

PRELIMINARY NOTE

The homolytic reduction of polychloroalkanes by triorganosilicon hydrides

Quite recently, Young and co-workers¹ have investigated the photochemical chain reaction between trichlorosilane and simple alkyl chlorides in the gas phase.

TABLE I

THE REACTION OF TRIORGANOSILANES WITH CARBON TETRACHLORIDE (80°, 10h)^a

| Run | Reactants (mmol) | | Products (mmol) ^b | | Recovered (mmol) ^b | |
|-----|-----------------------|------|--|-------|-------------------------------|------|
| 1 | Et ₃ SiH | 4.0 | Et ₃ SiCl | trace | Et ₃ SiH | 3.9 |
| | CCl ₄ | 10.0 | CHCl ₃ | trace | CCl ₄ | 9.6 |
| | BPO | none | | | | |
| 2 | Et ₃ SiH | 20.8 | Et ₃ SiCl | 15.2 | Et ₃ SiH | 5.0 |
| | CCl ₄ | 41.3 | CHCl ₃ | 15.1 | CCl ₄ | 25.3 |
| | BPO | 0.11 | | | | |
| 3 | Et ₃ SiH | 20.7 | Et ₃ SiCl | 12.8 | Et ₃ SiH | 7.9 |
| | CCl ₄ | 41.3 | CHCl ₃ | 12.5 | CCl ₄ | 27.7 |
| | BPO | 0.10 | | | | |
| 4 | PhMe ₂ SiH | 6.0 | PhMe ₂ SiCl | trace | PhMe ₂ SiH | 5.6 |
| | CCl ₄ | 12.3 | CHCl ₃ | 0.0 | CCl ₄ | 12.1 |
| | BPO | none | | | | |
| 5 | PhMe ₂ SiH | 20.1 | PhMe ₂ SiCl | 15.4 | PhMe ₂ SiH | 2.1 |
| | CCl ₄ | 40.1 | CNCl ₃ | 16.5 | CCl ₄ | 24.3 |
| | BPO | 0.12 | Ph ₂ SiMe ₂ ^c | 0.0 | | |
| 6 | PhMe ₂ SiH | 20.1 | PhMe ₂ SiCl | 13.2 | PhMe ₂ SiH | 3.7 |
| | CCl ₄ | 33.9 | CHCl ₃ | 15.5 | CCl ₄ | 17.9 |
| | BPO | 0.12 | Ph ₂ SiMe ₂ ^c | 0.0 | | |
| 7 | Ph ₂ MeSiH | 5.0 | Ph ₂ MeSiCl | 0.0 | Not determined | |
| | CCl ₄ | 9.0 | CHCl ₃ | trace | | |
| | BPO | none | | | | |
| 8 | Ph ₂ MeSiH | 20.0 | Ph ₂ MeSiCl | 13.7 | Ph ₂ MeSiH | 8.6 |
| | CCl ₄ | 40.5 | CHCl ₃ | 16.9 | CCl ₄ | 20.0 |
| | BPO | 0.11 | PhMeSiH ₂ ^c | 0.0 | | |
| 9 | Ph ₂ MeSiH | 20.2 | Ph ₂ MeSiCl | 13.9 | Ph ₂ MeSiH | 10.4 |
| | CCl ₄ | 47.3 | CHCl ₃ | 17.2 | CCl ₄ | 26.9 |
| | BPO | 0.11 | PhMeSiH ₂ ^c | 0.0 | | |
| 10 | Ph ₃ SiH | 4.9 | Ph ₂ MeSiCl | 0.0 | Not determined | |
| | CCl ₄ | 9.8 | CHCl ₃ | trace | | |
| | BPO | none | | | | |
| 11 | Ph ₃ SiH | 20.0 | Ph ₂ MeSiCl | 12.5 | Ph ₃ SiH | 6.6 |
| | CCl ₄ | 43.8 | CHCl ₃ | 13.8 | CCl ₄ | 30.0 |
| | BPO | 0.12 | Ph ₂ SiH ₂ ^c | 0.0 | | |
| 12 | Ph ₃ SiH | 20.0 | Ph ₂ MeSiCl | 8.4 | Ph ₃ SiH | 10.0 |
| | CCl ₄ | 40.9 | CHCl ₃ | 9.4 | CCl ₄ | 27.9 |
| | BPO | 0.13 | Ph ₂ SiH ₂ ^c | 0.0 | | |

^a Each of the experiments was carried out in a sealed tube which was kept in a constant temperature bath.

^b Analyses were made by means of vapor phase chromatography (Silicone Rubber, QF-1). ^c These compounds are expected products of the radical redistribution reactions.

We have found that a similar reaction occurs in the liquid phase at 80° between triorganosilanes and carbon tetrachloride in the presence of benzoyl peroxide to give the respective triorganochlorosilane and chloroform in a ratio of 1 : 1. The data listed in Table 1 were obtained by vapor phase chromatographic analysis. The results show the principal reaction to proceed through a radical chain mechanism,



where In^\cdot is a radical produced from the initiator.

Organosilyl radicals bearing aryl groups on silicon are known to undergo the homolytic aromatic displacement reaction of type (5)². In our cases, however,



such radicals produced are seen to enter into the chlorine atom abstraction exclusively, behavior which has been noted by others previously^{1,3-5}. This fact may well be explained by the considerable exothermicity of reaction (3)⁶⁻⁸.

