Reactions of Chlorosilanes and 5-Chloro-2-hydroxybenzophenone

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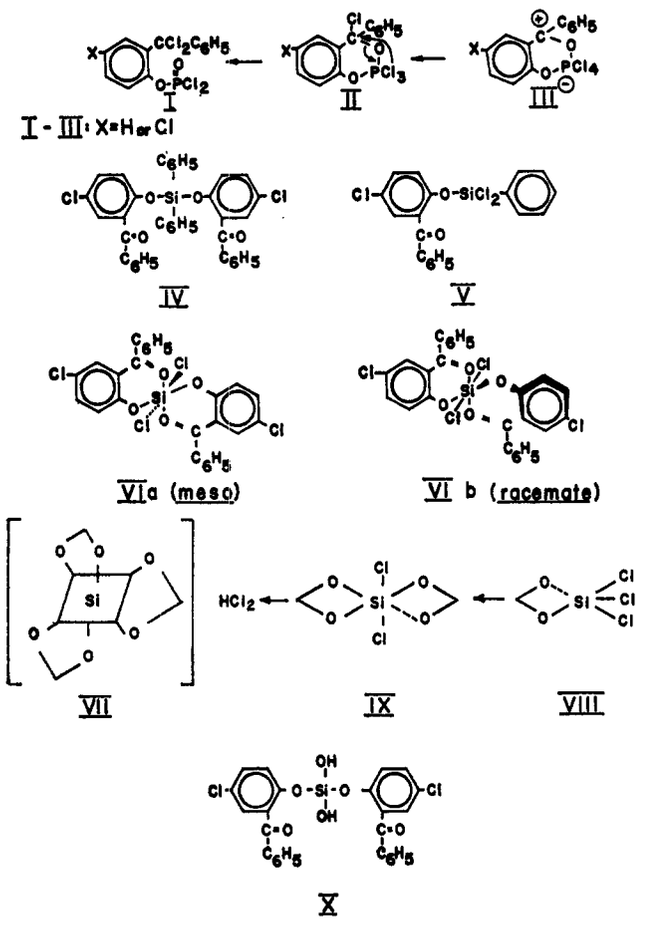
The following results were obtained in reactions with 5-chloro-2-hydroxybenzophenone. Diphenyldichlorosilane reacts in the presence of 1 equiv of triethylamine to form a 1:2 ratio product, IV. Phenyltrichlorosilane reacts in refluxing benzene or in the presence of 1 equiv of triethylamine to form a 1:1 ratio product, V. Silicon tetrachloride reacts in benzene solvent to form a 1:2 ratio product, VI, in which silicon is hexacoordinate. Structure VI is the first example of an intermediate of type IX originally postulated by Dilthey as formed (but not isolated) during reactions of silicon tetrachloride with acetylacetone and related compounds. The structures are based on evidence from elemental analyses, molecular weight determinations, quantitative hydrolytic determinations, and infrared spectra. Possible explanations are given for formation of 1:2 and not 1:1 ratio products, and the absence of coordination with silicon in IV and V as compared with VI.

Phosphorus pentachloride reacts with 2-hydroxybenzophenones to form (*o*-phenyldichloromethyl)-phenyl phosphorodichloridates (I).[1] The d orbitals of phosphorus were postulated to participate in the mechanism of the reaction by forming intermediates II and III (Scheme I) in which phosphorus is sp^3d and

SCHEME I



sp^3d^2 hybridized, respectively. It was of interest to investigate the corresponding reactions of silicon tetrachloride and other phenylchlorosilanes as representatives of group IVA of the second period where d orbitals would also be available.[2-7] Results of the investigation are reported in the present paper.

