H), 4.86 (m, 1 H), 6.48 (d, $J$ = 10 Hz, 1 H), 7.2–7.7 (m, 10 H).

Oxidation and workup as in preceding runs gave 5-methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one (65% NMR yield): NMR $\delta$ 0.32 (s, 9 H), 1.04 (d, $J$ = 7 Hz, 6 H), 1.80 (m, 1 H), 2.18 (t, $J$ = 7 Hz, 2 H), 6.10 (d, $J$ = 16 Hz, 1 H), 6.60 (dt, $J$ = 16, 7 Hz, 1 H).

**Acknowledgment.** We thank the National Science Foundation and National Institutes of Health for partial financial support of this work.

**Registry No.** (*E*)-**2b**, 80780-63-8; (*Z*)-**2b**, 80780-64-9; (*Z*)-**4**, 80780-65-0; (*E*)-**4**, 80780-66-1; (*Z*)-**5**, 80780-67-2; (*E*)-**5**, 80789-27-1; **6**, 80780-68-3; i, 80780-69-4; ii, 80796-73-2; $Ph_2Se_2$, 1666-13-3; 1,3-dichloropropene, 542-75-6; thiophenol, 108-98-5; *trans*-3-trimethylsilyl-2-propenal, 33755-86-1; *trans*-6-methyl-2-heptenal, 80780-70-7; 1,3-bis(phenylseleno)allyllithium, 80780-71-8; isoamyl bromide, 107-82-4; 1,3-bis(phenylseleno)-6-methyl-1-heptene, 80780-72-9; *trans*-4-methyl-2-hexenal, 80780-73-0; 2-bromobutane, 78-76-2; 1,3-bis(phenylseleno)-4-methyl-1-hexene, 80780-74-1; *trans*-5-acetoxy-2-hexenal, 31849-96-4; propylene oxide, 75-56-9; 1,3-bis(phenylseleno)-5-acetoxy-1-hexene, 80780-75-2; 4-acetoxy-5-methyl-*trans*-2-hexenal, 80780-76-3; isobutyraldehyde, 78-84-2; 1,3-bis(phenylseleno)-4-acetoxy-5-methyl-1-hexene, 80780-77-4; cyclohexene oxide, 286-20-4; *trans*-2-[1,3-bis(phenylseleno)allyl]cyclohexyl acetate, 80780-78-5; *trans*-3-(*trans*-2-acetoxycyclohexyl)-2-propenal, 31849-91-9; 4-*tert*-butylcyclohexanone, 98-53-3; 1-[1,3-bis(phenylseleno)allyl]-4-*t*-butyl-cyclohexanol, 80780-79-6; 3-pentanone, 96-22-0; (*E*)-4,6-bis(phenylseleno)-3-ethyl-5-hexen-3-ol, 80780-80-9; (*Z*)-4,6-bis(phenylseleno)-3-ethyl-5-hexen-3-ol, 80780-81-0; 4-ethyl-4-hydroxy-*trans*-2-hexenal, 80780-82-1; (*E*)-phenylseleno-4-methyl-1,3-pentadiene, 80780-83-2; (*Z*)-1-phenylseleno-4-methyl-1,3-pentadiene, 80780-84-3; 4-methyl-1-trimethylsilyl-trans-2-hexen-1-one, 80780-85-4; 1,3-bis(phenylseleno)-4-methyl-1-trimethylsilyl-1-hexene, 80789-28-2; 4-methyl-1-trimethylsilyl-*trans*-2-penten-1-one, 73341-03-4; 2-bromopropane, 75-26-3; 1,3-bis(phenylseleno-4-methyl-1-trimethylsilyl)-1-pentene, 80780-86-5; 4-hydroxy-4-methyl-1-trimethylsilyl-*trans*-2-penten-1-one, 80789-29-3; acetone, 67-64-1; (*E*)-1,3-bis(phenylseleno)-1-(trimethylsilyl)-4-hydroxy-4-methyl-1-pentene, 80780-87-6; (*Z*)-1,3-bis(phenylseleno)-1-trimethylsilyl)-4-hydroxy-4-methyl-1-pentene, 80780-88-7; 5-methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one, 80780-89-8; isobutyl bromide, 78-77-3; 1,3-bis(phenylseleno)-1-(trimethylsilyl)-5-methyl-1-hexene, 80780-90-1.

