as in the product of sodium amalgam reduction but show distinct differences in the splitting patterns.

Reduction of 8.3 mmol of 9 with 2.39 mmol of sodium borodeuteride in 20 ml of 2 M methanolic sodium methoxide was worked up after 2 hr by separating the mixture from a 73% yield of mercury and pouring it into 100 ml of water. The aqueous phase was extracted with three portions of pentane. The pentane solution was worked up as described above to give a 63% yield of the ether, bp 51–52° (21 mm). Infrared analysis indicated 81% of the exo-3- (c-12) and 19% of the endo-3-deuterated ether (t-12) and no undeuterated compound. It was determined that 3% of the latter could have been detected. The aqueous phase from the work-up was titrated to pH 2 with hydrochloric acid. The precipitate was extracted with chloroform and the solution was evaporated to dryness to leave 0.648 g (22%) of 9, mp 120–122.5°, free of trans isomer (10) by ir analysis.

Reduction of cis,exo-3-Methoxy-2-norbornylmercuric Chloride (9) with Sodium Borodeuteride in the Presence of Diisopropylbenzene.—A solution of 2.0 g (5.54 mmol) of 9 and 2.5 g (15.4 mmol) of p-diisopropylbenzene (Shell Chemical Corp.) in 15 ml of 0.7 M methanolic sodium methoxide was treated with 0.082 g (1.92 mmol) of sodium borodeuteride and worked up after 3.5 hr as described above. Mercury was obtained in 82% yield. The ether was partially separated from the aromatic hydrocarbon by fractionation on a 15-in. Podbielniak column and further purified by preparative vpc and was obtained in 71% yield. Infrared analysis showed no undeuterated material. Acidification of the aqueous phase gave 0.255 g (13%) of unchanged mercurial.

Reduction of exo-3-Methoxy-endo-2-norbornylmercuric Chloride (10) with Sodium Borohydride and Borodeuteride.—A 2.02-g (5.6 mmol) sample of 10 in 20 ml of D$_2$O containing seven sodium hydroxide pellets was reduced with 0.24 g (5.6 mmol) of sodium borodeuteride and worked up after 2.5 hr in the manner described above for reduction of the cis,exo mercurial. Mercury was obtained in 96% yield. The organic products (72% yield) were 84% exo-3-deuterio- (c-12) and 16% endo-3-deuterio-exo-2-methoxynorbornane (t-12) by ir analysis.

Reduction of 0.5 g (1.4 mmol) of the mercurial with 0.026 g (0.7 mmol) of sodium borohydride in 5 ml of heavy water containing two sodium hydroxide pellets gave, after 2 hr, a 94%

yield of mercury and a 62% yield of exo-2-methoxynorbornane (12) which was undeuterated (ir analysis).

A mixture of 1.0 g (2.77 mmol) of 10 and 0.0146 g (0.35 mmol) of sodium borodeuteride in 10 ml of 2 M methanolic sodium methoxide gave, after 2 hr, 0.116 g (41% based on borodeuteride) of free mercury and 0.738 g of unchanged 10, mp 89.5–92°, free of 9 (ir analysis). A small amount of the reduction product was isolated by vpc for ir analysis and found to be 82% exo-3-deuterio- (c-12) and 18% endo-3-deuterio-exo-2-methoxynorbornane (t-12). No undeuterated ether was detected.

Reduction of cis,endo-3-Methoxy-2-norbornylmercuric Chloride (11) with Sodium Borodeuteride.—A 1.0-g (2.77 mmol) sample of pure 11 was reduced with sodium borodeuteride in basic deuterium oxide as described above for the borodeuteride reduction of the cis,exo isomer. Mercury was isolated in 97% yield. Methoxycyclohexane was added to the organic phase as an internal standard and the yield of methoxynorbornane by vpc analysis, assuming equal thermal conductivities, was 109%. The bulk of the product was isolated by preparative vpc. In the pmr spectrum in carbon disulfide, H-2 absorbed at τ 6.45, methoxy protons at 6.84, H-1 and H-4 at 7.68 and 7.92, and the remaining seven hydrogens between 8 and 9.2. H-2 appears as an eight-line multiplet with $W_{h/2}$ = 9.3 Hz. Double irradiation of the downfield bridgehead proton (2.594 kHz, offset at 157 Hz, 100–200 mV input) simplified absorption of H-2 to a broad doublet of doublets with J = 3.0 and 1.3 Hz.