Results and Discussion

The main product isolated from the 1:1 ratio reaction of 5-chloro-2-hydroxybenzophenone[8] and diphenyldichlorosilane using triethylamine was the 1:2 product (diphenyldichlorosilane–5-chloro-2-hydroxybenzophenone) IV. The infrared spectrum of the 1:2 product was in accord with a benzophenone structure; it showed the absence of an OH stretching band indicating substitution at this position and the presence of a sharp carbonyl stretching band at 1670 cm^{-1} (5.98 μ). The position is close to those reported[9] for related benzophenones: 4-chloro at 1666, 4-bromo at 1665, 3-bromo at 1669 cm^{-1}. The closeness of the frequency correspondence indicates no interaction of the carbonyl group with silicon bonding orbitals. The structure was further confirmed by hydrolysis to 5-chloro-2-hydroxybenzophenone in 97.8% yield. A 1:1 condensation product could not be isolated even though the reaction was carried out in such a way as to favor a 1:1 product by adding the 5-chloro-2-hydroxybenzophenone slowly dropwise into the diphenyldichlorosilane solution, thus keeping the latter in excess at all times. On repeating the reaction using a 1:2 ratio of reactants, an 89.0% yield of 1:2 product (IV) was obtained.

The main component from the reaction of phenyltrichlorosilane was determined to be a 1:1 condensate.

(1) A. G. Pinkus and L. Y. C. Meng, *J. Org. Chem.*, **31**, 1038 (1966).

(2) Aspects of d orbital participation in phosphorus and silicon chemistry have been recently discussed by Bissey;[3] for discussion of d orbitals in silicon chemistry, see ref 4-7.

(3) J. E. Bissey, *J. Chem. Educ.*, **44**, 95 (1967).

(4) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, 1, 112 (1955).

(5) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960.

(6) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

(7) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, Inc., New York, N. Y., 1963; V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. I and II, Academic Press, New York, N. Y., 1965; D. Seyferth and R. B. King, "Annual Survey of Organometallic Chemistry," Elsevier, Publishing Co., Inc., New York, N. Y., Vol. I, 1965, pp 89 ff; Vol. II, 1966, pp 113 ff.

(8) 5-Chloro-2-hydroxybenzophenone was used as a representative 2-hydroxybenzophenone because of its commercial availability; the authors express appreciation to the Dow Chemical Co., Midland, Mich., for generous experimental samples.

(9) N. Fuson, M. L. Josien, and E. M. Shelton, *J. Amer. Chem. Soc.*, **76**, 2526 (1954). Structure IV is a 3-chlorobenzophenone; although the stretching band for this analog is not reported, the data show little difference between chloro and bromo analogs.

The infrared spectrum consisted of well-resolved bands and indicated a single product rather than a mixture. It showed the absence of the OH stretching band (*ca.* 3117 cm^{-1}) for 5-chloro-2-hydroxybenzophenone indicating substitution at this position and the presence of a carbonyl stretching band at 1670 cm^{-1} (5.98 μ), the same position as product VI from diphenyldichlorosilane. The 1:1 condensation product is in accord with structure V.

The product from the reaction of silicon tetrachloride in a 1:1 ratio of reactants was an orange solid having a 1:2 composition (silicon tetrachloride–5-chloro-2-hydroxybenzophenone) even though the various procedures were such as to favor a 1:1 product. The most interesting feature of the infrared spectrum of the 1:2 condensation product was the absence of absorption in the carbonyl stretching region and the appearance of strong bands at 1547 (6.46 μ) and 1500 cm^{-1} (6.67 μ). The shift of the absorption band to lower frequencies is indicative of chelation of the carbonyl oxygen with silicon. This behavior is found in metal chelates which show one or two strong bands in the 1500–1600-cm^{-1} (6.67–6.25-μ) region.[10] West[11] observed similar spectral behavior for compounds formed from reactions of acetylacetone with silicon tetrachloride, phenyltrichlorosilane, and methyltrichlorosilane. The products, formulated as $SiA_3^+HCl_2^-$, $PhSiA_2Cl$, and CH_3SiA_2Cl (A = acetylacetonyl group, $C_5H_7O_2$) showed absorption at 1555, 1553, 1550 cm^{-1}, respectively. Structure VI in which both carbonyl groups are chelated and in which sp^3d^2 orbitals of silicon are utilized is in accord with the data. Three isomers are possible: a *mesa* form VIa in which the rings are coplanar and an enantiomeric pair VIb (and its mirror) in which the rings are perpendicular.

