degree of separation of the new isomer from the mixtures with δ-heptachlorocyclohexane and with γ-BHC. The micro crystals separated as a result of these fractionations melted at 124–125°. Insufficient pure isomer was available for recording the spectrum.

(3) **Heptachlorocyclohexane Isomers.**—Three heptachlorocyclohexane isomers have been identified in the products of chlorination of ϵ-BTC. Recrystallization from hexane of a composite of the eluate, 2600–3000 ml. (Fig. 3), yielded crystals of γ-heptachlorocyclohexane, m.p. 84.0–84.5° (cor.).[17,18] Upon alkaline dehydrochlorination, a mixture of 1,2,3,4- and 1,2,4,5-tetrachlorobenzene was formed. The same heptachlorocyclohexane, which has the structure (ea)aeeee, also was formed by the chlorination of γ-BTC (2700–3200 ml., Fig. 2).

A composite of the residues recovered from the eluate, 3600–3800 ml., from ϵ-BTC (Fig. 3) was identified as an isomer of heptachlorocyclohexane by means of alkaline dehydrohalogenation which yielded 1,2,3,4-tetrachlorobenzene chiefly, together with some 1,2,3,5- and a trace of the 1,2,4,5-isomer. Inasmuch as the melting point of a sample purified by sublimation, 101.2–101.7° (cor.), did not correspond to any reported value in the literature, the compound was presumed to be a new heptachlorocyclohexane. In a private communication, however, Prof. Riemschneider has indicated that it is probably identical with η-heptachlorocyclohexane, (ea)aeeae, which he stated to have a melting point of 101°, although no value was cited in his paper.[18]

The heptachlorocyclohexane (4600–5300 ml., Fig. 3) which preceded θ-BHC in the chromatography of the chlorination product of ϵ-BTC and interfered with the purification of the latter melted at 142–143°. *Anal.* Calcd. for $C_6H_5Cl_7$: Cl, 76.08. Found: Cl, 75.98. Comparison of the spectrum of the heptachlorocyclohexane with that of an authentic sample of δ-heptachlorocyclohexane, m.p. 139.6–140.2°,[19] indicated them to be the same isomer. Its structure has been established as (ea)eeaae.[18,20]

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[17] T. Oiwa, R. Yamada, H. Araki and M. Ohno, *Botyu-Kagaku*, **13**, 23 (1949); G. Scheuing and C. Vogelbach, *Naturwissenshaften*, **37**, 211 (1950); M. L. Coutier, *Compt. rend.*, **232**, 532 (1951).

[18] R. Riemschneider, H. Karl and R. Bös, *Ann.*, **580**, 191 (1953).

[19] We are indebted to Dr. J. T. Clarke for the reference spectrum of pure δ-heptachlorocyclohexane which had been separated chromatographically from the chlorination product of δ-BHC.

[20] M. Nakazima, T. Okubo and Y. Katumura, *Botyu-Kagaku*, **15**, 97 (1950).

DETROIT 20, MICHIGAN

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Effect of Adjacent Silicon in Displacement Reactions: Kinetics of the Reaction of Chloromethylsilicon Compounds with Iodide Ion[1]

BY GLENN D. COOPER AND MAURICE PROBER

RECEIVED FEBRUARY 27, 1954

Second-order rate constants and heats and entropies of activation for the reaction of chloromethyltrimethylsilane, chloromethylpentamethyldisiloxane, chloromethylheptamethylcyclotetrasiloxane and *n*-butyl chloride with potassium iodide in acetone have been determined. Chloromethyltrimethylsilane reacts twenty-five times as fast as *n*-butyl chloride at 20°. The activating effect of silicon is due to a lowering (by about 4 kcal.) of the heat of activation; the entropy of activation is less favorable by about 6 e.u. The rate of reaction decreases with increasing oxygen substitution on silicon.

