electrochemical step, forms anaerobically stable reaction intermediates under both protic and aprotic reduction conditions. Whereas normally under protic conditions a two-electron change and addition of two protons to a double bond to form a dihydro product is found for alternant hydrocarbons, fluorene reduction under the same conditions does not lead to a dihydro or any other stable reduction product.

As was pointed out earlier, fluorenone is also formed as a major product of the electrochemical reduction of fluorene under aprotic conditions, as expected, but in greater amounts than the ECE mechanism would allow; unexpectedly, no dihydrofluorene is found here either. It appears as if one of the reaction intermediates, possibly the product of $RH_3\cdot$ reaction with solvent, in the presence of oxygen, reacts very readily with unelectrolyzed fluorene, in a second pathway to the ketone besides that through the carbanion. A significant solvent effect is observed in that addition of oxygen to the electrolyzed aprotic fluorene solution leads to different colored intermediates in MeCN than in DMF and DMSO. The major and final product in all three solvents is, however, fluorenone.

As different intermediates are observed depending on whether protic or aprotic conditions obtain, it is clear that different pathways to the ketone exist. One fact seems consistent, however, that the second electrochemical step ($RH_3\cdot + e^- \rightarrow RH_3^-$) does not occur in either case, and up to reaction 10 the sequences are probably the same.

Further study is necessary to establish the nature of the differencs in the reaction pathways and intermediate stabilities (the inability to isolate the purple cation species is puzzling, and further investigation is in progress) and to define the nature of the reaction products formed in both protic and aprotic conditions. Nevertheless, it seems clear from this work that fluorene does not follow the normal ECE sequence. It would be of interest to study other nonalternant hydrocarbons to determine if the above behavior is common with nonalternant species or peculiar to the fluorene-type structure.[24]

Registry No.—Fluorene, 86-73-7; dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5; acetonitrile 75-05-8; fluorene anion radical, 34484-03-2; fluorene carbanion, 35782-20-8; fluorenone anion radical, 37439-74-0.

Acknowledgment.—The authors wish to express their thanks to David B. Knight and Philip J. Hamrick, Jr., for helpful discussions concerning this investigation. Professor Hamrick was also kind enough to provide us with some 9-substituted fluorene compounds used in this study.

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[24] We have some evidence that 9,10-dihydrophenanthrene also exhibits an n value of about 3.0 under protic conditions in DMF, but further study of this system is necessary. It should be noted that this species is also a cross-conjugated, biphenyl-related compound.

Reduction with Trichlorosilane. II.
Mechanistic Study of Reduction of Methyl Acetate to Ethyl Methyl Ether

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The kinetics of the previously reported reduction of alkyl aliphatic carboxylates with trichlorosilane under γ and photoirradiations was studied by using methyl acetate as a starting material. Initially the stoichiometry corresponded to $CH_3COOCH_3 + 3Cl_3SiH \rightarrow C_2H_5OCH_3 + SiCl_4 + HSiCl_2OSiCl_3$. However, since trichlorosiloxydichlorosilane behaved similarly to trichlorosilane, the amount of trichlorosilane consumed at the later stage of the reaction was smaller than 3 mol and the amount of trichlorosiloxydichlorosilane produced was less than 1 mol. Acetaldehyde was detected together with ethyl methyl ether by glpc analysis. The formations of intermediates, acetal type and α-chloroethyl methyl ether, were supported by several results. These intermediates gave acetaldehyde during glpc analysis, and were converted to ethyl methyl ether under irradiations with trichlorosilane. A free-radical chain mechanism *via* these intermediates was proposed. The rate of methyl acetate consumption is derived as $-d[\text{methyl acetate}]/dt = k(\text{dose rate})^{1/2} \times [\text{trichlorosilane}]$ by assuming that recombination of $CH_3\dot{C}(OSiCl_3)OCH_3$ radicals predominates over other termination steps. This rate equation is consistent with the results obtained by kinetic determinations. A small amount of benzene added to the reaction system was found to strongly retard the reaction, suggesting that benzene acts as a scavenger of trichlorosilyl radical.