We have next turned our attention to the relative rates of chlorine atom abstraction by triorganosilyl radicals from several aliphatic carbon-chlorine bonds. In this connection, Young and co-workers¹ recently have determined the relative reactivities of simple alkyl chlorides toward the trichlorosilyl radical. Their results indicate the importance of resonance stabilization of the incipient free alkyl radicals, thus the reactivity order being primary (C-Cl) < secondary (C-Cl) < tertiary (C-Cl).

In our present investigation, six different polychloroalkanes were allowed to compete in pairs for an insufficient amount of phenyldimethylsilane or triethylsilane at 80°, benzoyl peroxide being used as catalyst. Relative rate constants were calculated using the equation of Ingold and Shaw⁹ from concentrations of the reactants or products as determined by vapor phase chromatography. The applicability of the Ingold-Shaw equation was tested by determining relative reactivities of 1,1,1-trichloroethane and chloroform at several concentrations. The relative rates are independent of the initial concentrations of the two polychloroalkanes (Table 2), and thus chlorine atom abstraction by the organosilyl radicals is the rate-determining step.

TABLE 2

THE COMPETITIVE REDUCTION OF 1,1,1-TRICHLOROETHANE AND CHLOROFORM WITH PHENYLDIMETHYLSILANE

| <i>Init. concn.</i> CCl_3CH_3 (mmoles) | <i>Init. concn.</i> CHCl_3 (mmoles) | <i>Init. concn.</i> PhMe_2SiH (mmoles) | $k(\text{CH}_3\text{CCl}_3)/k(\text{CHCl}_3)$ |
|---|---|---|---|
| 9.73 | 3.66 | 1.16 | 1.42 |
| 14.27 | 5.00 | 1.48 | 1.33 |
| 3.13 | 5.08 | 1.14 | 1.58 |
| 9.78 | 5.13 | 1.04 | 1.36 |
| 14.30 | 5.61 | 1.46 | 1.42 |
| 7.56 | 7.01 | 1.45 | 1.57 |

Relative reactivities per chlorine atom of the trichloromethyl groups in $X-CCl_3$ toward the two triorganosilyl radicals were obtained from the competitive experiments for all of the polychloroalkanes and are listed in Table 3*. The reactivity of one of the chlorine atoms in chloroform was taken as unity.

TABLE 3

RELATIVE REACTIVITIES TOWARD TRIORGANOSILYL RADICALS OF C-Cl BONDS IN $X-CCl_3$ AT 80°C

| Substituent <i>X</i> | Relative reactivity | |
|-------------------------|------------------------|----------------------|
| | Toward $PhMe_2Si^*$ | Toward Et_3Si^* |
| Me | 1.45 ± 0.03 | 1.40 ± 0.01 |
| H | 1.00 | 1.00 |
| CH_2Cl | 4.21 ± 0.3 | 3.07 ± 0.01 |
| $CHCl_2$ | 6.16 ± 0.3 | 6.19 ± 0.2 |
| CCl_3 | 6.50 ± 0.02 | 7.18 ± 0.3 |
| Cl | 11.6 ± 0.4 | 11.4 ± 0.8 |

Results of the two sets of measurements are plotted in Fig. 1 against Taft σ^* values¹⁰ for the substituents. With the exception of chloroform, they yield satisfactory straight lines with a ρ^* value of +0.26 for the reaction of the phenyldimethylsilyl radical and with a ρ^* value of +0.29 for that of the triethylsilyl radical. The deviation for chloroform is real and the greater reactivity of 1,1,1-trichloroethane over chloroform can be rationalized in terms of resonance stabilization by hyperconjugation for the incipient radical derived from the former substance. Satisfactory Hammett-type correlations for the remaining five polychloroalkanes imply that, within this class of substrates, the polar factor is primarily important in determining the react-

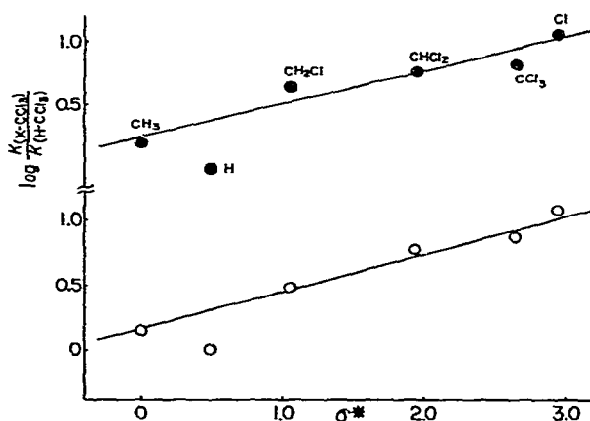


Fig. 1. Plot of the relative rate versus σ^* . Open circles represent the reaction of Et_3Si^* and solid circles the reaction of $PhMe_2Si^*$. The σ^* value for Cl was calculated from multiplying the value for CH_2Cl by 2.8.

* It was found that reactivities of the dichloromethyl and chloromethyl groups are too small to be measured conveniently under the analytical conditions employed.

ivities of the chlorine atoms. Positive signs of the ρ^* values are what should be anticipated from the electropositive character of the organosilicon free radical serving as an electron donor to the electronegative chlorine atom. This trend is in harmony with the observations of Kuivila and co-workers¹¹⁻¹³ concerning the halogen atom abstraction by organotin free radicals.

Comparison of the reaction constants for the two triorganosilyl radicals is of considerable interest, but the rather small difference in the observed ρ^* values does not permit any detailed discussion. Studies on the homolytic reductions by organosilicon hydrides are being continued.

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Received April 17th, 1967; in revised form May 16th, 1967.

J. Organometal. Chem., 9 (1967) P21-P24