# Reactions of Bis(acetoxymethyl) Ether and Several of Its Aryloxy Analogues

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Displacement of acetoxy groups from bis(acetoxymethyl) ether by a variety of phenols is demonstrated. The effect of various catalysts on the reaction is documented, and a possible role of the catalyst is discussed. Several (aryloxy)methyl ethers are used for the preparation of (alkylthio)methyl ethers.

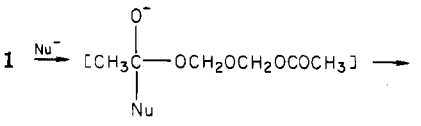
Bis(acetoxymethyl) ether (1), known for many years[1] and easily prepared in large quantity from acetic anhydride and *s*-trioxane (eq 1a), has found very little use because of its facile hydrolysis and decomposition (eq 1b). We report here the efficient displacement of acetoxy in 1 by aryloxy to form intermediates more useful in subsequent displacement reactions.[2]

$$(CH_2O)_3 + (CH_3CO)_2O \xrightarrow{H^+} (CH_3COOCH_2)_2O \qquad (1a)$$

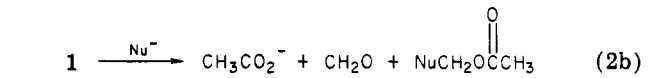
$$\underset{1}{(CH_3COOCH_2)_2O} \xrightarrow{H^+ \text{ or } OH^-} [(HOCH_2)O] \rightarrow CH_2O + CH_3COOH \qquad (1b)$$

## Results and Discussion

An attempt to develop a synthesis of bis(phenoxymethyl) ether and bis[(alkylthio)methyl] ethers[3] without using bis(chloromethyl) ether[4,5] prompted investigation of bis(acetoxymethyl) ether (1) as an intermediate. Many attempts to displace the acetoxy groups in 1 with strong nucleophiles such as mercaptide or aryl oxide gave either disubstituted methylenes or intractable mixtures of paraformaldehyde and other polymeric compounds, with no formation of substituted methyl ether. Attack on the carbonyl carbon or cleavage of the formal ether linkage is the predominant reaction (eq 2a,b). To minimize these



$$CH_3CONu + CH_2O + CH_3COO^- \qquad (2a)$$



(2b)

$Nu^-$ = strong nucleophile

undesirable additions, reactions with weak nucleophiles such as phenols and mercaptans, which might hydrogen bond with the carbonyl oxygen of 1, were investigated. At

(1) Tomiska, J.; Spousta, E. *Angew. Chem.* **1962**, *74*, 248.
(2) Wadsworth, D. H.; Vinal, R. S. U.S. Patent 4021475, 1977.
(3) Burness, D. M.; Wright, C. J.; Perkins, W. C. *J. Org. Chem.* **1977**, *42*, 2910.
(4) Iovy, M.; Cimpeanu, G. *Rev. Roum. Chim.* **1973**, *18*, 883; **1974**, *19*, 881.
(5) Head, Frank S. H. *J. Chem. Soc.* **1963**, 2972.
(6) Cleveland, J. P. U.S. Patent 3954878, 1976.

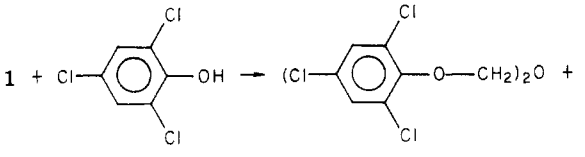
0022-3263/82/1947-1623$01.25/0 

Table I. Effect of Catalyst on Preparation of Bis[(2,4,6-trichlorophenoxy)methyl] Ether

