroxides are known to disproportionate to nitrones and hydroxylamines. Whether any induced decomposition leads to *O*-benzhydryloxime is not known.

Reaction of Allylic and Benzylic Methyl Ethers with Sodium and Trimethylchlorosilane. Evidence for the Intermediacy of Allylic Radicals and Anions

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Allyl methyl ether and benzyl methyl ether react with sodium and trimethylchlorosilane to yield, respectively, allyltrimethylsilane and benzyltrimethylsilane. α,α-Dimethylallyl methyl ether and γ,γ-dimethylallyl methyl ether react with sodium and trimethylchlorosilane to yield γ,γ-dimethylallyltrimethylsilane. α-Methylallyl methyl ether and *trans*-γ-methylallyl methyl ether react with trimethylchlorosilane and sodium to yield similar product mixtures of α-methylallyltrimethylsilane and *cis*- and *trans*-γ-methylallyltrimethylsilane. These results are discussed in terms of a mechanism involving electron transfer to yield allylic radicals and allylic anion intermediates.

We report herein a novel synthesis of allylic trimethylsilanes. Specifically, allylic methyl ethers react with trimethylchlorosilane and sodium metal in hydrocarbon solvents such as *n*-decane or toluene to yield the corresponding allylic trimethylsilane and methoxytrimethylsilane in good yields. There is considerable interest in allylic trimethylsilanes since they have been shown to be versatile intermediates in organic synthesis which react

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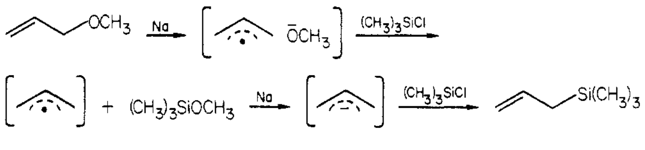
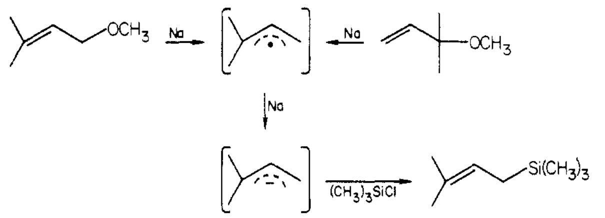
regiospecifically with a wide range of electrophilic reagents to give substitution with allylic rearrangement.[1-13]

We believe that the reaction reported occurs by the following sequence of events. Electron transfer from sodium to the allylic methyl ether yields an anion radical which undergoes heterolysis of the allylic C–O bond to yield an allylic radical–methoxide anion pair. The methoxide anion reacts with spectral to yield methoxytrimethylsilane. Transfer of a second electron from sodium to the allylic radical yields an allylic anion which reacts with trimethylchlorosilane to yield an allylic trimethylsilane.

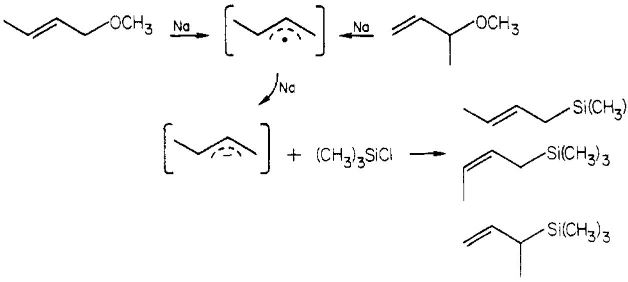


A similar mechanism has been proposed for the reaction of allylic chlorides with trimethylchlorosilane and sodium naphthalide which likewise yields allylic trimethylsilanes.[14] In this case, electron transfer occurs from the naphthalene anion radical. Related reactions of allylic methyl ethers with trimethylchlorosilane and magnesium in HMPT solvent have been observed.[15]

