clohexyl radicals before they react with oxygen, and (4) the utilization of oxygen to oxidize trivalent phosphorus and regenerate chlorine atoms. By suitable adjustment of concentration of oxygen and phosphorus trichloride, the reaction has been diverted so that 68% of the cyclohexane reacting was converted to cyclohexyl esters (section 3). Graf[4] reported the formation of substantial proportions of EtOPOCl$_2$ as well as of EtPOCl$_2$ from the liquid phase reaction of ethane, phosphorus trichloride, and oxygen under superatmospheric pressure at 0 to 40°, but not at atmospheric pressure at −75°. He ascribed the increasing yields of ester with increasing temperatures to the effect of temperature. However, the higher reaction temperatures were maintained by faster supplies of oxygen, and it now seems that he was observing an effect of oxygen concentration rather than of temperature.

The limiting conversion of phosphorus trichloride to cyclohexylphosphonyl chloride is about 36% over a wide range of feed ratios which contain excess cyclohexane. Here, reaction 2 is largely eliminated and the limit is apparently set by reaction 7.

Competition between reactions 6 and 7 now accounts for several puzzling results in the literature on the chlorophosphonation of hydrocarbons. When the alkyl group has considerable resonance stabilization, then the alkyl group is lost more easily than the chlorine atom and reaction 7 predominates. Thus the alkyl group acts as a catalyst for the oxidation of phosphorus trichloride and conceivably may react several times through the sequence 4, 5, 7, with little net change. When the alkyl group has little resonance stabilization, then the chlorine atom is released and reaction 6 pre-

dominates. Jensen and Noller[2c] report that toluene gave only 13% yield of benzylphosphonyl chloride; that ethylbenzene gave 11% of β-phenethylphosphonyl chloride and none of the α-isomer; that diphenylmethane gave only 2% of substitution product, and that triphenylmethane did not react. Lesfauries and Rumpf[24] report that tetralin reacts to give only one product, apparently the β-phosphonyl chloride. All of these results suggest that benzyl radicals undergo reaction 7 readily and that secondary and tertiary benzyl radicals undergo reaction 7 exclusively, while β-tetralyl and β-phenethyl radicals favor reaction 6.

Those radical properties which favor reaction 7 should also favor reaction 14. Indeed, if benzyl radicals are relatively more reactive than alkyl radicals toward oxygen (section 4.8), then reaction 14 rather than reaction 7 may account for the low yields of benzylphosphonyl chlorides.

The present work suggests that phosphorus trichloride, and perhaps many other trivalent phosphorus compounds, may be excellent scavengers for free radicals, as good as oxygen or iodine, but that to take advantage of this reaction, a scavenger for RPX$_3$ radicals is necessary.

(24) P. Lesfauries and P. Rumpf, *Bull. soc. chim.*, 542 (1950).

[CONTRIBUTION FROM THE RESEARCH CENTER OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

Displacement Reactions on Silicon. The Reaction of 2-Propanol with Chlorotriphenylsilane in Carbon Tetrachloride

BY RAYMOND C. PETERSEN AND SIDNEY D. ROSS

The rates of reaction of 2-propanol with chlorotriphenylsilane have been measured in carbon tetrachloride at 24.8° with and without added benzyltriethylammonium chloride. The observations indicate that in the absence of the salt the reaction proceeds only through autocatalysis by associated HCl. This is further interpreted to support the concept of a pentavalent silicon intermediate. Apparent catalysis observed with the added salt is attributed to uncatalyzed attack by associated benzyltriethylammonium isopropoxide.

A number of basic questions with respect to the mechanism of nucleophilic displacements on organosilicon halides are still incompletely resolved. One of the questions is whether these reactions involve an intermediate with pentacovalent silicon or proceed by an S$_N$2 mechanism with synchronous bond-making and bond-breaking. Another pertains to the kinds of catalysis that operate in these reactions.