| catalyst (0.2 g/0.10 mol) | reaction time, h | yield, % | comment[a] |
|---|---|---|---|
| $Zn(OCOCH_3)_2$ | 4 | 73 | ++$CH_2O$, dark brown |
| ZnO | 4 | 73 | ++$CH_2O$, dark brown |
| ZnO + $(C_2H_5O)_3P$ | 4 | 82 | +$CH_2O$, light yellow |
| $ZrSO_4$ | 4 | 64 | +++$CH_2O$, no color |
| $Zr(NH_4SO_4)_2$ | 4 | 48 | +++$CH_2O$, no color |
| $Al[CH_3C(O)CHC(O)CH_3]_3$ | 4 | 71 | +$CH_2O$, dark brown |
| $Al[OCH(CH_3)_2]_3$ | 3.5 | 74 | +$CH_2O$, dark brown |
| $Al[OCH(CH_3)_2]_3$ + EDTA | 5 | 79 | +$CH_2O$, light yellow |
| $Al[OCH(CH_3)_2]_3$ + $(C_4H_9O)_3P$ | 5.5 | 72 | +$CH_2O$, dark brown |
| $Al_2(SO_4)_3$ (dried in vacuo) | 3 | 77 | +$CH_2O$, very light yellow |
| $Al_2(SO_4)_3 \cdot 18H_2O$ | 3.5 | 69 | +++$CH_2O$, light yellow |
| $Al_2(SO_4)_3$ (dried in vacuo) | 4 | 81 | +$CH_2O$, very light yellow |
| $Al_2(SO_4)_3$ (dried in vacuo) | 4.5 | 82 | +$CH_2O$, very light yellow |
| $Al_2O_3$ (pellets)[a] | 3 | 89 | +$CH_2O$, very light yellow |
| $Al_2O_3$ + $(C_2H_5O)_3P$[a] | 5 | 0 | no trace of product on VPC |
| $Al_2O_3$ + $SiO_2$[a] | 4 | 43 | +++$CH_2O$ |
| molecular sieves (pellets)[b] | 4 | 60 | +$CH_2O$ |
| $CuBr_2$ | 4 | 60 | +++$CH_2O$, very light yellow |

[a] One, two, and three plus signs indicate increasing amounts of $CH_2O$. [b] 2.0 g of catalyst/0.10 mol.

temperatures below 200 °C, no reaction of 1 with either mercaptans or phenols was observed. At ca. 240–250 °C, however, 1 and 2,4,6-trichlorophenol (2) evolved acetic acid and, in some instances, gave substantial amounts of bis[(2,4,6-trichlorophenoxy)methyl] ether (3, eq 3). The

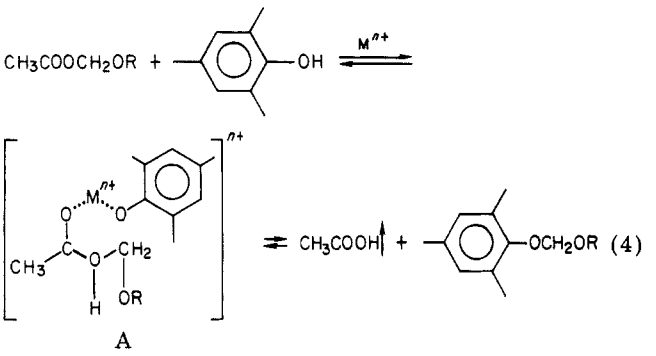



2 3

$CH_3COOH$ (3)

reaction was not reproducible, however, since small temperature variations, changes in nitrogen purge rate, and/or minor contaminants in phenol 2 caused longer reaction times or gross decomposition. To allow the use of lower boiling phenols and to avoid thermal decomposition, we sought an effective catalyst (see Experimental Section). As illustrated in Table I, several catalysts were effective in forming 3 in substantial yield. The zinc catalysts performed well in small-scale reactions (0.10 mol) but were unreliable in larger equipment, producing a zinc-containing tar. The aluminum catalysts (aluminum isopropoxide, aluminum sulfate, aluminum oxide) were the most effective, forming 3 in good yield and purity and showing reliability on scale-up (2.0 mol) and in continuous reactions.

The best catalysts containing Al(III) or Zn(II) are hard acids. One can rationalize the catalytic effect with a cyclic intermediate such as A in which the hard acid metal ion coordinates and stabilizes the hard base oxygen atoms of both reactants (eq 4) in the required geometry. This




proposed six-membered chelate reactive intermediate would allow concerted acetoxy displacement by phenoxy with the loss of acetic acid as the driving force.