In paper I of this series,[1] we reported that trichlorosilane can reduce alkyl aliphatic carboxylates, in some cases quantitatively, to dialkyl ethers under γ irradiation, and proposed that the reaction may proceed by a free-radical chain mechanism. However, the detailed mechanism has remained unsettled.

$$RCOOR' \xrightarrow[Cl_3SiH]{\gamma\ \text{ray}} RCH_2OR'$$

Also, one could not explain why carboxylic esters containing an aryl group in either R or R′ of RCOOR′ could not be reduced by this reaction. In the present paper we have established the reaction mechanism of methyl acetate with trichlorosilane under γ and photoirradiations. In addition, we found that addition of a catalytic amount of benzene to the reaction system greatly retarded the reaction. This retarding effect is interpreted by assuming that benzene acts as a scavenger of trichlorosilyl radical. This effect explains why carboxylic esters containing an aryl group cannot be reduced.

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

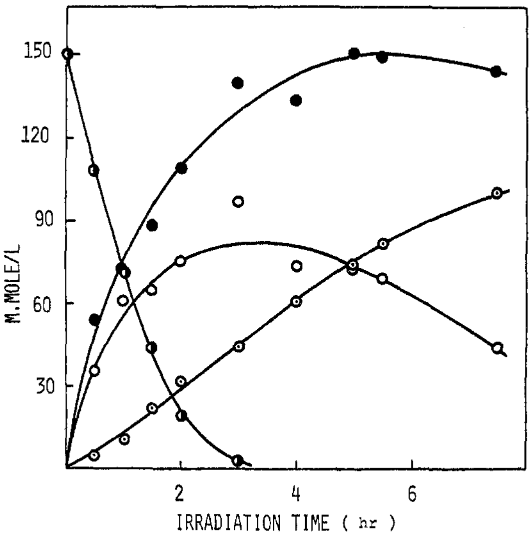

Figure 1.—Time plot of γ-irradiated mixture in cyclohexane: $[CH_3COOCH_3]_0$ = 0.150 and $[Cl_3SiH]_0$ = 0.600 mol/l., dose rate, 1.85 × 10^5 R/hr; ○, CH_3CHO; ⊙, $C_2H_5OCH_3$; ●, $CH_3CHO + C_2H_5OCH_3$; ◑, CH_3COOCH_3. As seen in text, the amount of acetaldehyde actually corresponds to the amount of intermediate. This also holds for all the succeeding figures.

Results and Discussion

The reaction in cyclohexane indicates that a prominent amount of acetaldehyde together with ethyl methyl ether was produced as compared with the result in neat reaction (Figure 5). Figure 1 shows the amounts of the products and methyl acetate remaining *vs.* γ-irradiation time. The products and methyl acetate remaining were determined by glpc. Figure 1 seems, at first glance, to support the assumption that acetaldehyde is the intermediate of the reaction because the sum total of acetaldehyde and ethyl methyl ether corresponds to the consumption of methyl acetate. However, this assumption is contradicted by subsequent experiments.

The cyclohexane solution of the same mixture sealed in a photoabsorption cell was photoirradiated. Determination of uv-absorption spectra of the irradiated mixture indicates a decrease of absorption of methyl acetate, but no absorption of acetaldehyde. This result indicates no production of acetaldehyde during the irradiation. However, glpc identified acetaldehyde from this irradiated mixture. Addition of a small amount of water to the same irradiated mixture in the same photocell was found to cause the formation of acetaldehyde. Assuming that the same mechanism prevails both in γ and photoirradiations, these results support the formation of an intermediate other than acetaldehyde and the decomposition of this intermediate to acetaldehyde during glpc separation process.

In another experiment acetaldehyde was added to the reaction system prior to the irradiation. After uv irradiation, this mixture indicated a decrease of acetaldehyde but no decrease of methyl acetate nor formation of ethyl methyl ether. This result suggests that the reaction of acetaldehyde with trichlorosilane[2] predominates over that of methyl acetate with trichlorosilane. If acetaldehyde was an intermediate in the reaction system, the reaction of methyl acetate with trichlorosilane would not proceed. All these results clearly indicate that acetaldehyde determined by glpc is a decomposition product from the intermediate other than acetaldehyde.