Swain, Esteve, and Jones[1] studied the hydrolysis of triphenylsilyl fluoride in 50% aqueous acetone and proposed that an intermediate was involved. The pertinent considerations were that the fluoride reacts with hydroxide ion 10^6 times as fast as with water, that the reaction with water was retarded by p-methyl substituents but accelerated by both neutral salts and increasing polarity of medium, and that triphenylsilyl chloride is much more reactive than the fluoride. Hughes, however, suggested[2] that these observations are equally consistent with a modified S$_N$2 mechanism in which bond-making influences are dominant.

This latter position was supported by Allen, et al.,[3,4] after a detailed kinetic study of the reactions of several trisubstituted silyl chlorides with alcohols and water in a variety of solvents. The reactions were facilitated by increasing polarity of the medium, and in some, but not all, cases a high order with respect to the hydroxylic reagent was observed. When the concentration of the hydroxylic reagent was low, both autocatalysis and strong catalysis by added chloride salts were noted.

The aforementioned studies included measurements of the rates of hydrolysis of chlorotriphenylsilane in both nitromethane and dioxane at 25.1°. These determinations were complicated by the high reactivity of the substrate, the occurrence of autocatalysis, and a significant reverse reaction. The combination of these factors necessitated the measurement of initial rates by extrapolation to zero time.

Such extrapolations can introduce major uncertainties, particularly in cases where the instantaneous

(1) C. G. Swain, R. M. Esteve, Jr., and R. H. Jones, *J. Am. Chem. Soc.*, **71**, 965 (1949).
(2) E. D. Hughes, *Quart. Rev.* (London), **5**, 245 (1951).

(3) A. D. Allen, J. C. Charlton, C. Eaborn, and G. Modena, *J. Chem. Soc.*, 3668 (1957).
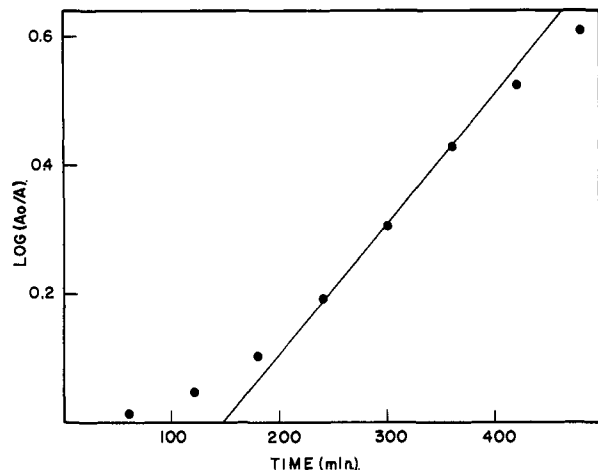(4) A. D. Allen and G. Modena, *ibid.*, 3671 (1957).

Fig. 1.—Pseudo-first-order plot for the 2-propanolysis of chlorotriphenylsilane in CCl_4 at 24.8°; initial concentrations: $(C_6H_5)_3SiCl$, 0.03420 M; i-PrOH, 0.5164 M; HCl, 0.0011 M.

rate constants are changing rapidly owing to autocatalysis.

It is our present purpose to report the results of measurements of the rate of reaction of chlorotriphenylsilane with 2-propanol in carbon tetrachloride at 24.8 ± 0.1°. In this system it was possible to analyze the rate data without resorting to extrapolations to zero time in spite of the fact that autocatalysis is still very important. We have also investigated the effect of added benzyltriethylammonium chloride on the rate of this reaction.

Experimental

Rate Measurements.—Separate determinate solutions of the reactants in CCl_4 at 24.8° were mixed at zero time and placed in a constant-temperature bath maintained at 24.8 ± 0.1°. Aliquots (10 ml.) were removed at appropriate times, added to 50 ml. of benzene, extracted once with 25 ml. of 1:4 nitric acid and twice with 25-ml. portions of distilled water. Chloride in the aqueous extract was determined by Volhard titration.

Chlorotriphenylsilane.—Purified grade chlorotriphenylsilane from the Dow Corning Corp. was crystallized repeatedly from hexane and dried *in vacuo*; m.p. 96°.