At lower temperatures and under noncatalytic conditions, phenols are not strong enough nucleophiles to attack the carbonyl carbon. The product formed at high temperatures near the decomposition point may arise from an intermediate analogous to A in which a proton may be the bridge occupied by M (eq 4).

To our knowledge, the literature reports only one acetoxy displacement by aryloxy, the reaction apparently occurring only with compounds containing an electrophilic methylene.[7] Indeed, we observed no reaction in an attempted catalyzed displacement of acetoxy by trichlorophenoxy from dodecyl acetate.

Table II summarizes the preparation of many (aryloxy)methyl ethers under various conditions. Methoxyphenol and methylphenol (with electron-donating substituents) were much less reactive, requiring long reaction times that resulted in side reactions and lower product yields. *p*-Nitrophenol (with an electron-withdrawing substituent), on the other hand, reacted rapidly to evolve acetic acid but gave none of the desired phenoxymethyl ethers, perhaps because of an undesirable nucleophilic attack on the carbonyl carbon.

As demonstrated by the successful preparation of bis[(pentafluorophenoxy)methyl] ether, bis[(2,4,6-trichlorophenoxy)methyl] ether, and bis[(2,4,6-tribromophenoxy)methyl] ether, the reaction can accommodate considerable steric crowding. However, 2,6-dimethyl- or 2-*tert*-butyl-substituted phenols do not displace the acetoxy group. Only the preparation of bis[(2,4,6-trichlorophenoxy)methyl] ether was optimized for yield. It is possible that higher yields of the other ethers could be realized by selection of a different catalyst and/or solvent.

Acetoxy displacement by softer bases should not be as susceptible to catalysis by hard acids in this proposed mechanism. Indeed, the catalyzed acetoxy displacement method failed with mercaptans; either no reaction occurred, or a variety of byproducts were formed. Although VPC indicated the formation of some of the desired sulfur-substituted methyl ethers, no pure product could be isolated (eq 5).

$$RSH + (CH_3COOCH_2)_2O \not\rightarrow (RSCH_2)_2O \quad (5)$$

In sharp contrast to the behavior of bis(acetoxymethyl) ether, the bis[(aryloxy)methyl] ethers react readily with

(7) Alimov, E.; Razakov, R.; Tulyaganov, S. R. *Zh. Org. Khim.* 1973, *9*, 330.

Table II. Preparation of Bis[(aryloxy)methyl] Ethers from Bis(acetoxymethyl) Ether[a,b]

$$ArOH + (CH_3COOCH_2)_2O \xrightarrow[o\text{-}Cl_2C_6H_4]{Al_2O_3} (ArOCH_2)_2O + CH_3COOH$$

| no. | Ar | reaction time, h | yield, % | mp, °C | ref |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | 4 | 32 | 80-81 | 4 |
| 2 | 4-$ClC_6H_4$ | 4 | 61 | 48-49 | 10 |
| 3 | 2-$ClC_6H_4$ | 3 | 79 | 60-61 | 11 |
| 4 | 2,4-$Cl_2C_6H_3$ | 1[c] | 61 | 98-99 | |
| 5 | 2,4,6-$Cl_3C_6H_2$ | 4 | 89[d] | 178-179 | 12 |
| 6 | 2,3,4,5,6-$F_5C_6$ | 7 | 29 | 69-70 | |
| 7 | 2,4,6-$Br_3C_6H_2$ | 4 | 43 | 203-204 | 5 |
| 8 | 4-$CH_3C_6H_4$ | 4 | 25 | 83-84 | |
| 9 | 2-$CH_3C_6H_4$ | 8 | 18 | 74 | 4 |
| 10 | 2,6-$(CH_3)_2C_6H_3$ | 5 | 2[e] | | 4 |
| 11 | 2-$[(CH_3)_3C]C_6H_4$ | 5 | 0 | | |
| 12 | 4-$CH_3OC_6H_4$ | 4 | 19 | 55-56 | |
| 13 | 2-$CH_3OC_6H_4$ | 4 | 0 | | |
| 14 | 4-$NO_2C_6H_4$ | 4 | 0 | | |

[a] 0.30 mol with 2.0 mol of $^1/_8$-in. pelletized $Al_2O_3$ catalyst in 75 mL of refluxing $o$-$Cl_2C_6H_4$. Pot temperatures were not monitored. [b] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table. [c] 0.02 g of $Zn(OCOCH_3)_2$ was used as the catalyst. [d] Prepared in a hot-tube reactor in 53% yield. [e] By vapor-phase chromatography.