The first hexacovalent complex SiA_3X (X = –Cl·HCl) containing Si–O bonds was prepared by Dilthey[12] in 1903 by reacting silicon tetrachloride with acetylacetone. In 1906, Dilthey[13] proposed structure VII for the compound. This structure was confirmed by the infrared studies of West[11] and the resolution of the cation into optical isomers by Dhar, Doron and Kirschner.[14] Dilthey suggested[13] that formation of VII occurred in stages which involved precursers VIII and IX[15] which could not be isolated because "... die Tendenz zur Oniumsalzbildung ist ebenzu gross ...". Structure VI obtained in the present investigation appears to be the first example of a type IX intermediate. It is interesting to note that a germanium analog of type IX had been previously prepared[16] (by reacting germanium tetrachloride and acetylacetone). In two recent communications, Pike and coworkers[17] reported the "first example of a neutral silicon chelate having β-diketo ligands prepared from a tetrafunctional silicon reagent." Their compound obtained from the reaction of tetraacetoxysilane and acetylacetone, is an example of type IX with two acetoxy groups in place of the chlorines. They determined the configuration to be *trans* in the solid state isomerizing to a *cis/trans* mixture in solution.

A possible reason the reaction with silicon tetrachloride stops at the type IX stage in the present work is the insolubility of product VI which lessens its reactivity toward the substrate, 5-chloro-2-hydroxybenzophenone. A pentacoordinate intermediate[18–23] of type VIII (with sp^3d hybridization) was not obtained in the present investigation; this would have been the silicon analog of the sp^3d^2-hybridized phosphorus intermediate (II) previously postulated[1] in the mechanism of the reaction with phosphorus pentachloride. However, it is notable that an sp^3d^2-hybridized product (VI) is isolable from the silicon tetrachloride reaction. A limited number of chelated hexacoordinate silicon compounds have been reported.[3–6,10–12,14]

Another interesting aspect of the present results is the fact that whereas the ligands in product VI from the silicon tetrachloride reaction are chelated with silicon, the products from phenyltrichlorosilane and diphenyldichlorosilane (V and IV, respectively) are nonchelated. It has been pointed out[5] that the presence of organic groups on silicon markedly lowers the tendency to form complexes. Thus the compounds $PhSiA_2Cl$ and $MeSiA_2Cl$ which West[11] obtained from the reaction of acetylacetone with phenyltrichlorosilane and methyltrichlorosilane, respectively, resembled the compounds SiA_3X in having structures of the chelated type but when two or three alkyl groups were present on silicon, as in the compounds Me_2SiA_2, Me_3SiA and Et_3SiA, the structures were of the nonchelated type.[11,21,24] West[11] stated that steric hindrance alone did not explain the lack of chelation in Me_2SiA_2 since the steric requirement of a chlorine is about equal to that of a methyl group and Me_2SiA_2Cl was chelated. Chelation was attributed to the presence of electronegative chlorine on silicon which increased the acidity of silicon by withdrawal of electrons. In $SiA_3^+HCl_2^-$, acetylacetonate groups were sufficiently electron withdrawing so that the compound adopted a chelated structure. The importance of electronegativity of the group attached to silicon in connection with the availability of the d orbitals for bonding was also noted by others.[4,6] In the case of compound VI the use of silicon d orbitals can be rationalized on the basis of electron withdrawal by electronegative chlorine and oxygen atoms thus contracting

(10) J. Lecomte, *Discussions Faraday Soc.*, **9**, 125 (1950); R. West and R. Riley, *J. Inorg. Nucl. Chem.*, **5**, 295 (1958); L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, pp 145–146.

(11) R. West, *J. Amer. Chem. Soc.*, **80**, 3246 (1958).

(12) W. Dilthey, *Ber.*, **36**, 923 (1903).

(13) W. Dilthey, *Ann.*, **344**, 300 (1906).

(14) S. K. Dhar, V. Doron, and S. Kirschner, *J. Amer. Chem. Soc.*, **80**, 753 (1958); **81**, 6372 (1959).

(15) The formulations VIII and IX are those used by Dilthey.[13]

(16) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **125**, 1261 (1924).

(17) R. M. Pike and R. R. Luongo, *J. Amer. Chem. Soc.*, **87**, 1403 (1965); C. E. Holloway, R. R. Luongo, and R. M. Pike, *ibid.*, **88**, 2060 (1966); see also R. M. Pike and R. R. Luongo, *ibid.*, **88**, 2972 (1966).