Registry No.—2, 36807-31-5; 3, 20556-05-2; 4, 20556-07-4; 5, 36807-34-8; c-6, 21438-85-7; t-6, 36807-36-0; c-7-d, 6372-64-1; t-7-d, 36807-38-2; 8, 21438-92-6; 8-d, 36794-38-4; 9, 36807-39-3; 10, 36807-40-6; 11, 36807-41-7; 12, 10395-53-6; c-12, 36807-43-9; t-12, 36807-44-0; 13, 10395-55-8; c-13, 36807-46-2; t-13, 36807-47-3; mercury, 7439-97-6; deuterium, 7782-39-0; sodium borodeuteride, 15681-89-7; sodium amalgam, 11, 110, 524.
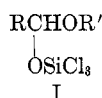

Reduction with Trichlorosilane. IV. Ether from Acetal[1]

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The reduction of acetals derived from formaldehyde, acetaldehyde, acetone, and diethyl ketone to the corresponding ethers with trichlorosilane under γ irradiation has been studied. An acetal reacts at first with chlorosilane to give an α-chloro ether, which is in turn reduced with the silicon hydride under γ irradiation. The present study, especially the reduction of mixed acetal containing a triethylsilyl group, makes clear the reduction sequence of an ester through an acetal type intermediate mentioned in our preceding paper.

Our previous paper reported the reduction of aliphatic esters to dialkyl ethers with trichlorosilane under free-radical conditions.[2] There we considered that the reduction proceeds via an acetal type intermediate I. If

$$\underset{\underset{I}{\overset{|}{\text{OSiCl}_3}}}{\overset{\text{RCHOR}'}{}}$$

this consideration were true, it might be expected that acetals, in general, are reduced with trichlorosilane to give the corresponding ethers. Furthermore, it might also be expected that the elucidation of the reduction mechanism of acetals may add to understanding the

mechanism of the reduction of esters. From these viewpoints, acetals of formaldehyde, acetaldehyde, acetone, and diethyl ketone and some mixed acetals were allowed to react with trichlorosilane in the present paper. Although several papers reported that acetals can be reduced to ethers with lithium aluminum hydride[3] and sodium borohydride,[4] the present method will provide a new synthetic route to ethers in high yields.

Results and Discussion

A degassed mixture of acetal and trichlorosilane was irradiated with γ rays in a sealed tube. The results are summarized in Table I, which indicates comparatively

(1) Paper III in this series: R. Nakao, T. Fukumoto, and J. Tsurugi, *J. Org. Chem.*, **37**, 76 (1972).

(2) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Amer. Chem. Soc.*, **91**, 4587 (1969).

(3) E. L. Eliel, V. G. Badding, and M. N. Rerick, *ibid.*, **84**, 2371 (1962). and references cited therein.

(4) J. R. Dias and G. R. Pettit, *J. Org. Chem.*, **36**, 3485 (1971).

TABLE I

REDUCTION OF ACETALS TO ETHERS WITH TRICHLOROSILANE[a]

| Registry no.	Run	Acetal	Product (yield, %)
77-76-9	1	$(CH_3)_2C(OCH_3)_2$	$(CH_3)_2CHOCH_3$[d] (85), HCl_2SiOCH_3 (90)
36749-09-4	2	$(C_2H_5)_2C(OC_2H_5)_2$	$(C_2H_5)_2CHOC_2H_5$[e] (89), $HCl_2SiOC_2H_5$ (95)
534-15-6	3	$CH_3CH(OCH_3)_2$	$C_2H_5OCH_3$[f] (79), HCl_2SiOCH_3 (94)
	4[b]	$CH_3CH(OCH_3)_2$	$C_2H_5OCH_3$ (61), HCl_2SiOCH_3 (34)
			Cl_3SiOCH_3 (58)
105-57-7	5	$CH_3CH(OC_2H_5)_2$	$C_2H_5OC_2H_5$ (82), $HCl_2SiOC_2H_5$ (96)
462-95-3	6[c]	$H_2C(OC_2H_5)_2$	$CH_3OC_2H_5$ (85), $HCl_2SiOC_2H_5$ (92)
10471-14-4	7	CH_3CHOCH_3 $\vert$ OC_2H_5	$C_2H_5OC_2H_5$ (52), HCl_2SiOCH_3 (50) $C_2H_5OCH_3$ (35), $HCl_2SiOC_2H_5$ (43)
17841-50-8	8	$CH_3CHOC_2H_5$ $\vert$ $OSi(C_2H_5)_3$	$C_2H_5OC_2H_5$ (93), $HCl_2SiOSi(C_2H_5)_3$ (96)