Table III. Reactions of Mercaptides with Several (Aryloxy)methyl Ethers

$$RS^- + (ArOCH_2)_2O \longrightarrow (RSCH_2)_2 + ArO^-$$

| R | Ar | solvent/base | time, h/temp, °C | yield, % |
|---|---|---|---|---|
| $n$-$C_4H_9$ | $C_6H_5$ | DMF/NaH | 5/150 | 85[a] |
| $n$-$C_4H_9$ | $p$-$ClC_6H_4$ | DMF/NaH | 24/95 | 65[b] |
| $n$-$C_4H_9$ | $C_6H_5$ | DMF/$NaOCH_3$ | 24/150 | 5[b] |
| $HOCH_2CH_2$ | $C_6H_5$ | DMF/NaH | 6/150 | 0[a] |
| $HOCH_2CH_2$ | $C_6H_5$ | DMF/NaH | 24/105 | 0[a] |
| $HOCH_2CH_2$ | 2,4,6-$Cl_3C_6H_2$ | BuOH/NaOH | 7/115 | 90[a] |
| $HOCH_2CH_2$ | 2,4,6-$Cl_3C_6H_2$ | $EtOCH_2CH_2OH$/NaOH | 1/1 | 90 |

[a] Isolated. [b] By NMR.

mercaptide anions to give the commercially useful bis(alkylthiomethyl) ethers[6] (Table III). Although formaldehyde acetals are generally resistant to cleavage under alkaline conditions,[7] the work of Feutrill and Mirrington[8] and of Bartlett and Johnson[9] provides an analogy for the reaction illustrated by eq 6.

$$(ArO\text{—}CH_2)_2O + RS^- \longrightarrow (RSCH_2)_2O + ArO^- \qquad (6)$$

In hot, polar, aprotic solvents, butanethiol, sodium hydride, and bis(phenoxymethyl) ether (4) gave bis[(butylthio)methyl] ether in good yield. Although this reaction appears general for the simple alkanethiols, the less reactive 2-mercaptoethanol (5) failed to react with 4 under these conditions. In contrast, 5 and 3 reacted smoothly even in protic media. In a typical run, 3 and 5 in refluxing 1-butanol or 2-alkoxyethanol with aqueous sodium hydroxide as base gave bis[[(2-hydroxyethyl)thio]methyl] ether in 80–90% yield, with no evidence of attack at the aromatic centers or of undesirable acetal cleavage (eq 2b). Table III summarizes the pertinent results.

Electron-withdrawing substituents on the (aryloxy)methyl ether are apparently necessary to make the acetal methylene electrophilic enough for attack by the weak nucleophile $HOCH_2CH_2S^-$. The electronegative substituent would also suppress undesirable acetal cleavage (as illustrated in eq 2b).

## Summary and Conclusions

Although bis(acetoxymethyl) ether is, in general, too susceptible to hydrolytic decomposition to be useful as a substitute for bis(chloromethyl) ether, its conversion to a variety of bis[(aryloxy)methyl] ethers by treatment with suitable phenols and an appropriate catalyst furnishes materials more suitable for nucleophilic displacement reactions. Bis(phenoxymethyl) ether and bis[(2,4,6-trichlorophenoxy)methyl] ether, for example, are stable intermediates of low toxicity which react smoothly with mercaptides to form the corresponding thiomethyl ethers.