Anal. Calcd. for $C_{18}H_{15}ClSi$: Cl, 12.03. Found: Cl, 12.03, 11.86.

2-Propanol.—Baker and Adamson A.C.S. reagent grade 2-propanol was distilled from calcium hydride and a middle fraction was used; b.p. 81° (747 mm.).

Carbon Tetrachloride.—A.C.S. reagent grade CCl_4 was used without further purification.

Benzyltriethylammonium chloride was prepared by refluxing benzyl chloride and triethylamine (10% excess) in acetone for 3 hr. The crude product, obtained by adding ether to the cooled reaction mixture, was crystallized from 2-propanol–ether, then from ethanol–ether and was finally dried 8 hr. *in vacuo* at 100°; m.p. 185° dec.

Anal. Calcd. for $C_{13}H_{22}ClN$: Cl, 15.57. Found: Cl, 15.37.

Triphenylisopropoxysilane.—Chlorotriphenylsilane (1 g.) in 2-propanol (10 ml.) and carbon tetrachloride (90 ml.) was left standing for 240 hr. at room temperature. Benzene (250 ml.) was added and the mixture was extracted with two 200-ml. portions of water. The benzene solution was dried over magnesium sulfate. The benzene was removed and the crude product was crystallized from hexane; yield 0.9 g. (83%), m.p. 86–89°; after recrystallization from 2-propanol, m.p. 87–89°.

Anal. Calcd. for $C_{21}H_{22}OSi$: C, 79.19; H, 6.96; Si, 8.82. Found: C, 79.37; H, 6.07; Si, 9.01.

Conductivity Measurements.—Electrolytic conductances of HCl and benzyltriethylammonium chloride in CCl_4, 0.517 M in 2-propanol, were measured with the aid of a Keithley 610A electrometer. Benzyltriethylammonium chloride, 0.92 × 10^{-2} M, gave ρ = 0.16 × 10^{10} ohm-cm. (equivalent conductance Λ = 6.8 × 10^{-5} mho), while 1.4 × 10^{-2} M HCl gave ρ = 5.7 × 10^{10} ohm-cm. (Λ = 0.13 × 10^{-5} mho).

Results and Discussion

Figure 1 shows a typical pseudo-first-order plot for the rate of the reaction of $(C_6H_5)_3SiCl$ with 2-propanol
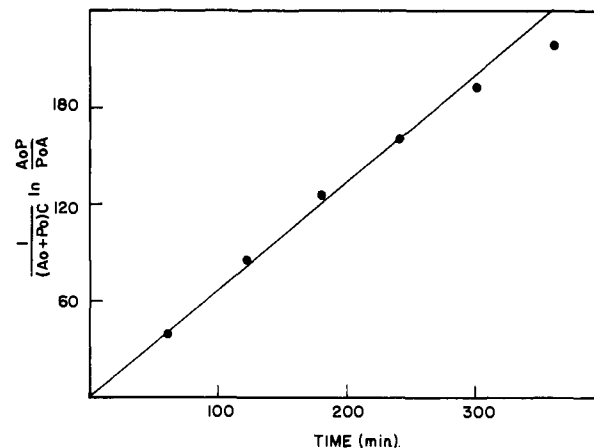

Fig. 2.—Plot of eq. 2 for the HCl-catalyzed 2-propanolysis of chlorotriphenylsilane in CCl_4 at 24.8°; initial concentrations: $(C_6H_5)_3SiCl$, 0.03420 M; i-PrOH, 0.5164 M; HCl, 0.0011 M.

(i-PrOH). One sees immediately an apparent induction period for the reaction and a slowing at later times. The slowing is presumably due to the reverse reaction, as was mentioned earlier.[4] The rate of the reverse reaction is almost certainly dependent on the product of the concentrations of at least two species, both of which start at or near zero and increase with time. In such a situation, involving at least a square term, the transition from negligible to substantial magnitude for the reverse reaction can be fairly sharp, and in fact we have been able to fit the rate data to about 50% reaction while ignoring the reverse reaction. By contrast, Allen and Modena[4] had found it necessary to use only extrapolated zero-time rates in their analysis of the hydrolysis of $(C_6H_5)_3SiCl$ in dioxane.