[a] Trichlorosilane/acetal = 3; dose rate = 0.3 Mrad/hr, total dose = 5.1 Mrad. [b] Trichlorosilane/acetal = 1. [c] Irradiated after mixing and standing for 5 days. [d] Registry no., 598-53-8. [e] Registry no., 36749-13-0. [f] Registry no., 540-67-0.

high yields of dialkyl ethers from several types of acetals. Besides the products cited in Table I, tetrachlorosilane was always found among the products when a 3:1 molar ratio of trichlorosilane/acetal was used. Although the mixed acetal, $CH_3CH(OCH_3)OC_2$-H_5 of run 7, yields two types of ether, the mixed acetal, $CH_3CH(OC_2H_5)OSi(C_2H_5)_3$ of run 8, gave predominantly diethyl ether. The formation of tetrachlorosilane and the products from the latter mixed acetal will be discussed later in this paper.

We found that simple mixing of trichlorosilane with acetaldehyde dimethylacetal (3:1 molar ratio) caused eq 1 to shift to the right-hand side, because the forma-

$$CH_3CH(OCH_3)_2 + HSiCl_3 \longrightarrow$$
$$CH_3CHClOCH_3 + HCl_2SiOCH_3 \quad (1)$$
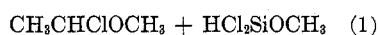
tion of α-chloro ether and complete disappearance of the acetal were confirmed by nmr. The quantitative formation of dichloromethoxysilane was further confirmed by glpc. Identification and determination of α-chloroethyl methyl ether by glpc were unsuccessful because of its sensitivity to the decomposition. The results confirmed by nmr and glpc indicate that eq 1 proceeds quantitatively immediately after the simple mixing except run 6 for ethylal.[5] The reduction of acetal with trichlorosilane then turned out to be the reduction of α-chloro ether with trichlorosilane. After γ irradiation of the mixture, nmr spectra showed that ethyl methyl ether was produced together with the complete disappearance of the spectra of α-chloro ether and maintenance of the spectra of dichloromethoxysilane. This result indicates eq 2 for γ-induced reduction.

$$CH_3CHClOCH_3 + HSiCl_3 \xrightarrow{\text{--}/\!/\!/\backslash\text{--}} CH_3CH_2OCH_3 + SiCl_4 \quad (2)$$
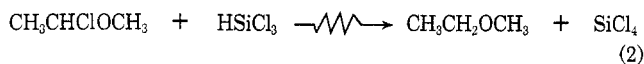
A number of papers[6] reported the reduction of alkyl chlorides to alkanes with trichloro- and trialkylsilanes. These reactions are believed to proceed by a radical chain mechanism. We irradiated the mixture

(5) γ irradiation of the mixture of run 6 immediately after the mixing did not give ethyl methyl ether. After the mixture was left for a sufficient time period, γ irradiation gave a high yield of ethyl methyl ether as indicated in run 6, Table 1. This may be attributed to the slower rate of eq 1 in the case of ethylal, because immediately after the mixing chloromethyl ethyl ether could not be detected by nmr. Chlorination was accelerated by adding a very small amount of water to the reduction system.

(6) (a) R. N. Haszeldine and J. C. Young, *J. Chem. Soc.*, 4503 (1960); (b) R. A. Jackson, *Advan. Free-Radical Chem.*, **3**, 231 (1969); (c) I. M. T. Davidson, *Quart. Rev., Chem. Soc.*, **25**, 111 (1971).

of trichlorisilane and acetaldehyde dimethylacetal (3:1 molar ratio) in a Pyrex tube with uv lights for 1 hr and obtained a 51% yield of ethyl methyl ether. We also obtained an 86% yield of the ether by uv irradiation (for 1 hr) of the same mixture containing 2 molar % of di-*tert*-butyl peroxide/acetal. From Figure 1, which will be mentioned later, the G value (number of molecules formed per 100 eV of energy absorbed) is calculated as 5000. These results clearly support a radical chain mechanism.