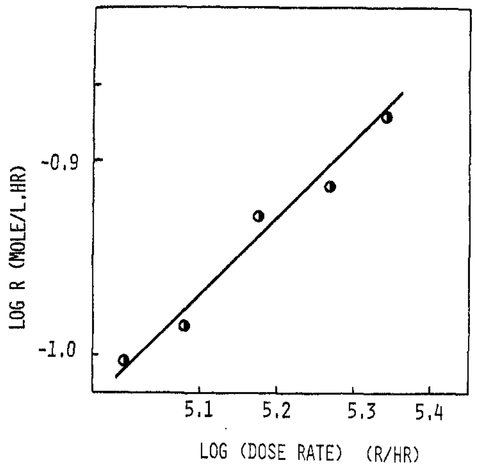

Figure 2.—Dependence of rate of methyl acetate consumption on dose rate (from 0.98 to 2.20 × 10^5 R/hr).

In our previous communications, the acetal type intermediate $RCH(OSiCl_3)OR'$ was assumed by analogy to the reaction of ketones with trichlorosilane.[1] Also acetals were found to be converted to α-chloro ethers through the reaction with trichlorosilane.[3] To confirm the structure of the intermediate, a mixture of methyl acetate and trichlorosilane (CH_3COOCH_3/Cl_3SiH, 1:4 molar ratio) in cyclohexane-d_{12} sealed in a nmr tube was irradiated with γ rays at room temperature. After the irradiation, nmr spectra indicated the presence of a methyne proton coupled with an adjacent methyl proton which was identical with the methyne proton of α-chloroethyl methyl ether (II). When the irradiation and nmr analysis were carried out at low temperatures (−20°), the resulting spectrum indicated the presence of a methyne proton which was also coupled with an adjacent methyl proton but different from that of II. It was concluded that this methyne proton was derived from acetal type intermediate I,[4] since this spectra changed into that of II[4] on standing at room temperature. From the results cited above we can write the reaction sequence as

$$CH_3COOCH_3 + Cl_3SiH \xrightarrow{\gamma} \underset{\text{I}}{CH_3CH(OSiCl_3)OCH_3}$$

$$\text{I} + Cl_3SiH \longrightarrow \underset{\text{II}}{CH_3CHClOCH_3} + HSiCl_2OSiCl_3$$

$$\text{II} + Cl_3SiH \xrightarrow{\gamma} CH_3CH_2OCH_3 + SiCl_4$$

In the presence of water, *e.g.*, by glpc process,

$$\text{II (or I)} + H_2O \longrightarrow CH_3CHO + CH_3OH + HCl \text{ (or } Cl_3SiOH)$$

Although methanol, the counterpart of acetaldehyde, has not been identified by glpc, methanol should further react with excess trichlorosilane to yield poorly characterized products. The equimolar relation between the intermediates and acetaldehyde is clear from the results in Figure 1. The sum total of acetaldehyde

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(2) R. Calas, *Pure Appl. Chem.*, **13** (1–2), 61 (1966).

(3) R. Nakao, T. Fukumoto, and J. Tsurugi, *J. Org. Chem.*, in press.

(4) Nmr spectra for $CH_3CH(OSiCl_3)OCH_3$ δ 1.45 (d, 3, J = 5 Hz, CCH_3), 5.20 (q, 1, J = 5 Hz, CH), 3.38 (s, 3, OCH_3); for $CH_3CHClOCH_3$ δ 1.70 (d, 3, J = 5 Hz, C CH_3), 5.50 (q, 1, J = 5 Hz, CH), 3.40 (s, 3, OCH_3).