## Experimental Section

**Catalyst Screening Method.** A solution of 60 g (0.3 mol) of 2,4,6-trichlorophenol and 16.2 g (0.1 mol) of bis(acetoxymethyl) ether in 75 mL of $o$-dichlorobenzene was treated with the appropriate amount of catalyst (Table I) and refluxed with vigorous stirring. Distillate was collected at 10 mL/h to remove the acetic acid as it was formed. The disappearance of 1, appearance and disappearance of the half-substituted product, and appearance of the final product were monitored by VPC. Upon completion of the reaction, the mixture was cooled to 120 °C and poured into ethanol. The product was collected by filtration and crystallized from cyclohexanone. Table I summarizes pertinent experimental details.

**Preparation of Bis[(aryloxy)methyl] Ethers.** Reactions were run as above by using 0.3 mol of the appropriate phenol and 2 g of activated alumina ($^1/_8$-in. tablets; Matheson Coleman and Bell; 98%). Isolation procedures were as described; however, when purification was difficult, no attempt was made to optimize yields (as noted in Table II).

**Bis[[(2-hydroxyethyl)thio]methyl] Ether.** A mixture of 174.5 g (0.4 mol) of bis[(2,4,6-trichlorophenoxy)methyl] ether, 36 g (0.9 mol) of NaOH in 36 mL of water, 70.5 g (0.9 mol) of 2-mercaptoethanol, and 800 mL of 2-ethoxyethanol was stirred

(8) Feutrill, G. I.; Mirrington, R. N. *Aust. J. Chem.* **1972**, *25*, 1719.
(9) Bartlett, Paul A.; Johnson, William S. *Tetrahedron Lett.* **1970**, 4459.
(10) Reiche, A.; Gross, H. *Chem. Ber.* **1960**, *93*, 259.
(11) Mamedov, S.; Ozhailov, T. N. *Zh. Obshch. Khim.* **1963**, *33*, 346.
(12) Reiche, A.; Gross, H. German Patent 1 138 790, 1962.

and refluxed until an aliquot of the resulting clear red solution showed no precipitate when drowned in water. About 650 mL of solvent was then distilled, and the remaining deep red liquid was drowned with 500 mL of water. The red solution was neutralized with 66 g (1.1 mol) of acetic acid and extracted with 1 L of hot heptane and then 300 mL of cold heptane. The aqueous layer was made alkaline with 32 g of 50% aqueous NaOH, saturated with sodium chloride, and extracted with three 200-mL portions of 1,2-dichloroethane. Removal of the dichloroethane in vacuo gave 75 g (94%) of medium-red oil which was identical with the bis[[(2-hydroxyethyl)thio]methyl] ether made from bis(chloromethyl) ether.

**Bis[(*n*-butylthio)methyl] Ether.** A solution of 12 g (0.13 mol) of butanethiol and 4.6 g (0.02 mol) of bis(phenoxymethyl) ether in 50 mL of DMF was treated with 2.9 g (0.13 mol) of sodium hydride and refluxed for 5 h at 150 °C. The resulting solution was drowned in water and taken up in 200 mL of ether. After the solution was washed with 20% aqueous NaOH and water, the solvent was removed, giving 5.4 g of an oily product shown by VPC to contain 70% bis[(*n*-butylthio)methyl] ether (85% yield) and 30% butyl sulfide and disulfide. Analysis by NMR was consistent with that of authentic product prepared from butyl mercaptan and bis(bromomethyl) ether.

**Registry No.** 1, 4082-91-1; 2, 88-06-2; 3, 60093-93-8; 4, 3807-05-4; 5, 60-24-2; bis[[(2-hydroxyethyl)thio]methyl] ether, 36727-72-7; butanethiol, 109-79-5; bis[(*n*-butylthio)methyl] ether, 62609-74-9; bis[(4-chlorophenoxy)methyl] ether, 60093-88-1; bis[(2-chlorophenoxy)methyl] ether, 60093-87-0; bis[(2,4-dichlorophenoxy)methyl] ether, 60093-89-2; bis[(2,3,4,5,6-pentafluorophenoxy)methyl] ether, 80484-50-0; bis[(2,4,6-tribromophenoxy)methyl] ether, 61454-70-4; bis[(4-methylphenoxy)methyl] ether, 42818-09-7; bis[(2-methylphenoxy)methyl] ether, 42818-07-5; bis[(4-methoxyphenoxy)methyl] ether, 63195-89-1; phenol, 108-95-2; 4-chlorophenol, 106-48-9; 2-chlorophenol, 95-57-8; 2,4-dichlorophenol, 120-83-2; 2,3,4,5,6-pentafluorophenol, 771-61-9; 2,4,6-tribromophenol, 118-79-6; 4-methylphenol, 106-44-5; 2-methylphenol, 95-48-7; 2,6-dimethylphenol, 25134-01-4; 2-*tert*-butylphenol, 88-18-6; 4-methoxyphenol, 150-76-5; 2-methoxyphenol, 90-05-1; 4-nitrophenol, 100-02-7.