(18) Chelated pentacoordinate compounds of silicon have been reported.[19] In addition to the examples of chelated hexacoordinated silicon compounds in references listed in the present paper, the following are added. Products from reactions of silicon tetrachloride and/or silicon tetrabromide with acetoacetic ester,[20,21] benzoylacetone,[22] dibenzoylmethane,[13] and silicon esters of picolinic acids.[23]

(19) R. Müller and L. Heinrich, *Ber.*, **94**, 1943 (1961); C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Amer. Chem. Soc.*, **83**, 996 (1961); J. Y. Corey and R. West, *ibid.*, **85**, 4034 (1963); E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 159 (1967); R. Rudman, W. C. Hamilton, S. Novick, and T. D. Goldfarb, *J. Amer. Chem. Soc.*, **89**, 5157 (1967), and references in these papers.

(20) A. Rosenheim, W. Loewenstamm, and L. Singer, *Ber.*, **36**, 1833 (1903).

(21) R. West, *J. Org. Chem.*, **23**, 1552 (1958).

(22) W. Dilthey, *Ber.*, **36**, 1595 (1903).

(23) G. H. Searle and C. J. Wilkins, *J. Chem. Soc.*, 3897 (1961).

(24) L. H. Sommer and W. H. Knoth, unpublished work as quoted in ref 6; *cf.* W. H. Knoth, Ph.D. Thesis, Pennsylvania State University, 1954.

the d orbitals and making possible bonding of carbonyl oxygen electrons with available silicon d orbitals.[25]

In the present work, the main product V from phenyltrichlorosilane which is of the $PhSiACl_2$ type with only one phenyl group is nonchelating in comparison with results of West[11] on $PhSiA_2Cl$ which was chelated. One factor which may have an important bearing on the difference between the two cases may be the greater electronegativity of the groups attached to silicon in West's compound (two oxygens, one chlorine, and one phenyl) as compared with compound V (one oxygen, two chlorines, and one phenyl). There is also the possibility that $d\pi$–$p\pi$ bonding from phenyl to silicon might also contribute to the lack of chelation in compounds IV and V. In a recent review on this topic, Eaton and McClellan[26] discuss the published evidence for $d\pi$–$p\pi$ bonding involving group IV elements; their results in which nmr contact shifts of substituted paramagnetic nickel chelates were measured showed a negligible amount of conjugation between aromatic residues linked by tetrahedral silicon, germanium and tin atoms.

Although West[11] represented compounds $PhSiA_2Cl$ and $MeSiA_2Cl$ as hexacoordinate, Sommer[6] pointed out the possibility that ionic Si–Cl bonds in these compounds would make silicon pentacovalent, the nature of these bonds being unknown. Their germanium analog,[16] however, has been shown to have a hexacoordinate covalent structure. Thus, in 1965, Ong and Prince[27] found a small molecular conductivity for $GeAc_2Cl_2$ which they concluded showed that it was essentially a nonelectrolyte. Similar considerations would apply to compound VI prepared in the present investigation.

Experimental Section

Materials, Instruments, and Procedures.—Diphenyldichlorosilane[28] was distilled, bp 160° (<1 mm). Phenyltrichlorosilane[28] was used without further purification. Silicon tetrachloride was distilled, bp 56.0–56.5°. 5-Chloro-2-hydroxybenzophenone was recrystallized from cyclohexane, mp 96.5–98.0°. Benzene, cyclohexane and ethyl ether were dried by refluxing with sodium ribbon and were distilled. Triethylamine was dried by refluxing with sodium hydroxide pellets and was distilled. Melting points are corrected; they were determined by procedures referred to in a previous paper[1] using techniques for moisture-sensitive compounds. Infrared spectra were obtained by procedures referred to in an earlier paper[1] in which precautions against moisture were observed. X-Ray diffraction patterns as Debye–Scherrer camera powder photographs were obtained on a Norelco–North American Philips instrument using Cu Kα radiation with a nickel filter.

Reaction of Diphenyldichlorosilane and 5-Chloro-2-hydroxybenzophenone.—The reaction was run using drybox techniques and sweeping with dry nitrogen gas for several minutes before mixing the reagents. Procedures and precautions are those referred to in a previous paper.[1] The following quantities of reagents were used: 5-chloro-2-hydroxybenzophenone (13.98 g, 6.008×10^{-2} mol) and triethylamine (6.080 g, 6.008×10^{-2} mol) in benzene (100 ml); diphenyldichlorosilane (7.608 g, 3.004×10^{-2} mol) in benzene (60 ml). Solvent was removed *in vacuo* in a drybox. The residue was extracted with dry ether to leave a white powder which was dried *in vacuo*, 17.3 g (89.0% yield). Solid IV was recrystallized from cyclohexane (86.6% yield): mp 163.8–164.8°.