The two-step sequence, chlorination of acetal to α-chloro ether and reduction of α-chloro ether to ether, is supported by the results shown in Table II. Chlorinat-

TABLE II

REDUCTION OF ACETALEDHYDE DIMETHYLACETAL TO
METHYL ETHYL ETHER WITH SILICON HYDRIDES COMBINED
WITH CHLORINATING AGENTS[a]

Run	Chlorinating agent (mol)	Silicon hydride (mol)	Yield, %
1		$HSi(C_2H_5)_3$ (1)	0
2		$HSi(C_6H_5)_3$ (1)	0
3	$HClSi(CH_3)_2$ (2)		68
4	$SiCl_4$ (1)	$HSi(C_2H_5)_3$ (1)	83
5	$SiCl_4$ (1)	$HSi(C_6H_5)_3$ (1)	64
6	CH_3COCl (1)	$HSi(C_2H_5)_3$ (1)	71

[a] Dose rate = 0.3 Mrad/hr, total dose = 5.1 Mrad.

ing agents such as tetrachlorosilane and acetyl chloride[7] combined with triethyl- or triphenylsilane can yield methyl ethyl ether from acetaldehyde dimethylacetal, while triethyl- or triphenylsilane alone cannot. Dimethylchlorosilane (run 3, Table II) can behave similarly to trichlorosilane. Tetrachlorosilane (runs 4 and 5, Table II) also chlorinated the acetal similarly to eq 1. Acetyl chloride (run 6, Table II) is well known[7] to give α-chloro ether from acetal as indicated in eq 3. Methyl

$$RR'C(OR'')_2 + CH_3COCl \longrightarrow$$
$$RR'CClOR'' + CH_3COOR'' \quad (3)$$
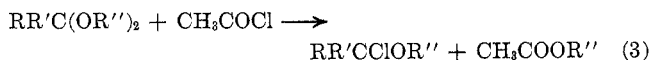
acetate,[8] expected to be produced in eq 3, was found in 75% yield by glpc. The two-step sequence was further supported by the following result. The mixture of trichlorosilane with chloromethyl ethyl ether (purified

(7) L. Summers, *Chem. Rev.*, **55**, 301 (1955).

(8) Methyl acetate is reduced to ethyl methyl ether with trichlorosilane under γ irradiation, but is not reduced with triethylsilane. Therefore, methyl acetate remained unaltered under the conditions of run 6, Table II.

commercial material) gave an 87% yield of ethyl methyl ether under γ irradiation.

The two-step sequence at first glance seems to require 2 mol of trichlorosilane to reduce 1 mol of acetal, because both eq 1 and 2 consume each 1 mol of trichlorosilane. However, run 4, Table I, indicates that an equimolar amount is sufficient. Since eq 1 is fast, 1 mol of trichlorosilane is consumed by eq 1. The reduction of α-chloro ether must be performed with dichloromethoxysilane produced in eq 1. As seen in run 4, Table I, the amount of dichloromethoxysilane decreases as compared with other runs, and trichloromethoxysilane was found anew instead of tetrachlorosilane. This result suggests that eq 4 proceeds under γ

$$CH_3CHClOCH_3 \ + \ HCl_2SiOCH_3 \ \text{—/\/\/—→}$$
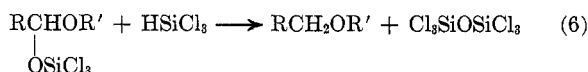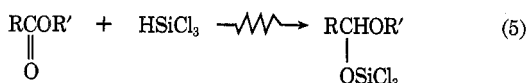$$CH_3CH_2OCH_3 \ + \ Cl_3SiOCH_3 \quad (4)$$
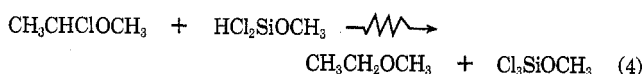
irradiation. Figure 1 shows yields of ethyl methyl ether by the reductions of 3:1 and 1:1 molar ratios of trichlorosilane/acetaldehyde dimethylacetal. This result indicates that dichloromethoxysilane can reduce α-chloro ether, but more slowly than trichlorosilane can.