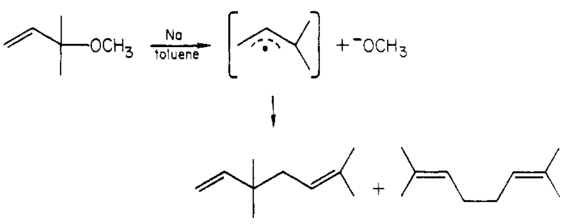
The following facts are consistent with this mechanistic proposal. As expected, both α,α-dimethylallyl methyl ether and γ,γ-dimethylallyl methyl ether react with trimethylchlorosilane and sodium metal to yield only γ,γ-dimethylallyltrimethylsilane.[6]



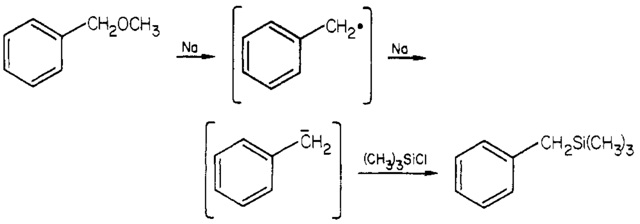
Both γ-methylallyl methyl ether and α-methylallyl methyl ether react with trimethylchlorosilane and sodium metal to yield similar product mixtures: α-methylallyltrimethylsilane (5–6%), *cis*-γ-methylallyltrimethylsilane (25%), and *trans*-γ-methylallyltrimethylsilane (18-20%). The preferential formation of *cis*-γ-methylallyltrimethylsilane is consistent with previous results with allylic anion–sodium cation pairs.[16]



Yields may be limited by competitive reactions of the allylic radical intermediates. For example, reaction of allyl methyl ether, trimethylchlorosilane, and sodium metal yields allyltrimethylsilane (52%), methoxytrimethylsilane (50%), and propene (2%). Propene may result from hydrogen abstraction by the allylic radical. Similarly, reaction of α,α-dimethylallyl methyl ether with sodium metal in toluene in the absence of trimethylchlorosilane, yields 2,7-dimethyl-2,6-octadiene (38%) and 3,3,6-trimethyl-1,5-heptadiene (3%), the expected products of dimerization of the α,α-dimethylallyl radicals.[17]



Finally, we find that benzyl methyl ether reacts with trimethylchlorosilane and sodium metal in toluene solvent to yield benzyltrimethylsilane in high yield. A similar reaction sequence involving the formation of benzylic radicals and benzylic anions by electron transfer can account for these results.[14]



Experimental Section

IR spectra were recorded as 2% CCl_4 solutions on a Perkin-Elmer 281 spectrometer. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode using 1% solutions in $CDCl_3$ with an internal standard of chloroform. Samples of all compounds for spectral analysis were purified by preparative vapor-phase chromatography on a Hewlett-Packard F&M 700 using a 26 ft × 0.25 in. 20% SE-30 on Chromosorb W 60/80-mesh column. GC analyses of reactions were performed in a temperature-programming mode with the oven temperature increasing at a rate of 0.5 °C/min. Yields of products were determined by GC with bis(trimethylsilyl)acetylene (Silar) as standard. They are based on the amount of allylic methyl ether consumed. Mass spectra were run on a Du Pont 21-492 spectrometer at 70-eV ionizing voltage. All reactions were run under an atmosphere of dry nitrogen.

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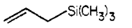
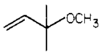
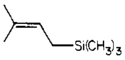
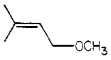
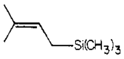
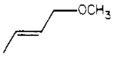
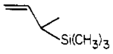
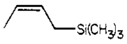
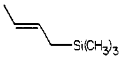
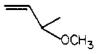
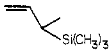
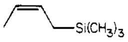
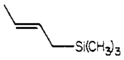
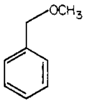
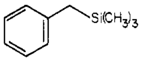
Table I. Reaction of Allylic and Benzylic Methyl Ethers with Trimethylchlorosilane and Sodium

ethers	solvent	products	% yield
	*n*-decane		52
	*n*-decane		53
	*n*-decane		68
	*n*-decane		5
			25
			20
	*n*-decane		6
			25
			18
	toluene		82

The starting materials and products are known compounds. They had physical and spectral properties in complete agreement with literature values. In those cases where spectral data have not been previously reported, we have included these data.