Anal. Calcd for $C_{38}H_{26}O_4Cl_2Si$: C, 70.70; H, 4.06; Cl, 10.98; Si, 4.35; mol wt (cryos, benzene), 645. Found:[29] C, 70.21,[29a] 69.24,[29a] 71.91,[29a] 71.14,[29b] 71.24;[29c] H, 4.11,[29a] 4.29,[29a] 4.31,[29a] 4.41,[29b] 4.35;[29c] Cl, 10.89,[29a] 10.50,[29a] 11.45;[29c] Si, 5.58,[29a] 4.42,[29a] 4.03,[29b] 1.54;[29c] mol wt, 664.

Hydrolysis Studies on IV.—A 3.239-g sample of IV was hydrolyzed with dilute sodium hydroxide. A 2.28-g crude yield (97.8%) of 5-chloro-2-hydroxybenzophenone, mp 91–92°, was obtained; mp 96–97° (after recrystallization from cyclohexane); identification by mixture melting point and infrared spectral comparison. A quantitative determination of the amount of 5-chloro-2-hydroxybenzophenone formed from hydrolysis was obtained by analysis using the ultraviolet absorption curve of the cyclohexane solution. It was found that 1 mol of IV on hydrolysis formed 1.93 mol of 5-chloro-2-hydroxybenzophenone.

Reaction of Phenyltrichlorosilane and 5-Chloro-2-hydroxybenzophenone. A. No Base.—The reaction was carried out as described for diphenyldichlorosilane using phenyltrichlorosilane (0.7720 g, 3.648×10^{-3} mol) in benzene (10 ml), and 5-chloro-2-hydroxybenzophenone (0.8488 g, 3.648×10^{-3} mol) in benzene (20 ml). No hydrogen chloride evolution was observed at room temperature and the infrared spectrum showed that no reaction had taken place after *ca.* 1 hr. Hydrogen chloride was evolved on heating the reaction; the mixture was heated until gas evolution ceased. On removal of solvent *in vacuo*, a viscous orange oil was obtained, crude yield 1.39 g (93.3% based on 1:1 product, V).

B. Triethylamine.—The following quantities of reagents were used: phenyltrichlorosilane (6.240 g, 2.949×10^{-2} mol) in benzene (20 ml); 5-chloro-2-hydroxybenzophenone (6.851 g, 2.949×10^{-2} mol), and triethylamine (2.984 g, 2.949×10^{-2} mol) in benzene (80 ml). After removal of triethylamine hydrochloride precipitate by filtration and benzene from the filtrate *in vacuo*, a viscous orange oil was obtained; crude yield 11.9 g (98.8%) based on 1:1 product VI. The molecular weight determined on the product by cryoscopy in benzene was 433 (calcd for 1:1 product V $C_{19}H_{13}O_2Cl_3Si$, 407). Analysis for hydrolyzable chlorine was carried out on the hydrolysate of a sample from a 5:1 mixture[30] of 1,4-dioxane and water. Chloride was precipitated as silver chloride which was determined gravimetrically. The average percentage of chlorine found (four samples) was 14.20% (17.38% calcd for 1:1 product; 5.87% for 1:2 product).

In order to demonstrate that the reaction product did not consist of a fortuitous mixture of 1:2 product and unreacted phenyltrichlorosilane, the infrared spectrum of the product was examined; no detectable amount of the latter appeared to be present and the relatively simple spectrum indicated the presence of mainly a single compound rather than a mixture. In addition a vacuum distillation was attempted on the reaction product and no phenyltrichlorosilane [bp 74° (10 mm)][31] was obtained at 140° (<1 mm). In a check experiment in which phenyltrichlorosilane was deliberately added to the reaction mixture, most of it was recovered by distillation. These experiments indicate the presence of a 1:1 condensation product V.