As a summary, the reduction in the presence of a 2:1 or more molar ratio of trichlorosilane/acetal proceeds *via* eq 1 and 2. On the other hand, equimolar amount of trichlorosilane leads to the sequence indicated by eq 1 and 4.

Frainnet, *et al.*,[9] reported the reduction of acetals with trialkylsilanes in the presence of zinc chloride as a catalyst. The reduction sequence, which had not been mentioned by them, seems to differ from ours.

Connection with the Reduction of Esters.—It seems interesting to discuss the reduction of ester to ether in connection with the present results. In our previous paper[2] on the reduction of alkyl aliphatic esters we reported that the reduction proceeds *via* eq 5 and 6. In

$$\begin{array}{c} RCOR' \ + \ HSiCl_3 \ \text{—/\/\/—→} \ RCHOR' \\ \parallel \qquad\qquad\qquad\qquad\qquad | \\ O \qquad\qquad\qquad\qquad\qquad OSiCl_3 \end{array} \quad (5)$$

$$\begin{array}{c} RCHOR' \ + \ HSiCl_3 \ \longrightarrow \ RCH_2OR' \ + \ Cl_3SiOSiCl_3 \\ | \\ OSiCl_3 \end{array} \quad (6)$$

this sequence we considered mixed acetal as an intermediate, and held eq 6 ambiguous. Later, in part III of this series, we proposed a sequence[10] for the reduction of lactones with trichlorosilane. However, on the basis of the results of the present paper, this sequence should be corrected to eq 7 and 8 (X = Cl). In the present paper, as a model of mixed acetal containing the trichlorosilyl group, which is very susceptible to moisture, we used in run 8, Table I, the mixed acetal containing the triethylsilyl group. The mixture of the latter acetal with trichlorosilane gave diethyl ether and triethylsiloxydichlorosilane both in nearly quantitative
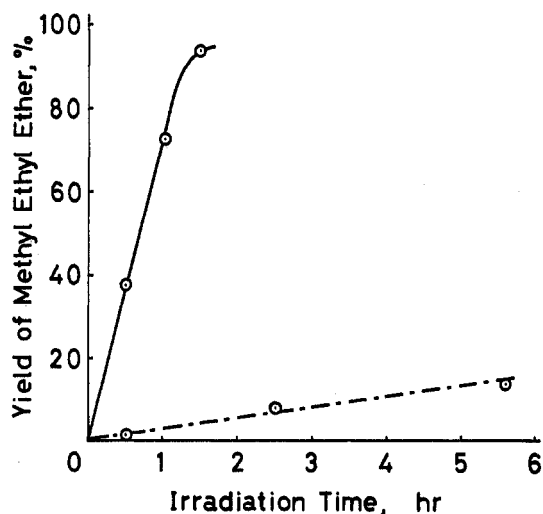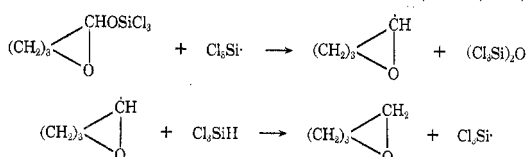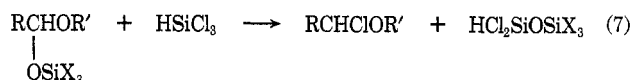

Figure 1.—Reduction of acetaldehyde dimethylacetal with trichlorosilane for various irradiation times. Dose rate = 0.3 Mrad/hr: —·○·—, HSiCl₃/acetal = 1; —○—, HSiCl₃/acetal = 3.

yields under γ irradiation (X = C₂H₅, R = CH₃, and R' = C₂H₅ in eq 7 and 8).

$$\begin{array}{c} RCHOR' \ + \ HSiCl_3 \ \longrightarrow \ RCHClOR' \ + \ HCl_2SiOSiX_3 \\ | \\ OSiX_3 \end{array} \quad (7)$$

$$RCHClOR' \ + \ HSiCl_3 \ \text{—/\/\/—→} \ RCH_2OR' \ + \ SiCl_4 \quad (8)$$

As a summary, the reduction of ester to ether in the presence of a 3:1 or more molar ratio of trichlorosilane can be concluded to proceed *via* eq 5, 7, and 8. However, in the presence of a 2:1 molar ratio of trichlorosilane the reduction proceeds *via* eq 5, 7, and 9, because our previous paper reported that ethyl acetate and trichlorosilane (1:2.2 molar ratio) gave hexachlorodisiloxane besides diethyl ether. Equation 9 is quite similar to eq 4.