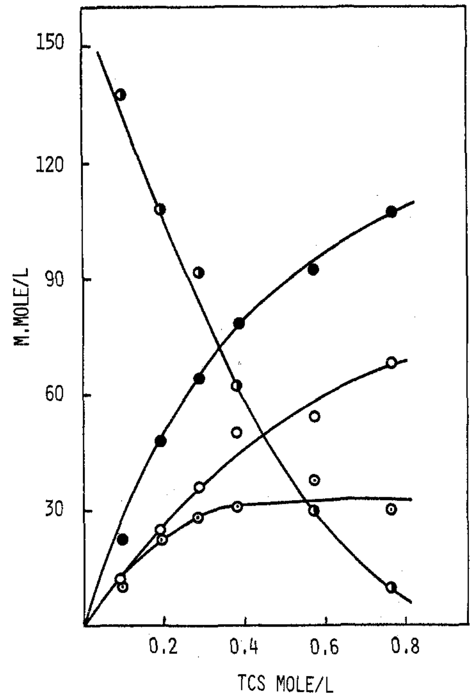

Figure 3.—Dependence on initial trichlorosilane concentration at a given dose of 3.7×10^5 *R*: $[CH_3COOCH_3]_0 = 0.156$ mol/l. in cyclohexane; ○, CH_3CHO; ⊙, $C_2H_5OCH_3$; ◑, CH_3COOCH_3; and ●, $CH_3CHO + C_2H_5OCH_3$.

and ethyl methyl ether in Figure 1 and all the figures cited hereafter corresponds to the amount of methyl acetate consumed.

Figure 2 shows a logarithmic plot of methyl acetate consumption rate $-d[CH_3COOCH_3]/dt$ *vs.* dose rate and gives

$$-d[CH_3COOCH_3]/dt = k(\text{dose rate})^{0.40}$$

The exponent value of this equation suggests that the termination process consists predominantly of recombination of the propagating species, this value (0.40) being near to 0.5.

Kinetic orders were determined (in Figures 3 and 4) by varying the concentration of the starting materials in cyclohexane under the γ irradiations at a constant dose. The rate of consumption of methyl acetate was proportional to $[Cl_3SiH]$ in a range where $[Cl_3SiH]/[CH_3COOCH_3]$ is small, and almost independent of $[CH_3COOCH_3]$.

This reaction proceeds under γ and photoirradiations. Taking into consideration the free-radical chain mechanism suggested by the observed high *G* value (400–500), and the structures of the intermediates mentioned in the present paper, we propose the following mechanism.

$$\text{initiator} \longrightarrow R\cdot \quad (1)$$

$$R\cdot + Cl_3SiH \longrightarrow RH + Cl_3Si\cdot \quad (2)$$

$$Cl_3Si\cdot + CH_3COOCH_3 \longrightarrow CH_3\dot{C}(OSiCl_3)OCH_3 \quad (3)$$

$$CH_3\dot{C}(OSiCl_3)OCH_3 + Cl_3SiH \longrightarrow I + Cl_3Si\cdot \quad (4)$$

$$I + Cl_3SiH \longrightarrow II + HSiCl_2OSiCl_3 \quad (5)$$

$$II + Cl_3Si\cdot \longrightarrow CH_3\dot{C}HOCH_3 + SiCl_4 \quad (6)$$

$$CH_3\dot{C}HOCH_3 + Cl_3SiH \longrightarrow CH_3CH_2OCH_3 + Cl_3Si\cdot \quad (7)$$

$$2CH_3\dot{C}(OSiCl_3)OCH_3 \longrightarrow \text{nonradical product(s)} \quad (8)$$

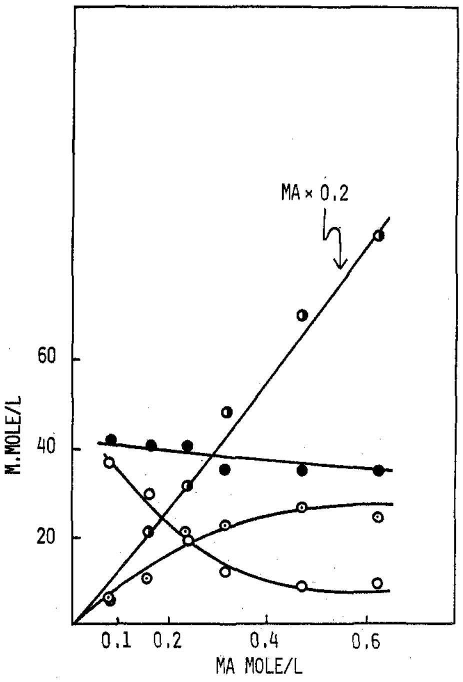

Figure 4.—Dependence of initial methyl acetate concentration: dose 3.7×10^5 *R*; $[Cl_3SiH]_0 = 0.156$ mol/l. in cyclohexane; ○, CH_3CHO; ⊙, $C_2H_5OCH_3$; ◑, CH_3COOCH_3; and ●, $CH_3CHO + C_2H_5OCH_3$.