The induction period clearly indicates autocatalysis, and the shape of the curve further suggests that there is little or perhaps no reaction in the absence of product. Experiments were performed in which $(C_6H_5)_3SiOCH(CH_3)_2$, a major product of the reaction, and $(C_6H_5)_3SiOH$, a possible impurity product, were added to the reaction mixture. In the former case there was no change in rate while in the latter there appeared a small decrease in the apparent rate of the reaction. Catalysis was thus attributed to the other product, HCl, either as H^+, Cl^-, or associated HCl.

Attempts to fit the data were successful only with the rate equation

$$dP/dt = k_1 CAP \qquad (1)$$

where C = [i-PrOH], A = [$(C_6H_5)_3SiCl$], and P is total HCl concentration.

The reaction is initiated by a small amount of impurity HCl which is present (shown by analysis) in the starting solution of $(C_6H_5)_3SiCl$. Equation 1 was integrated, treating C as a constant since i-PrOH is present in large excess, with the result

$$\ln (A_0 P/P_0 A) = k_1 (A_0 + P_0) Ct \qquad (2)$$

where zero subscripts refer to zero time and A = (A_0 + P_0 − P). This equation has been satisfactorily fitted to runs containing various initial concentrations of HCl (small amounts added in some runs) and varying concentrations of i-PrOH. Figure 2 shows a plot of eq. 2 using the same run as was illustrated in Fig. 1; note again that at long times the reaction seems to slow, due again to the reverse reaction.

Table I lists the rate constants for several runs, these having been computed from plots of eq. 2 (Fig. 2) ignoring points above 45% reaction. The average value of k_1 is 0.641 $l.^3$ $mole^{-3}$ $min.^{-1}$. The maximum deviation is 5.6% and the average deviation is 3.0%.
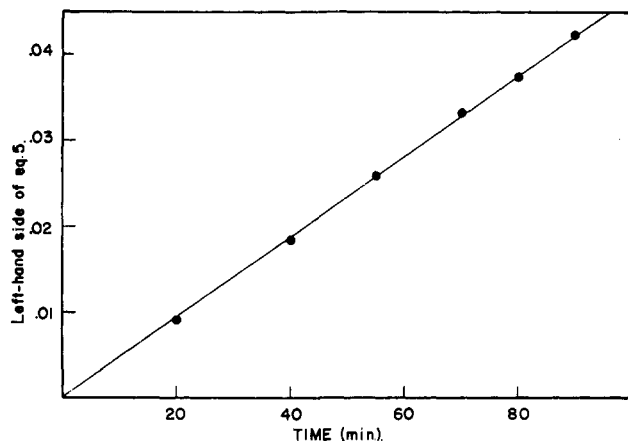
Fig. 3.—Plot of eq. 5 for the 2-propanolysis of chlorotriphenyl-silane in the presence of benzyltriethylammonium chloride in CCl_4 at 24.8°; initial concentrations: $(C_6H_5)_3SiCl$, 0.03383 M; i-PrOH, 0.5174 M; HCl, 0.0008 M; $(C_6H_5CH_2)(CH_3CH_2)_3NCl$, 0.00238 M.

Equations 1 and 2 are consistent with catalysis by molecular HCl or by the ion pair $(H^+ Cl^-)$. We shall not distinguish between these associated species. A kinetically equivalent alternative, concerted catalysis by both H^+ and Cl^-, is unreasonable in such a non-polar solvent as CCl_4.