$$CH_3CHClOC_2H_5 \ + \ HCl_2SiOSiCl_3 \ \text{—/\/\/—→}$$
$$CH_3CH_2OC_2H_5 \ + \ Cl_3SiOSiCl_3 \quad (9)$$
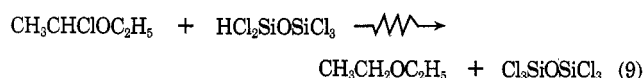
Experimental Section

All boiling points are uncorrected. Gas chromatographies were determined by a Yanagimoto GCG-5DH with a 2.5-m column containing 25% silicon DC-200 on Celit 545 and a 3-m column containing 30% dioctyl phthalate on Celit 545 both using helium as a carrier gas. Nmr spectra were recorded on a JNM 3H-60 with tetramethylslane as an external standard. Mass spectra were recorded on a Shimadzu-LKD 9000.

Materials.—Diethyl ketone diethylacetal was prepared by the method of Fife[11] from diethyl ketone and triethyl orthoformate, bp 155° (lit.[12] bp 154°). Acetaldehyde methyl ethylacetal was prepared by the modified procedure of Juvet.[13] Acetaldehyde diethyl acetal (0.6 mol) and methanol (0.2 mol) were refluxed in the presence of 1 drop of 12 N hydrochloric acid for 30 min. After neutralization with sodium hydroxide, two distillations gave the acetal: bp 83° (lit.[13] bp 84.5°); nmr (neat) δ 1.15 (t, 3, CH₂CH₃), 1.20 (d, 3, CHCH₃), 3.20 (s, 3, OCH₃), 3.45 and 3.50 (2 q, 2, CH₂), 4.55 (q, 1, CH). Acetaldehyde ethyl (triethyl)silylacetal[14] was synthesized by the addition reaction of

(9) E. Frainnet and C. Esclamadon, *C. R. Acad. Sci.*, **254**, 1814 (1962).

(10)

$$\begin{array}{l} (CH_2)_3 \diagup\raisebox{0.5ex}{CHOSiCl_3}\diagdown O \ + \ Cl_6Si \cdot \ \longrightarrow \ (CH_2)_3 \diagup\raisebox{0.5ex}{CH}\diagdown O \ + \ (Cl_3Si)_2O \end{array}$$

$$\begin{array}{l} (CH_2)_3 \diagup\raisebox{0.5ex}{CH}\diagdown O \ + \ Cl_3SiH \ \longrightarrow \ (CH_2)_3 \diagup\raisebox{0.5ex}{CH_2}\diagdown O \ + \ Cl_3Si \cdot \end{array}$$

(11) T. H. Fife and L. Hagopian, *J. Org. Chem.*, **31**, 1772 (1966).

(12) Beilstein's "Handbuch der Organichen Chemie," Vol. 1, 1918, p 680.

(13) R. S. Juvet, Jr., and J. Chiu, *J. Amer. Chem. Soc.*, **83**, 1560 (1961).

(14) M. F. Shostakovskii, K. A. Andrianov, I. A. Shikhiev, and D. A. Kochkin, *Dokl. Akad. Nauk SSSR*, **93**, 681 (1953); *Chem. Abstr.*, **49**, 1542a (1955).