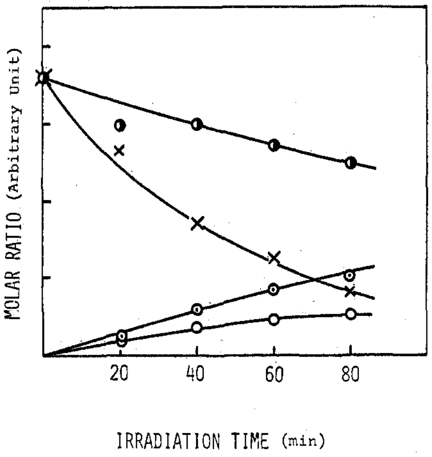

Figure 5.—Time plot of the irradiated mixture in neat reaction: ◑, CH_3COOCH_3; ⊙, $C_2H_5OCH_3$; ○, $HSiCl_2OSiCl_3$; and ×, Cl_3SiH; determined by nmr, dose rate 2.5×10^6 *R*/hr.

If we assume that the termination step (8) predominates over the other possible steps, by the standard steady-state treatment the rate of methyl acetate consumption is derived as

$$-d[CH_3COOCH_3]/dt = k_4k_8^{-1/2}I_a^{1/2}[Cl_3SiH]$$

where I_a is the rate of absorption of energy and is proportional to the dose rate. This equation is consistent with the results (Figures 2–4).

Figure 5 shows amounts of the products and the starting materials *vs.* γ-irradiation time in a neat reaction. In contrast to the reaction in cyclohexane, only a trace amount of the intermediates was formed. Figure 5 shows formation of 1 mol of ethyl methyl ether and less than 1 mol of trichlorosiloxydichlorosilane and the consumption of 1 mol of methyl acetate and 2–3 mol of trichlorosilane. Furthermore, Figure 5 indicates that the relationship $a - b = 2c$ holds, where

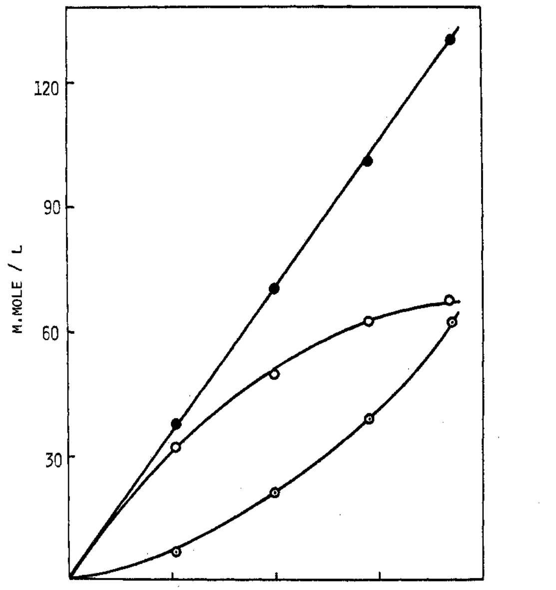

Figure 6.—Effect of the concentration of reactants in cyclohexane on the intermediate formation at a constant molar ratio of $[CH_3COOCH_3]_0/[Cl_3SiH]_0$ = 1:4; dose, 1.85 × 10^5 *R;* ○, CH_3CHO; ⊙, $C_2H_5OCH_3$; and ●, $CH_3CHO + C_2H_5OCH_3$.