Preparation of Allylic Methyl Ethers. Allyl methyl ether, bp 40–41 °C (lit.[18] bp 42.5–43 °C), α-methylallyl methyl ether, bp 54–56 °C (lit.[19] bp 53–55 °C), *trans*-γ-methylallyl methyl ether, bp 78–80 °C lit.[20] bp 79 °C), α,α-dimethylallyl methyl ether, bp 79–80 °C (lit.[21] bp 79.8–80.2 °C), and γ,γ-dimethylallyl methyl ether, bp 102–104 °C (lit.[21] bp 104.6–105.2 °C), were prepared as follows.

In a dry 250-mL three-neck round-bottom flask equipped with a reflux condenser, a pressure-equalizing addition funnel, and a Teflon-covered magnetic stirring bar were placed sodium hydride (2.4 g, 0.1 mol) and 100 mL of xylene. Allylic alcohol (0.1 mol) was placed in the addition funnel and added dropwise to the stirred solution. After the addition was complete, the solution was heated to reflux for 1 h. Dimethyl sulfate (6.9 g, 55 mmol) in 50 mL of xylene was placed in the addition funnel and added to the solution. The solution was refluxed overnight. The xylene solution was cooled, washed with water, and dried over anhydrous sodium sulfate. The allylic methyl ether was distilled from the xylene solution through a 25-cm Vigreux column. Samples of allylic methyl ethers were further purified by preparative GC.

Preparation of Benzyl Methyl Ether. Sodium methoxide (0.2 mol, 10.8 g) (Mallinckrodt), benzyl chloride (0.1 mol, 12.65 g) (Mallinckrodt), and 200 mL of MeOH were placed into a 500-mL round-bottom flask equipped with a reflux condenser and a magnetic stirring bar. The mixture was heated to reflux and stirred for 24 h. The solution was cooled to room temperature and the salts were removed by filtration. Methanol was removed from the filtrate by evaporation under reduced pressure. Ethyl ether (100 mL) was added to the residue. The ether solution was washed with three 10-mL portions of water. The ether solution was dried over anhydrous sodium sulfate and filtered, and the ether was removed by evaporation under reduced pressure. The residue was distilled through a 15-cm vacuum-jacketed Vigreux column. Benzyl methyl ether, bp 61–63 °C (14 mm) [lit.[22] bp 60 °C (12 mm)], was obtained (8.19 g, 67%).

Reaction of Allylic and Benzylic Methyl Ethers with Trimethylchlorosilane and Sodium. In a dry 300-mL three-neck round-bottom flask, equipped with a reflux condenser, a pressure-equalizing addition funnel, and a Teflon-covered magnetic stirring bar were placed 100–150 mL of toluene or *n*-decane and 210 mmol (4.83 g) of sodium. Freshly distilled trimethylchlorosilane (0.1 mol, 10.8 g) and 100 mmol of allylic (or benzylic) methyl ether were put into the addition funnel. The ether–silane mixture was added over 0.5 h to the rapidly stirred, refluxing solution. After the addition was complete, the solution was heated at reflux for 24 h. The reaction mixture was cooled and filtered to remove salts. The filtrate was subject to GC analysis or fractional distillation. The results are summarized in Table I. **Benzyltrimethylsilane** was found, bp 189–190.5 °C (lit.[23] bp 188–189 °C).