TABLE III

NMR SPECTRA OF REACTION MIXTURES

Mixture (molar ratio)	Reaction condition[a]	Spectra of products (molar ratio)
$CH_3CH(OCH_3)_2$ (1), $HSiCl_3$ (3)	Simple mixture	$CH_3CHClOCH_3$ (1) δ 2.01 (d, 3, CCH_3), 3.73 (s, 3, OCH_3), 5.84 (q, 1, CH);[b] HCl_2SiOCH_3 (1) δ 3.94 (s, 3, OCH_3), 5.82 (s, 1, SiH); $HSiCl_3$ (2) δ 6.40 (s, 1, SiH)
$CH_3CH(OCH_3)_2$ (1), $HSiCl_3$ (3)	Irradiation	$C_2H_5OCH_3$ (1) δ 1.41 (t, 3, CCH_3), 3.51 (s, 3, OCH_3), 3.62 (q, 2, CH_2); HCl_2SiOCH_3 (1) δ 3.93 (s, 3, OCH_3), 5.79 (s, 1, SiH); $HSiCl_3$ (1) δ 6.38 (s, 1, SiH)
$(CH_3)_2C(OCH_3)_2$ (1), $HSiCl_3$ (3)	Simple mixture	$(CH_3)_2CClOCH_3$ (1) δ 2.10 (s, 6, CCH_3), 3.70 (s, 3, OCH_3); HCl_2SiOCH_3 (1) δ 3.95 (s, 3, OCH_3), 5.82 (s, 1, SiH); $HSiCl_3$ (2) δ 6.40 (s, 1, SiH)
$(CH_3)_2C(OCH_3)_2$ (1), $HSiCl_3$ (3)	Irradiation	$(CH_3)_2CHOCH_3$ (1) δ 1.35 (d, 6, CCH_3), 3.48 (s, 3, OCH_3), 3.35–3.9 (m, 1, CH); HCl_2SiOCH_3 (1) δ 3.92 (s, 3, OCH_3), 5.79 (s, 1, SiH); $HSiCl_3$ (1) δ 6.35 (s, 1, SiH)
$H_2C(OC_2H_5)_2$ (1), $HSiCl_3$ (3)	A or B	$H_2ClOC_2H_5$ (1) δ 1.53 (t, 3, CH_3), 4.01 (q, 2, OCH_2C), 5.74 (s, 2, $ClCH_2O$); $HCl_2OSiOC_2H_5$ (1) δ 1.62 (t, 3, CH_3), 4.32 (q, 2, OCH_2C), 5.85 (s, 1, SiH); $HSiCl_3$ (2) δ 6.42 (s, 1, SiH)
$CH_3CH(OCH_3)_2$ (1), $SiCl_4$ (3)	Simple mixture	$CH_3CHClOCH_3$ (1) δ 2.11 (d, 3, CCH_3), 3.82 (s, 3, OCH_3), 5.91 (q, 1, CH); Cl_3SiOCH_3 (1) δ 4.11 (s, 3, OCH_3)
$CH_3CH(OCH_3)_2$ (1), HCl_2SiCH_3 (3)	Simple mixture	$CH_3CHClOCH_3$ (1) δ 1.92 (d, 3, CCH_3), 3.64 (s, 3, OCH_3), 5.78 (q, 1, CH); $HClSi(OCH_3)CH_3$ (1) δ 0.70 (d, 3, $J = 2$ Hz, $SiCH_3$), 3.74 (s, 3, OCH_3), 5.31 (q, 1, $J = 2$ Hz, SiH); HCl_2SiCH_3 (2) δ 1.07 (d, 3, $J = 2$ Hz, $SiCH_3$), 5.77 (q, 1, $J = 2$ Hz, SiH).

[a] A, allowing the mixture to stand for 5 days; B, adding a small amount of water to the mixture. [b] G. A. Olah and J. Sommer, *J. Amer. Chem. Soc.*, 90, 4323 (1968).

triethylsilanol to vinyl ether. A mixture of triethylsilanol[15] (0.2 mol), which was prepared by hydrolysis of triethylchlorosilane with aqueous sodium hydroxide, vinyl ethyl ether (0.4 mol), and hydrochloric acid (1 drop) was refluxed for 1 hr. The temperature of the mixture was raised to 55° at the later stage. After neutralization with sodium hydroxide, distillation gave the acetal, bp 81° (16 mm), n^{20}D 1.4235 [lit.[14] bp 78–79° (15–16 mm), n^{20}D 1.4232]. Other acetals, commercial materials, were distilled and stored in ampoules.

Trichlorosilane was treated with quinoline to remove hydrochloric acid and was distilled several times under vacuum.

The other reagents were purified by conventional methods.