Introduction

The extraordinary inertness of α-halosilanes toward electrophilic reagents is well established.[2] The situation with regard to attack by nucleophilic reagents is somewhat less clear. Whitmore and Sommer[2a] reported that chloromethyltrimethylsilane reacts much more rapidly with potassium iodide in acetone than does neopentyl chloride; this was attributed to a much smaller steric effect in the silicon compound, due to the larger silicon atom. It was also found that chloromethyltrimethylsilane was slightly less reactive than *n*-hexyl chloride toward sodium ethoxide in absolute ethanol, potassium hydroxide in aqueous ethanol, potassium acetate in acetic acid and potassium iodide in acetone.

The effect of oxygen bonded to silicon on the reactivity of chloromethylsilicon compounds has also been studied.[2b,3,4] Roedel[3] found that chloromethylpentamethyldisiloxane reacted slightly faster than chloromethyltrimethylsilane with sodium ethoxide in ethanol and potassium hydroxide in *n*-butyl alcohol, and much faster with potassium acetate in glacial acetic acid.

No kinetic investigation of S_N2 reactions of α-halosilanes has been reported. It appeared, therefore, that such an investigation should yield useful information concerning the effect of α-silicon. Since strongly basic reagents are known to cause silicon–carbon cleavage of α-halosilanes,[5,6] the system chosen was potassium iodide in anhydrous acetone, which is known to bring about replacement of chlorine by iodine without silicon–carbon cleavage or siloxane rearrangement.[2a,3,7]

Experimental

The chloro compounds were prepared by chlorination of the corresponding silicon compounds. The compounds were carefully fractionated just prior to use and a center cut was taken for these experiments. Acetone and potassium iodide were purified by the method of Conant and Kirner.[8]

Approximately 0.01 mole of the organic chloride was weighed into a flask which was immersed in a constant-temperature bath. Fifty milliliters of 0.03 M potassium iodide in acetone (previously brought to reaction temperature) was added by means of a pipet and a 5-ml. sample was immediately withdrawn and titrated for iodide ion by the procedure of Conant and Kirner. Five-milliliter samples

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[1] Presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March 25, 1954.

[2] (a) F. C. Whitmore and L. H. Sommer, THIS JOURNAL, **68**, 481 (1946); (b) L. H. Sommer, D. L. Bailey, W. A. Strong and F. C. Whitmore, *ibid.*, **68**, 1881 (1946); (c) F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 485 (1946).

[3] G. F. Roedel, *ibid.*, **71**, 269 (1949).

[4] J. L. Speier, B. F. Daubert and R. R. McGregor, *ibid.*, **71**, 1474 (1949).

[5] R. H. Krieble and J. R. Elliott, *ibid.*, **68**, 2291 (1946).

[6] J. L. Speier, *ibid.*, **70**, 4142 (1948).

[7] Personal communication from S. W. Kantor and A. R. Gilbert of this Laboratory.

[8] J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924).

were withdrawn and analyzed at appropriate intervals. No iodine was produced in any of the reactions except with chloromethylpentamethyldisiloxane, which showed a faint iodine coloration. The reactions were followed to 60–80% of completion, except for *n*-butyl chloride at 20°, which was very slow, and which was followed only to 30% completion. The rate constants reported are the average of two determinations. The average deviation of values of *k* observed in a single run was less than 3%; the averages agreed within 2%. Values obtained in a typical run are shown in Table I.

TABLE I

REACTION OF CHLOROMETHYLPENTAMETHYLDISILOXANE WITH POTASSIUM IODIDE IN ACETONE AT 20°

Time, hr.	% reacted	k, l. mole^{-1} hr.$^{-1}$
18.5	12.2	0.0363
46.3	28.5	.0387
68.3	38.6	.0387
93.8	48.2	.0383
119.0	56.5	.0387
159.9	66.1	.0381
183.7	71.0	.0384
	Average	0.0382

Results and Discussion

Second-order rate constants for the reaction of potassium iodide with chloromethyltrimethylsilane, chloromethylpentamethyldisiloxane, chloromethylheptamethylcyclotetrasiloxane and *n*-butyl chloride at 20, 30 and 40° are listed in Table II. Heats and entropies of activation are given in Table III.