TABLE I

REACTION RATES FOR THE HCl-CATALYZED 2-PROPANOLYSIS OF CHLOROTRIPHENYLSILANE IN CCl_4 AT 24.8 ± 0.1°

Concentrations, mole/l.			k_1, l.^{3}
$[(C_6H_5)_3SiCl]$	$[i$-PrOH]	[HCl]	mole^{-3} min.$^{-1}$
0.03430	0.5163	0.0092	0.677
.03427	.5184	.0060	.635
.03369	.5174	.0029	.624
.03349	.5146	.0011	.656
.03371	.5160	.0011	.613
.03420	.5164	.0011	.665
.03412	.2585	.0011	.623
.03420	1.0302	.0008	.631

Catalysis by individual free ions H^+ or Cl^- would involve $\sqrt{P}$ in place of P in eq. 1 since the extremely low conductance of the solution indicates that HCl is only very slightly dissociated in CCl_4. Attempts to fit the data to such an equation are successful for individual runs, but the resulting rate constants vary widely with changing initial concentrations of either HCl or i-PrOH.

An attempt was then made to fit the data to an equation of the form

$$dP/dt = k_1CAP + k_2CA\sqrt{P} \qquad (3)$$

Equation 3 contains contributions from catalysis by both associated HCl and the free ions. The ratio k_2/k_1 was varied in an effort to improve the fit provided by eq. 1 and 2, but the best fit was obtained with k_2 (and k_2/k_1) = 0. A fit was also attempted including a term for the uncatalyzed reaction, but again the fit provided by eq. 2 could not be improved.

The forward reaction of $(C_6H_5)_3SiCl$ with i-PrOH is thus adequately characterized by eq. 2 and we have no basis for suggesting any reaction at all in the absence of HCl catalysis and no evidence for catalysis by free H^+ or Cl^- ions. The apparent first-order dependence on i-PrOH concentration, shown by runs at three concentrations having the same k_1 (Table I), may also be contrasted to Allen and Modena's uncertainty in the order in water for the hydrolysis of $(C_6H_5)_3SiCl$ in dioxane.
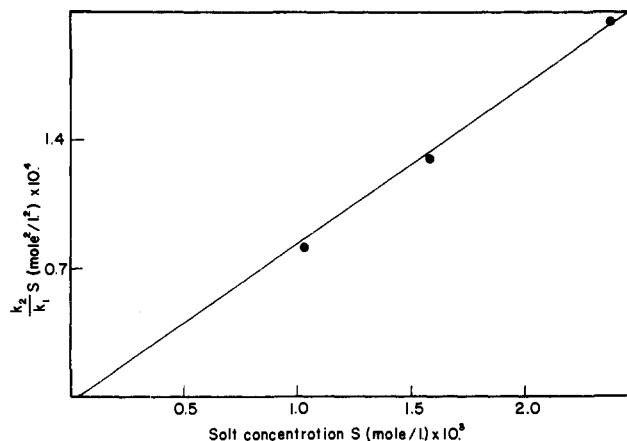

Fig. 4.—Plot of k_2S/k_1 (eq. 4 and 5) vs. salt concentration, S, for three runs; concentrations, from left to right: A_0, 0.03392, 0.03424, 0.03383; C, 0.5178, 0.5170, 0.5174; P_0, 0.00055, 0.0008, 0.0008; S, 0.00103, 0.00158, 0.00238.

Since Allen and Modena had claimed chloride ion catalysis for their reaction, a series of three experiments was performed with added benzyltriethylammonium chloride. Again conductance measurements indicate that this is almost entirely associated in CCl_4 although it apparently provides a much higher proportion of ions than does HCl.

With the added salt the rate data were found to fit the equation

$$dP/dt = k_1CAP + k_2CAS/P \qquad (4)$$

where S = salt concentration. Equation 4 is integrated to give

$$(A_0 + P_0)\ln\frac{A_0}{A} + \frac{A_0 + P_0}{2}\ln\frac{P^2 + \alpha S}{P_0^2 + \alpha S} =$$

$$\sqrt{\alpha S}\tan^{-1}\frac{\sqrt{\alpha S}\,(P - P_0)}{\alpha S + P_0P} = [(A_0 + P_0)^2 + \alpha S]k_1Ct \quad (5)$$

where $\alpha = k_2/k_1$. Using this equation, α can be evaluated for each run as a function of k_1, and knowing the correct value of k_1 from experiments without added salt the correct values of α can be obtained. Figure 3 is a plot of the left-hand side of eq. 5 vs. t for one run with the line drawn to have the slope indicated by the equation with $k_1 = 0.641$ l.^{3} mole^{-3} min.$^{-1}$ and with α having the same value as was used in computing the values of the left-hand side. The points shown in Fig. 3 go to 63% reaction and deviations due to the reverse reaction set in at later times for which points are not shown.