Reaction of Silicon Tetrachloride and 5-Chloro-2-hydroxybenzophenone.—Reaction was carried out at room temperature using procedures described above. The following quantities of reagents were used: redistilled silicon tetrachloride (3.196 g, 1.881×10^{-2} mol) in dry benzene (30 ml), 5-chloro-2-hydroxybenzophenone (4.377 g, 1.881×10^{-2} mol) in benzene (50 ml). Hydrogen chloride was evolved slowly during addition; an orange precipitate suddenly formed 5–6 min after all of the latter reagent had been added. On filtration, 0.90 g of product was obtained; more was recovered on evaporation of filtrates—total yield, 5.20 g (98.3% based on 1:2 condensation product VI). In another reaction carried out under reflux, a 63.4% yield was obtained. The product was only very slightly soluble in selected organic solvents; no suitable one was found for recrystallization. The material from the first crop of precipitate was used for quantitative characterization of the compound. The product melted at 197–204°.

(25) Report of Chemical Society Symposium on Valence and Reactivity Oxford, Jan 9–11, 1968; *Nature*, **217**, 220 (1968).

(26) D. R. Eaton and W. R. McClellan, *Inorg. Chem.*, **6**, 2134 (1967), In a more recent paper, nitrogen-14 nmr evidence is presented for interaction between a phenyl ring and silicon in nitrophenyltrimethylsilanes [Y. Vignollet, J. C. Maire, and M. Witanowski, *Chem. Commun.*, 1187 (1968)].

(27) W. K. Ong and R. H. Prince, *J. Inorg. Nucl. Chem.*, **27**, 1037 (1965).

(28) The authors express appreciation to the Dow Corning Corp., Midland, Mich., for experimental samples.

(29) Analyses on separately prepared samples as designated: (a) Galbraith Laboratories, Knoxville, Tenn.; (b) Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; (c) Geller Laboratories, Charleston, W. Va.; (d) Clark Microanalytical Laboratory, Urbana, Ill.

(30) The sample was incompletely hydrolyzed with dilute aqueous sodium hydroxide even after 3 days at room temperature.

(31) "Selection Guide to Dow Corning Reactive Organosilicon Chemicals," Dow Corning Corp., Midland, Mich.

Hydrolysis Studies on VI. A. Hydrolyzable Chlorine Determination.—Hydrolyzable chlorine was determined by potentiometric titration of a hydrolyzed sample using standardized silver nitrate solution and a Beckman pH meter with a calomel reference electrode and a silver indicator electrode. The percentage of hydrolyzable chlorine found was 12.65% (average of three samples), calcd for 1:2 product $C_{26}H_{16}O_4Cl_4Si$ (VI), 12.61%.

B. Hydrolysis Product Isolation and Analysis.—A 5.945-g sample of VI was hydrolyzed by allowing it to stand overnight with water (*ca.* 50 ml) in a stoppered flask. The residue was collected by filtration and dried to constant weight (5.277 g) and consisted of a mixture of white and yellow solids. The solid mixture was extracted with hot cyclohexane (see below for filtrate), the white residue being collected by filtration and washed with cyclohexane, yield 0.659 g. The solid did not melt when heated to 295° and was insoluble in organic solvents. The X-ray diffraction pattern showed that the material was amorphous. A sample of the material (0.1275 g) was heated at 1100° to a constant weight of 0.0905 g. Comparison of the X-ray diffraction pattern of the product with that of the standard ASTM *d/n* values for silicon dioxide identified the former as cristobalite.

On removal of cyclohexane *in vacuo* from the filtrate and combined washings from above 4.61 g (93.7% yield) of 5-chloro-2-hydroxybenzophenone, mp 94.5–96.0°, was obtained. Identification was by mixture melting point and comparison of the infrared spectrum with an authentic sample. In another experiment in which more care was taken to recover 5-chloro-2-hydroxybenzophenone quantitatively, 0.8910 g (97.91%) was obtained from hydrolysis of a 1.1000-g sample of VI.

Although preparation and handling of the compound were carried out under drybox conditions, results of commercial laboratory analysis of the analytical sample (sent in a sealed tube) indicated hydrolysis which probably occurred during handling[32] of the compound for analysis. Low chlorine and high carbon percentages are in the correct direction expected for hydrolysis.