TABLE II

RATES OF REACTION OF CHLORIDES WITH POTASSIUM IODIDE IN ACETONE

Chloride	Temp., °C. (±0.05°)	k (l. mole^{-1} hr.$^{-1}$)^a
$CH_3CH_2CH_2CH_2Cl$	20	0.00304
	30	.0123
	40	.0467
$(CH_3)_3SiCH_2Cl$	20	.0801
	30	.268
	40	.815
$(CH_3)_3SiOSi(CH_3)_2CH_2Cl$	20	.0377
	30	.126
	40	.385
$O[Si(CH_3)_2O]_3Si(CH_3)CH_2Cl$	20	.0211
	30	.0708
	40	.223

^{a} Average of two determinations at each temperature.

TABLE III

ENERGIES AND ENTROPIES OF ACTIVATION FOR THE REACTION OF CHLORIDES WITH POTASSIUM IODIDE IN ACETONE

Chloride	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$CH_3CH_2CH_2CH_2Cl$	24.9 ± 0.4	-1.4 ± 1.0
$(CH_3)_3SiCH_2Cl$	21.1	-7.7
$(CH_3)_3SiOSi(CH_3)_2CH_2Cl$	21.2	-9.1
$O[Si(CH_3)_2O]_3Si(CH_3)CH_2Cl$	21.5	-9.2

It is apparent that the silicon atom strongly activates the adjacent carbon in this reaction; chloromethyltrimethylsilane reacts 20–30 times faster with potassium iodide than does *n*-butyl chloride. The entropy of activation is less favorable by 6.3 e.u. for chloromethyltrimethylsilane; possibly this indicates a considerable amount of steric hindrance by the trimethylsilyl group, as an examination of the models leads one to expect. However, the 3.9 kcal. lower activation energy for chloromethyltrimethylsilane more than compensates for its lower entropy of activation.

The displacement of chloride ion from a saturated carbon atom by iodide ion, in the absence of important steric effects, is usually favored by electron-withdrawing groups.[9] In any case the fact that the trimethylsilyl group, like the vinyl group, can function either as an electron donor or an electron acceptor, depending on the requirements of the system,[10] furnishes a satisfactory explanation for the activating effect of silicon.[11]

These results seem to contradict the report by Whitmore and Sommer[2a] that chloromethyltrimethylsilane is less active than *n*-hexyl chloride toward ethoxide ion in ethanol, acetate ion in acetic acid, and iodide ion in acetone. It appears likely that the lower activity of chloromethyltrimethylsilane toward ethoxide ion and acetate ion is due to greater steric requirements of these highly solvated ions, but the statement that *n*-hexyl chloride is more active toward iodide ion in acetone than chloromethyltrimethylsilane appears to be in error, since *n*-hexyl chloride is only very slightly more active than *n*-butyl chloride.[12]

The replacement of methyl groups attached to silicon by oxygen causes a slight decrease in the rate of reaction (approximately 50% for each methyl group replaced; see Table I). This is in contrast to previous reports that chloromethylpentamethyldisiloxane reacts to produce chloride ion slightly faster with sodium ethoxide in absolute ethanol and potassium hydroxide in moist butanol than does chloromethyltrimethylsilane, and much faster with potassium acetate in glacial acetic acid. With strong bases such as ethoxide ion, however, considerable cleavage of chloromethyl groups occurs, particularly with the siloxane.[3] Since the methyl chloride thus formed reacts rapidly to give chloride ion, the rate of the displacement reaction on the α-carbon cannot be determined by measurement of chloride ion.