Preparation of Standard Materials for Glpc and Nmr.—Standard materials for glpc and nmr were purified from the corresponding commercial materials by conventional methods except for the compounds cited below. Isopropyl methyl ether was prepared from methyl iodide and sodium isopropoxide by the conventional method, bp 32° (lit.[16] bp 32–33°). 1-Ethylpropyl ethyl ether was prepared by γ-induced reduction of diethyl ketone diethylacetal (0.15 mol) with trichlorosilane (0.45 mol). To the irradiated mixture was added aqueous sodium hydroxide for decomposition of chlorosilanes. Two distillations gave the ether: bp 106°; nmr (neat) δ 0.87 (t, 6, CCH_2CH_3), 1.14 (t, 3, OCH_2-CH_3), 1.44 (m, 4, $CHCH_2CH_3$), 3.08 (m, 1, OCH), 3.42 (q, 2, OCH_2); mass spectrum (70 eV) m/e (rel intensity) 116 (0.2, M⁺), 87 (54), 59 (100), 55 (37), 41 (23), 29 (29). Dichloromethoxysilane was prepared by methanolysis of trichlorosilane. A benzene solution of trichlorosilane (0.2 mol) was placed in a two-necked flask equipped with a dropping funnel and a reflux condenser which was fitted with a calcium chloride tube. Methanol (0.2 mol) was added dropwise for 1 hr with magnetic stirring at 0°. The resulting mixture was refluxed for 30 min for the completion of the reaction and the exclusion of hydrogen chloride produced. Dichloromethoxysilane was obtained by two distillations: bp 51° (lit.[17] bp 50.5°); nmr (neat) δ 3.88 (s, 3, OCH_3), 5.74 (s, 1, SiH). Dichloroethoxysilane was prepared in the same manner as mentioned above by using ethanol instead of methanol and toluene instead of benzene: bp 75° (lit.[17] bp 75.7°); nmr (neat) δ 1.53 (t, 3, CH_3), 4.23 (q, 2, OCH_2), 5.78 (s, 1, SiH). Triethylsiloxydichlorosilane was separated from the irradiated mixture of acetaldehyde ethyl (triethyl)silyl acetal and trichloro-

silane. A degassed mixture of the acetal (0.1 mol) and trichlorosilane (0.3 mol) was irradiated by γ rays (dose rate = 0.3 Mrad/hr, total dose = 5.1 Mrad) in a Pyrex tube equipped with a breakable seal. After the irradiation, the mixture was distilled under vacuum. Triethylsiloxydichlorosilane was collected in a trap cooled by Dry Ice and the others (diethyl ether, tetrachlorosilane, and unchanged trichlorosilane) were trapped by liquid nitrogen. Five distillations gave a gas chromatographically pure sample, nmr (neat) δ 0.5–1.3 (m, 15, $SiCH_2CH_3$), 5.70 (s, 1, SiH).

Procedure for Irradiation.—A given amount of acetal and trichlorosilane or di-*tert*-butyl peroxide was degassed in a Pyrex tube or nmr sample tube by the same way as stated earlier.[1] The mixture was irradiated by γ rays from a ⁶⁰Co source or uv rays from a medium-pressure mercury lamp at room temperature.

Identification and Estimation of Products.—The products were identified by glpc or nmr and estimated by glpc, except for Figure 1. The yields of methyl ethyl ether in Figure 1 were estimated by comparison of nmr intensity of the methyl signal (δ 1.40, triplet) of the ether with that of the methyl absorption (δ 2.00, doublet) of unchanged α-chloroethyl methyl ether.

Nmr Spectra of the Products. A. From Acetals and Chlorosilanes.—Simple mixing of an acetal with a chlorosilane gave a superimposed spectrum which consisted of α-chloro ether, chloroalkoxysilane, and excess chlorosilane. When chlorosilane was trichlorosilane, γ irradiation changed the spectrum into that consisted of an ether, a dichloroalkoxysilane, and unchanged trichlorosilane with the disappearance of the spectrum of α-chloro ether. The nmr spectrum of each product is summarized in Table III.

B. From Acetaldehyde Dimethylacetal and Acetyl Chloride.—An equimolar mixture of the titled compounds, after standing for 4 days, gave a spectrum which consisted of the following four components: α-chloroethyl methyl ether, δ 1.83 (d, 3, CCH_3), 3.69 (s, 3, OCH_3), 5.78 (q, 1, CH) (relative ratio 0.8); methyl acetate, δ 2.08 (s, 3, CCH_3), 3.57 (s, 3, OCH_3) (relative ratio 0.8); unchanged acetal, δ 1.30 (d, 3, CCH_3), 3.33 (s, 6, OCH_3), 4.61 (q, 1, CH) (relative ratio 0.2); and unchanged acetyl chloride, δ 2.80 (s, 3, CH_3) (relative ratio 0.2).

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