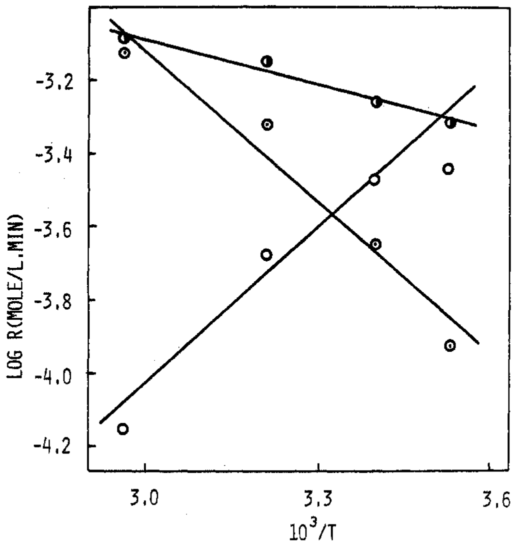

Figure 7.—Arrhenius plot of R($-CH_3COOCH_3$), ◑; R(CH_3CHO), ○; and R($C_2H_5OCH_3$), ⊙; under 3.70 × 10^5 *R;* $[CH_3COOCH_3]_0$ = 0.156 and $[Cl_3SiH]_0$ = 0.312 mol/l. in cyclohexane.

a signifies the amount of trichlorosilane consumed, *b* the amount of trichlorosiloxydichlorosilane formed, and *c* the amount of ethyl methyl ether formed. This relationship suggests that trichlorosiloxydichlorosilane produced *via* eq 5 reacts almost identically to trichlorosilane.

Figure 6 shows the effect of the concentration of the reactants at a constant molar ratio on the amount of the intermediates formed at a given γ-irradiation dose. Figure 6 indicates the tendency of an increasing amount of cyclohexane to increase the ratio of the intermediates to ethyl methyl ether. To find a reason for the intermediates[3] formation in cyclohexane, we utilized *n*-hexane and tetrahydrofuran as alternant solvents[5] and ran the reaction under the same conditions as those in Figure 1. Using *n*-hexane, we observed similar results to that of cyclohexane. However, while the use of tetrahydrofuran resulted in the same reaction rate, it gave only a small amount of acetaldehyde[6] as compared with the reaction in cyclohexane. The above results suggests that, while eq 4 and 6 are not dependent on solvent, eq 5 is. This results because the dielectric constant of tetrahydrofuran (7.4) is near that of methyl acetate (7.03) and greater than those of cyclohexane (2.02) and *n*-hexane (1.89).

Arrhenius plots of R (−methyl acetate), R (intermediate), and R (ethyl methyl ether) are shown in Figure 7, where R (X) denotes initial rate of the formation of X. From the results in Figure 7, the apparent activation energies of ethyl methyl ether formation, intermediate formation, and methyl acetate consumption are calculated as 8.2, −6.5, and 1.9 kcal/mol, respectively.

As stated above, the present reaction mechanism consists of three sequences; the first is the radical formation of acetal type intermediate I (eq 3 and 4), the second is ionic transformation of the intermediate I to II (eq 5), and the third is radical formation of ethyl methyl ether from the intermediate II (eq 6 and 7). The rate of the first radical sequence is considered much slower than the rate of the third radical sequence.[7] Therefore, the amount of acetaldehyde derived from the intermediate II and/or I depends on the rate of eq 5. Equation 5 is faster in neat reaction (as in tetrahydrofuran) than in nonpolar solvents. Hence, in neat reaction the amount of acetaldehyde derived from II and/or I becomes smaller than in nonpolar solvents. On the contrary, in nonpolar solvent the concentration of I in the reaction system becomes higher during the irradiation, and hence acetaldehyde derived from II and/or I becomes larger than in the neat reaction. For the same reason the reaction at higher temperatures favors a decreased amount of acetaldehyde because the activation energy of eq 5 is much larger than those of the other steps.