It is probable that the much greater activity of chloromethylpentamethyldisiloxane toward potassium acetate in acetic acid is due to a different mechanism of reaction. Extensive siloxane rearrangement occurs under these conditions; hexamethyldisiloxane, acetoxymethylpentamethyldisiloxane and 1,3-bis-(acetoxymethyl)-tetramethyldisiloxane are isolated in the statistical proportion.[4]

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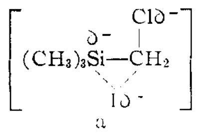
[9] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935); G. Baddely and G. M. Bennett, *ibid.*, 1819 (1935); F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951).

[10] R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953); H. Soffer and T. DeVries, *ibid.*, **73**, 5817 (1951).

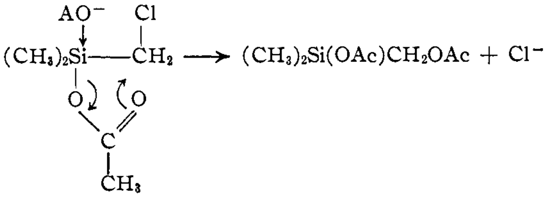
[11] It has been suggested (P. D. Bartlett in Gilman's "Organic Chemistry," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 35) that the reactivity of α-haloketones in displacement reactions is due to participation of the carbonyl carbon in the transition state. Since silicon is known to be able to expand its valence shell, it is possible that a similar process accounts for the reactivity of the α-halosilanes; the transition state for the reaction with iodide ion would be (a).



a

[12] J. B. Conant and R. E. Hussey, THIS JOURNAL, **47**, 476 (1925).

Acetoxysilanes are almost certainly intermediates in this rearrangement.[13] The acetoxysilane could then react intramolecularly with acetic acid or acetate ion to displace chloride ion



Acknowledgment.—We wish to thank Dr. J. R. Ladd for the preparation of the chloro compounds.

SCHENECTADY, N. Y.

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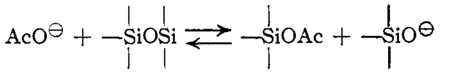
(13) Decamethyltetrasiloxane rearranges when heated with glacial acetic acid. The rearrangement proceeds much more rapidly in a 1 *M* solution of potassium acetate in acetic acid, presumably due to cleavage of silicon–oxygen bonds by acetate ion



$$\mathrm{AcO^{\ominus}} + {-}\underset{|}{\overset{|}{\mathrm{Si}}}\mathrm{O}\underset{|}{\overset{|}{\mathrm{Si}}} \rightleftarrows {-}\underset{|}{\overset{|}{\mathrm{Si}}}\mathrm{OAc} + {-}\underset{|}{\overset{|}{\mathrm{Si}}}\mathrm{O^{\ominus}}$$

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

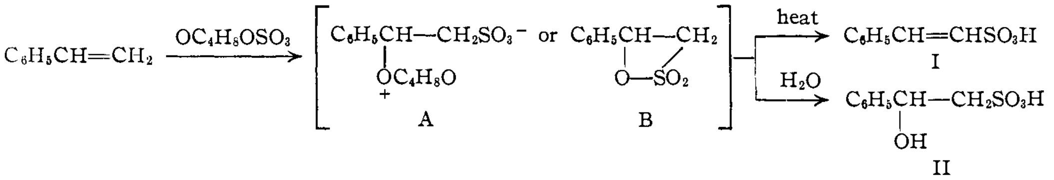
Sulfonation of Olefins. III. Nature and Reactions of the Intermediate from Styrene

BY F. G. BORDWELL, MARVIN L. PETERSON[1] AND CHRISTIAN S. RONDESTVEDT, JR.[2]

RECEIVED SEPTEMBER 8, 1953

An unstable intermediate β-sultone (B) has been isolated by addition of pentane to the sulfonation solution prepared from styrene and an equimolar quantity of dioxane–sulfur trioxide complex in ethylene chloride. The reactions of the sulfonation solution with water, methanol, ethanethiol, aniline and pyridine have been formulated in terms of B as an intermediate. The product from the reaction of B with pyridine was a dipolar ion $C_6H_5CH(^+NC_5H_5)CH_2SO_3^-$ (VI). The pyridine group in VI was not displaced by reactions with thiourea or iodide ion, but was eliminated to give $C_6H_5CH{=}CHSO_3^-$ by the action of hydroxide ion. A dimer of B was obtained in small amounts when the sulfonation was run at a temperature of 40° instead of 0°; this dimer underwent reactions similar to those of B.