Anal. Calcd for $C_{26}H_{16}O_4Cl_4Si$: C, 55.54; H, 2.87; Cl, 25.22; Si, 4.99. Found:[29a] C, 56.68; H, 3.69; Cl, 22.39; Si, 5.27.

Analysis of a previous sample which had inadvertently been sent in a screwcap vial showed that the sample had practically hydrolyzed completely (Found:[29d] C, 47.99; H, 3.68; Cl, 13.23; Si, 5.57). If replacement of the two hydrolyzable chlorines by hydroxyl groups is assumed, hydrolytic product X would be expected.[33] Calculated analytical values for this structure ($C_{26}H_{18}O_6Cl_2Si$) are C, 59.44; H, 3.45; Cl, 13.49; Si, 5.35. All the analyses check closely for structure VI except for carbon which is slightly low. This low carbon value could be due to silicon carbide formation which is commonly observed[5] during combustion analyses.

Registry No.—5-Chloro-2-hydroxybenzophenone, 85-19-8; diphenyldichlorosilane, 80-10-4; phenyltrichlorosilane, 98-13-5; silicon tetrachloride, 10026-04-7; IV, 18964-24-4; VI a (*meso*), 18962-94-2; VI b (racemate), 18975-92-3.

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(32) West[11] pointed out similar difficulties experienced with hydrolytically sensitive compounds.

(33) No studies were made on the hydrolyzed product to determine the possibility of chelation which would be expected in view of four oxygen atoms bonded to silicon.

The Reaction of *cis*-9-Octadecene and Related Compounds with Aqueous Perchloric Acid[1]

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The heterogeneous reaction of *cis*-9-octadecene with aqueous 67% deuterioperchloric acid has been studied with respect to the reaction variables involved, *i.e.*, reaction time, stirring rate, temperature, molar ratio of reactants, and strength of inorganic acid. High yields of isomeric octadecenes were obtained. The rate of double-bond migration was significantly faster than the rate at which deuterium was incorporated into the product. Small amounts of octadecyl perchlorates are formed in the reactions. *cis*-9-Octadecene and 1-octadecene were allowed to read with aqueous deuterioperchloric acid in the presence of stearic acid; migration of the double bond occurs by means of a reversible acid–olefin esterification reaction. The octadecene product shows a more extensive isomerization than is obtained in the absence of stearic acid; it is aslo comparatively heavily deuterated. Reactions of 1- and 9-octadecanol, both in the presence and absence of stearic acid, emphasize the differences in behavior between primary and secondary compounds.

Past studies[4] in this laboratory have been concerned with the optimum conditions for the preparation of γ-stearolacetone from the reaction of aqueous 70% perchloric acid with various C_{18} monounsaturated and monohydroxy fatty acids and with an investigation of the types and amounts of reaction by-products. This has led us to an examination of the reaction of 9- and 1-octadecenes and -octadecanols with aqueous deuterioperchloric acid and the changes brought about in the system by the introduction of stearic acid. The addition of stearic acid to the reaction mixture has meant that, as in the past studies,[4] the functional groups, olefin (or hydroxyl) and carboxylic acid, are present, albeit in two molecules rather than in a single molecule.

The Reaction of *cis*-9-Octadecene with Aqueous Deuterioperchloric Acid.—A series of reactions of *cis*-9-octadecene with aqueous 67% deuterioperchloric acid was carried out changing one at a time the reaction variables of time, stirring rate, temperature, molar ratio of deuteroperchloric acid to *cis*-9-octadecene used, and strength of inorganic acid. The amount of *cis*-9-octadecene used and the size of the reaction vessel and magnetic stirring bar were kept fixed for all reactions.

(1) Presented in part at the 1965 Spring Meeting of the American Oil Chemists' Society, April 25–28, 1965, Houston, Texas.

(2) (a) National Science Foundation, 1800 G Street, N. W., Washington, D. C. 20550. (b) Unilever Research Laboratory, The Frythe, Welwyn, England. (c) This author wishes to thank the Agricultural Research Service in association with the National Academy of Sciences—National Research Council, for a Resident Research Associateship (1963–1965).

(3) Agricultural Research Service, U. S. Department of Agriculture.

(4) J. S. Showell, W. R. Noble, and D. Swern, *J. Org. Chem.*, **33**, 2697 (1968).