The effect of adding benzene to this reaction system is shown in Figure 8 for a mixture of methyl acetate and trichlorosilane (1:2) in cyclohexane irradiated with a fixed dose. In order to interpret the result in Figure 8, we assume that benzene acts as a scavenger

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(5) Alcohols,[5a] amines,[5b] amides,[5c] and nitriles[5d] are known to react with trichlorosilane. Ketones,[5c] aldehydes,[5e] haloalkanes,[5f] and alkenes[5g] react with trichlorosilane under free-radical conditions. Compounds containing *S*-oxide[5h] and *P*-oxide[5i] functions are easily deoxygenated. Aromatic hydrocarbons retard the present reaction as described in this paper. Therefore, solvents available are restricted only to alkanes and ethers. (a) B. Helferich and J. Hausen, *Ber.*, **57**, 795 (1924); (b) H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc.*, 705 (1967); (c) Y. Nagata, T. Dohmaru, and J. Tsurugi, *Chem. Lett.*, 989 (1972); (d) R. Calas and N. Duffaut, *C. R. Acad. Sci.*, 906 (1957); *Rev. Fse. Corps. Gras.*, **2**, 1 (1959); (e) R. Calas, E. Frainnet, and A. Bazouin, *C. R. Acad. Sci.*, **252**, 420 (1961); (f) J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *Chem. Commun.*, 157 (1966); (g) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Amer. Chem. Soc.*, **69**, 188 (1947); (h) T. H. Chan, A. Milnyk, and D. N. Harpp, *Tetrahedron Lett.*, 201 (1969); (i) L. Horner and W. D. Balzer, *ibid.*, 1157 (1965).

(6) Under the same conditions as those in Figure 1, molar ratios of (acetaldehyde)/(ethyl methyl ether) obtained from the reduction in tetrahydrofuran were 0.03 and 0.07 for 2.5- and 4-hr irradiations, respectively.

(7) In part IV of this series (ref 3) the *G* value (number of molecules formed per 100 eV energy absorbed) of the reduction of α-chloro ether to ether was reported as 5000. Compare this value with 400–500 in the present paper.

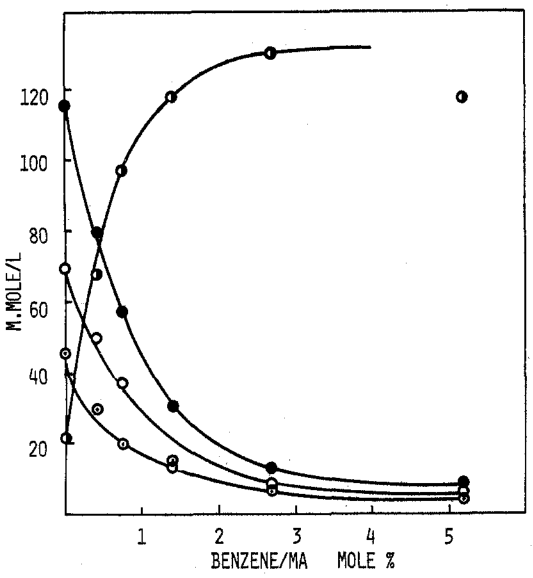


Figure 8.—Effect of benzene concentration; dose, 6.62 × 10^6 *R*; $[CH_3COOCH_3]_0$ = 0.156 mol/l; $[Cl_3SiH]_0$ = 0.312 mol/l. in cyclohexane; ○, CH_3CHO; ⊙, $C_2H_5OCH_3$; ●, CH_3CHO + $C_2H_5OCH_3$, and ◑, CH_3COOCH_3.

of trichlorosilyl radical and competes with methyl acetate for trichlorosilyl radical.

$$\text{benzene} + Cl_3Si\cdot \xrightarrow{k_b} \qquad (9)$$

$$\text{methyl acetate} + Cl_3Si\cdot \xrightarrow{k_m} \qquad (10)$$

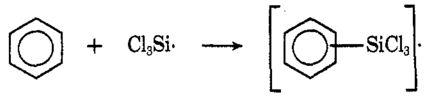
$$R = k_b[\text{benzene}][Cl_3Si\cdot] + k_m[\text{methyl acetate}][Cl_3Si\cdot] \qquad (11)$$

$$\Delta R = k_b[\text{benzene}][Cl_3Si\cdot] \qquad (12)$$

Here *R* signifies the rate of the methyl acetate consumed in the absence of benzene, and ΔR the decreased rate due to the presence of benzene. Equations 11 and 12 lead to

$$\Delta R^{-1} = R^{-1}\{1 + (k_m/k_b)[CH_3COOCH_3][\text{benzene}]\} \qquad (13)$$