# Preparation and Characterization of 2-Silanorbornanes

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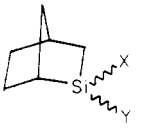
Four members of the new class of 2-silabicyclo[2.2.1]heptanes, or 2-silanorbornanes, were prepared: 2-silanorbornane (1), 2,2-dichloro-2-silanorbornane (2), 2-chloro-2-methyl-2-silanorbornane (3), and 2-methyl-2-silanorbornane (4); the ring-closure reaction involved a platinum-catalyzed, intramolecular hydrosilation. The silanes were characterized by carbon and hydrogen elemental analyses and by $^{1}H$, $^{13}C$, and $^{29}Si$ NMR, IR, and mass spectrometry. Isomer assignments for 3 and 4 were made on the basis of the NMR data. In the mass spectra, each compound gave an abundant molecular ion and a major mode of fragmentation peculiar to this bicyclic system. Some initial stereochemical studies of the reactions of 3 and 4 were performed, including fluoride-induced equilibration of the isomers of 4.

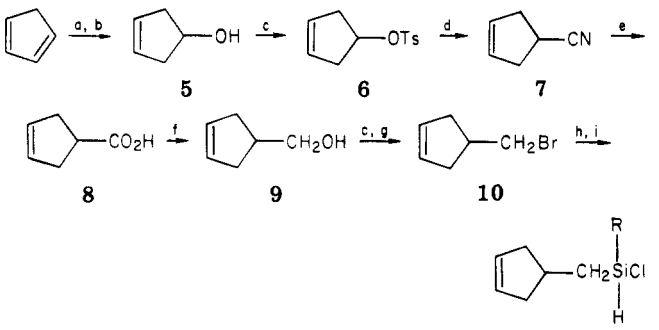
Studies of various bicyclo[2.2.1]heptanes (norbornanes) have provided great insight into the understanding of reaction mechanisms, spectral properties, and structure of organic molecules. As part of a program to prepare new organosilicons for study, we report the first unambiguous synthesis and characterization of 2-silabicyclo[2.2.1]heptane (1), or 2-silanorbornane, and some of its derivatives



1, X = Y = H
2, X = Y = Cl
3, X = Me; Y = Cl
4, X = Me; Y = H

(2-4). The synthetic route developed allows for the placement of different substituents at silicon, which makes systematic studies of this class of compounds possible. The only previous report of any compounds of this type describes the formation of the isomers of 3-neopentyl-2,2-dimethyl-2-silabicyclo[2.2.1]hept-5-ene in 30% yield from the cycloaddition reaction of cyclopentadiene with a silaethylene intermediate.[1] Some 1- and 7-silanorbornanes have been prepared, and a few of their chemical and physical properties have been studied.[2-5] Although 1 and its derivatives are interesting in their own right, another purpose for their preparation was for comparison with the chemistry of the homologous 3-silabicyclo[3.2.1]octanes, which we and others have prepared and studied.[6-8]

Scheme I[a]




[a] (a) 40% Peracetic acid; (b) LAH, ether; (c) *p*-toluenesulfonyl chloride, pyridine; (d) NaCN, HMPA; (e) NaOH, $H_2O$, EtOH, Δ; (f) LAH, THF, Δ; (g) LiBr, acetone, Δ; (h) Mg, THF; (i) $HSiCl_3$ or $MeSiHCl_2$.

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