Figure 4 is a plot of the values of $\alpha S = k_2S/k_1$ vs. salt concentration for the three runs. This should be a straight line through the origin with slope $= k_2/k_1$. The slope of the line is 0.0864 mole/l. and k_2 is then 0.0554 l.^{2} mole^{-2} min.$^{-1}$. Considering the magnitudes of S and P which occur in these three runs, the two terms on the right-hand side of eq. 4 are comparable in significance.

Equation 4 is just eq. 1 with an added term on the right-hand side. This additional term can be derived by considering it to describe a reaction path whose rate is given by $kA[Q^+ i\text{-PrO}^-]$ where $[Q^+ i\text{-PrO}^-]$ represents the concentration of associated quaternary ammonium isopropoxide, including the equilibrium

$$(Q^+Cl^-) + i\text{-PrOH} \rightleftharpoons (Q^+ i\text{-PrO}^-) + HCl \qquad (6)$$
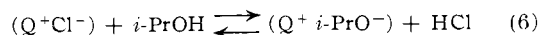
assuming it to lie well to the left and also recognizing that HCl and the quaternary ammonium salts are only very slightly dissociated. The expression $kA[Q^+ i\text{-PrO}^-]$ then converts directly to k_2CAS/P with k_2 being a product of rate constant k and the equilibrium

constant for eq. 6. The term $[Q^+ \ i\text{-PrO}^-]$ can be replaced by an equilibrium constant times the product of the concentrations of free quaternary ammonium ion and isopropoxide ion, but again this would be a mechanism requiring participation by not one, but two, free ions and in CCl_4 a mechanism involving an associated species is far more plausible.

Because Allen and Modena[4] had attributed catalysis to chloride ion, an attempt was made to fit the data by replacing the last term of eq. 4 with $kCA\,[\text{Cl}^-]$, and because their observed catalytic rate constants were in fact linear in total salt concentration rather than in ion concentration a term $kCAS$ was also tried, but in neither case could an acceptable fit be obtained.

Comparison of our findings with those of Allen and Modena[4] relative to catalysis by HCl in the absence of added salt is impossible, because we find that the rate at very short times is entirely dependent on the small amount of HCl initially present, while Allen and Modena determine rates at zero time and take no account of the possibility of impurity HCl being present. Our observations suggest that such rate constants must be meaningless without knowledge of the initial HCl concentrations.

From our own studies we can conclude with reasonable certainty that there is little or no uncatalyzed reaction in CCl_4 between $(C_6H_5)_3SiCl$ and 2-propanol, that the significant HCl catalysis is due to an associated species and not to free ions, and that the apparent catalysis by benzyltriethylammonium chloride results from uncatalyzed attack by an associated quaternary ammonium isopropoxide species on the $(C_6H_5)_3SiCl$.

These conclusions, initially somewhat surprising, are in fact quite reasonable. Failure to observe catalysis by H^+ or Cl^- may be attributed simply to the extremely low concentrations of the free ions, while catalysis by HCl, which must be similar in nature to that which might be predicted for H^+ or Cl^-, is measurable because of the very much greater concentration of HCl. The direct reaction between $(C_6H_5)_3SiCl$ and

the quaternary ammonium isopropoxide, with no equivalent reaction for the alcohol, is explained by the fact that charge separation in $(Q^+ \ i\text{-PrO}^-)$ is very much greater than in $i\text{-PrOH}$. The salt species, even though associated, is then a much stronger nucleophile than the alcohol.