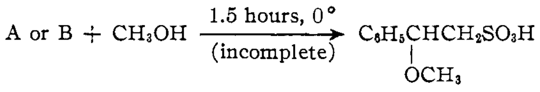
In the last paper in this series[3] the nature of the products from the reaction of styrene with the dioxane–sulfur trioxide addition complex[4] at 0° was shown to depend on the treatment of the resulting sulfonation solution. For example, heating the sulfonation solution prior to addition of water gave 2-phenylethenesulfonic acid (I) as the principal product, whereas direct hydrolysis gave chiefly 2-hydroxy-2-phenylethanesulfonic acid (II). These and other reactions of the sulfonation solution were rationalized[3] in terms of the presence of a dioxane-solvated-carbonium sulfonate (A). The results could also be explained on the basis of a β-sultone intermediate (B), but this was looked on with less favor.[5]



The rate of formation of the intermediate (A or B) has now been approximated by determining the amount of sulfate ion formed on hydrolysis after varied time intervals in a reaction of a 0.3 *M* solution of the dioxane–sulfur trioxide reagent with styrene in ethylene chloride at 0°. Under these conditions the reaction was 60% complete within one minute.

According to the representation formerly given,[3] A or B should be susceptible to attack by nucleophilic reagents other than water. This view has now been confirmed by observing similar reactions with methanol, aniline, ethanethiol and pyridine.

Reaction of the sulfonation solution with excess methanol for 1.5 hours at 0° gave, *on pouring into water*, approximately 30% of I, 25% of II and 45% of 2-methoxy-2-phenylethanesulfonic acid (III). The structure of III was established by synthesis of the sodium salt from 2-methoxy-2-phenyl-1-iodoethane and sodium sulfite, identity being established by comparison of the S-(*p*-chlorobenzyl)-thiuronium salts. The structure was further substantiated by hydrolysis of the pyridine salt of III to a salt of II in the presence of hot dilute acid. The 26% of II obtained in the original experiment was not derived, however, by hydrolysis of III, since no hydrolysis occurred in a model experiment using the pyridine salt of III under comparable conditions (at 20°). Instead, II must be formed from a portion of the sulfonation intermediate which did not react with methanol in the 1.5-hour period. In support of this conclusion, a sulfonation solution, which had stood with excess methanol at 0° for 15 days failed to yield II on addition of water.



$$\text{A or B} + CH_3OH \xrightarrow[\text{(incomplete)}]{\text{1.5 hours, 0°}} C_6H_5\underset{\substack{|\\ OCH_3}}{CH}CH_2SO_3H$$

III

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[1] Procter and Gamble Predoctoral Fellow, 1948–1951.

[2] National Research Council Predoctoral Fellow, 1946–1947.

[3] F. G. Bordwell and C. S. Rondestvedt, Jr., THIS JOURNAL, **70**, 2429 (1948).

[4] C. M. Suter, P. B. Evans and J. M. Kiefer, *ibid.*, **60**, 538 (1938).

[5] See also, F. G. Bordwell, C. M. Suter and A. J. Webber, *ibid.*, **67**, 827 (1945). The part of the argument against a β-sultam in this instance which was based on the reported stability of a β-sultone is invalid, since the compound referred to was later shown to have a different structure, see W. Autenrieth and P. Rudolph, *Ber.*, **34**, 3467 (1901).