γ,γ-Dimethylallyltrimethylsilane.[6] NMR δ 5.11 (t, 1 H, J = 8 Hz), 1.69 (br s, 3 H), 1.56 (br s, 3 H), 1.37 (d, 2 H, J = 8 Hz), −0.02 (s, 9 H); IR (CCl_4) 1260 and 860 (CH_3Si) cm^{-1}; mass spectrum, m/e 142 (P, 6.7%) (calcd for $C_8H_{18}Si$ 142.118, found 142.119), 127 (P − 15, 2.8%), 73 (100%).

α,α-Dimethylallyltrimethylsilane.[6] NMR δ 5.93 (d of d, 1 H, J = 17 and 11 Hz), 5.06 (d of d, 1 H, J = 17 and 1 Hz), 4.92 (d of d, 1 H, J = 11 and 1 Hz), 1.16 (s, 6 H), 0.08 (s, 9 H); IR (CCl_4) 1245 and 840 (CH_3Si) cm^{-1}; mass spectrum, m/e 142 (P, 22.4%), (calcd for $C_8H_{18}Si$ 142.118, found 142.118), 73 (100%) (calcd for C_3H_9Si 73.047, found 73.047).

α-Methylallyltrimethylsilane.[24] NMR δ 5.91 (d of d of d, 1 H, J = 18, 9, and 7 Hz), 4.98 (d, 1 H, J = 9 Hz), 4.92 (d, 1 H, J = 18 Hz), 1.57 (d of q (quintet), 1 H, J = 7 and 7 Hz), 1.12 (d, 3 H, J = 7 Hz), 0.035 (s, 9 H); IR (CCl_4) 1625 (C=C), 1250 and 830 (CH_3Si) cm^{-1}.

Allyltrimethylsilane[25] had spectral properties identical with those of an authentic sample (Aldrich).

***trans*-γ-Methylallyltrimethylsilane** and ***cis*-γ-methylallyltrimethylsilane** had spectral properties in agreement with those reported by Kwart.[26]

Formation of 2,7-Dimethyl-2,6-octadiene and 3,3,6-Trimethyl-1,5-heptadiene. The reaction was run as above with α,α-dimethylallyl methyl ether except that no trimethylchlorosilane was added. The spectral properties of 2,7-dimethyl-2,6-octadiene (38%) and 3,3,6-trimethyl-1,5-heptadiene (3%) were in agreement with literature values.[17]

Formation of Propene. The reaction of allyl methyl ether with trimethylchlorosilane and sodium was run as above except that dry nitrogen was flowing through the reaction system. The gas outlet of the system was immersed in a 20-mL solution of 2% Br_2 in CCl_4. When the reaction was complete, excess Br_2 and CCl_4 were removed by evaporation under reduced pressure. The concentrated solution was subjected to GLC analysis. 1,2-Dibromopropane was found in 2% yield. Its GC retention time and NMR spectrum were identical with those of an authentic sample (Aldrich).

Acknowledgment. This work has been supported by the Air Force Office of Scientific Research Grant No. 80-0006.

Registry No. Allyl methyl ether, 627-40-7; α,α-dimethylallyl methyl ether, 40426-44-6; γ,γ-dimethylallyl methyl ether, 22093-99-8; *trans*-γ-methylallyl methyl ether, 10034-14-7; α-methylallyl methyl ether, 17351-24-5; benzyl methyl ether, 538-86-3; allyltrimethylsilane, 762-72-1; γ,γ-dimethylallyltrimethylsilane, 18293-99-7; α-methylallyltrimethylsilane, 34584-84-4; *cis*-γ-methylallyltrimethylsilane, 17486-13-4; *trans*-γ-methylallyltrimethylsilane, 17486-12-3; benzyltrimethylsilane, 770-09-2; 2,7-dimethyl-2,6-octadiene, 16736-42-8; 3,3,6-trimethyl-1,5-heptadiene, 35387-63-4; 1,2-dibromopropane, 78-75-1; trimethylchlorosilane, 75-77-4.

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