In a case where three species are involved in the rate equation, as in the HCl-catalyzed path described here, it is far more reasonable to accommodate the observation by postulating an intermediate comprising at least two of the species than by requiring a three-body reaction. In the present case the most probable intermediate involves pentacovalent silicon, possibly as shown in structure I.

$$\begin{array}{ccc} H_5C_6 & & C_6H_5 \\ & \diagdown \ \diagup & \\ RO-&\!\!Si\!\!-&Cl \\ & | \quad | & \\ I & H \quad C_6H_5 & \end{array}$$
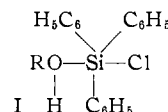
The fact that no reaction is observed in the absence of HCl suggests that the Si–Cl bond is stronger than the Si–O bond in the intermediate. The function of the HCl is then to aid in strengthening the Si–O bond relative to the Si–Cl bond. This may be done through hydrogen-bond formation with either the Cl or the hydroxyl H of I, although the latter possibility is not overly attractive when one considers that the solvent offers far more opportunities for similar interactions and CCl_4 is not a sufficient catalyst to effect reaction.

The preliminary formation of an intermediate hydrogen-bonded species $(C_6H_5)_3SiCl. \, . \, .HCl$ does not seem nearly as probable as the type represented by I, since the great excess of solvent CCl_4 competing with $(C_6H_5)_3 SiCl$ for the limited supply of HCl argues against any significant lifetime for such an intermediate and the mechanism would then not differ significantly from a three-body collision.

In view of these arguments, we conclude that our observations are best rationalized through an intermediate containing pentavalent silicon.

The Carborane Series: $B_nC_2H_{n+2}$. II. The Two Isomers of $B_4C_2H_6$

BY I. SHAPIRO,[1] B. KEILIN, ROBERT E. WILLIAMS, AND C. DAVID GOOD

RECEIVED FEBRUARY 6, 1963

Two isomers of carborane-4, $B_4C_2H_6$, have been isolated, and their structures deduced from the nuclear magnetic resonance, infrared, and mass spectral analyses of isotopic variants of the compounds. Some of the physical and chemical properties of the more stable carborane-4, $sym\text{-}B_4C_2H_6$, are given.

The carborane series of compounds have been prepared from the reaction of acetylene with boron hydrides. The simplest member of the series, $B_3C_2H_5$, has already been discussed.[2] The isomers of carborane-4 were prepared from the reaction of pentaborane and acetylene in a silent discharge tube. When these same reactants are confined under pressure at elevated temperatures, the product is another organoboron compound, $B_4C_2H_8$,[3] which differs structurally[4] from the

carboranes. Data on other carboranes and their derivatives will be published later.

Experimental

Materials.—The isotopic variants of acetylene and pentaborane have been described previously.[2]

Apparatus.—The apparatus used to prepare and analyze the isomers of carborane-4 are the same as described for carborane-3.[2]

Procedure.—Although carborane-4 can be prepared by the high-temperature reaction of acetylene with diborane or pentaborane at low pressures, it was found more convenient to prepare the carboranes by use of the silent discharge apparatus.[2] An equimolar mixture of pentaborane-9 and acetylene (25 mmoles) was circulated through the silent discharge apparatus (15 kv.) for 1 hr. at ambient temperature (the temperature of the reactor increased noticeably during the course of the experiment). During this time, the total pressure of the system gradually decreased, and a light yellow-brown deposit formed on the walls of the reactor. After the high-voltage discharge was discontinued, the condensable products were transferred to a fractionation train in the high vacuum apparatus. Inasmuch as the quantity of volatile product from any one experiment was low, this pro-

(1) Universal Chemical Systems, Inc., Culver City, Calif.

(2) I. Shapiro C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

(3) I. Shapiro and H. G. Weiss, experimental work performed 1953–1957, and declassified Nov. 5, 1962; I. Shapiro, paper presented at the XIX Meeting of the International Union of Pure and Applied Chemistry, London, July, 1963.

(4) Attention is called that the structure of B₄C₂H₈ cited recently⁵ was taken from the previous work³ without permission or acknowledgment of the senior investigator.

(5) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).