Figure 9 shows a plot of ΔR^{-1} *vs.* $[CH_3COOCH_3]/[\text{benzene}]$ and satisfies eq 13 in a range of lower concentrations of benzene. The value of k_m/k_b was calculated as 7.8 × 10^{-3}. The scavenging effect of benzene can be interpreted in two ways, eq 14 and 15 or eq 16 and 17.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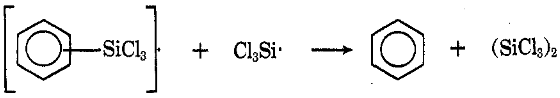
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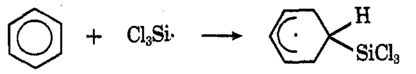
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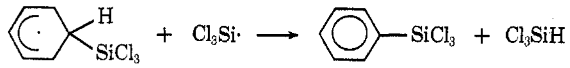
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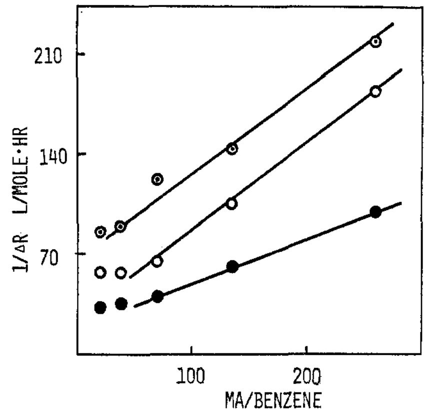

Figure 9.—Dependence of ΔR^{-1} values on CH_3COOCH_3/benzene: ○, CH_3CHO; ⊙, $C_2H_5OCH_3$; and ●, CH_3CHO + $C_2H_5OCH_3$.

The first results in the formation of hexachlorodisilane *via* the complex between benzene and trichlorosilyl radical (eq 14 and 15). The second describes the substitution of benzene with trichlorosilyl group. Which sequence is operative is not clear at the present time. The effect of adding some substituted benzenes is now under investigation at our laboratory.

Experimental Section

Trichlorosilane was treated with quinoline to remove hydrogen chloride and was distilled under atmospheric pressure. The distillate (boiling range 31.8–32.2°) was further purified by vacuum distillation. Methyl acetate was washed twice with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and distilled twice through a 50-cm fractionation column packed with glass Raschig rings. The fraction boiling at 56.0–56.5° was further distilled under vacuum from a trap at −60° to a trap at −196°. Cyclohexane, *n*-hexane, tetrahydrofuran, and benzene, all Spectrograde, were refluxed with lithium aluminum hydride and distilled under vacuum. All the materials thoroughly degassed were stored at −78°.

Sample preparations for γ and photoirradiations were performed on a vacuum line by bulb to bulb distillations, and irradiation tubes were sealed under vacuum. The pressure of each materials was measured on a mercury manometer. The γ irradiations were performed at constant temperature (22°) in a Pyrex tube (10 mm ϕ) or a nmr tube using ^{60}Co–10,000 Ci. Dose rates were determined by the standard Fricke method using $G(Fe^{3+})$ = 15.6. Irradiation was carried out at the dose rate of 1.85 × 10^5 *R*/hr unless otherwise stated.

The photochemical reactions were carried out in a 1-cm path length absorption cell using a 100-W medium-pressure mercury lamp (Toshiba SHL-100 uv). A Hitachi 063 glpc (equipped with FID using a 1-m column of Porapak-q at 200°), a JEOL JNM 3H-60 nmr spectrometer, and a Shimazu RS-27 spectrophotometer were used for analyses. Uv absorption spectra of methyl acetate (at λ 240 nm) and acetaldehyde (at λ 285 nm) contributed to the qualitative analyses.

Registry No.—I, 37676-11-2; II, 1538-87-0; trichlorosilane, 10025-78-2; methyl acetate, 79-20-9; ethyl methyl ether, 540-67-0.