[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

Two New Isomers of Benzene Hexachloride

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Two of the three hitherto unknown isomers of benzene hexachloride (BHC), eta and theta, have been synthesized by the photochlorination of individual benzene tetrachloride (BTC) isomers and their structures have been elucidated. η-BHC (aeaaee), m.p. 89.8–90.6° (cor.), was formed by *trans*-chlorine addition to ϵ-BTC and *cis* addition to β-BTC. Although θ-BHC (aeaeee), a product of *cis* addition to γ- and ϵ-BTC, was not isolated in pure form, strong evidence for its formation was provided by chromatographic, chemical and spectrophotometric data. These results establish that free radical chlorine addition to a cycloölefinic double bond takes place by two *cis* and two *trans* mechanisms to give four products in which the chlorine substituents thus introduced are oriented ea, ae, ee and aa. η-BHC also has been isolated from BHC prepared by the direct photochlorination of benzene.

The five known isomers of benzene hexachloride (BHC, 1,2,3,4,5,6-hexachlorocyclohexane) have been established by physical means as chair-formed cyclohexane derivatives which differ essentially in the spatial orientation of their hydrogen and chlorine substituents.[2,3] On the basis of the accepted concept of ring conversion,[4] the thirteen theoretically possible stereoisomers of BHC are reduced[5] to eight separable steric structures of which only one, α, can exist in separable enantiomeric forms.[6] In accordance with the recent recommendation of Barton, Hassel, Pitzer and Prelog,[7a] polar ("p") substituents in cyclohexane derivatives will be designated to this paper as axial ("a") whereas no change will be made in the accepted usage of the term equatorial ("e") for the remaining C–H or C–Cl bonds which are approximately orthogonal to the principal axis of the molecule. On this basis, the conformations[3] of the known BHC isomers are: α(aaeeee), β(eeeeee), γ(aaaeee), δ(aeeeee) and ϵ(aeeaee).[7b] A hexachlorocyclohexane, melting at 145° and exhibiting a zero dipole moment, was erroneously considered to be the sixth or ζ-isomer of BHC.[8] Subsequent investigations,[9] however, proved it to be a 1,1,2,4,4,5-positional isomer instead.

Of the three remaining benzene hexachlorides the molecules of two, aeaeee and aeaaee, are subject to an internal "*meta* axial strain"[5b] because of the presence of two chlorine substituents (1a, 3a) on the same side of the plane of the carbon ring. Although this orientation may result in some distortion of the molecule, as has been demonstrated by X-ray studies in the case of γ-BHC, it should not exclude the possibility of stable existence of the two isomers, aeaeee and aeaaee. The eighth theoretically separable hexachloride (aeaeae) has an even more highly strained structure since three *meta* axial chlorine substituents (1a, 3a, 5a) are present on the same side of the plane of the ring. For this reason, and because the latter molecule represents an all *cis* addition product, its formation appears improbable.

The separation in pure form of five steric isomers of benzene tetrachloride (3,4,5,6-tetrachlorocyclohexene-1, BTC)[10] provided a new approach to the synthesis of two of the hitherto unknown isomers of BHC. Theoretically, the addition of chlorine to the cycloölefinic double bond in BTC can proceed by two *cis* and two *trans* mechanisms to yield products in which the chlorine substituents are oriented ea or ae, and ee or aa, respectively. From the results of the additive photochlorination of individual BTC isomers, this hypothesis has been confirmed by the spectrophotometric detection of all five known benzene hexachlorides which were formed in accordance with the relationships shown in Table I.[10b] Unidentified bands in the infrared spectra of

TABLE I

BHC ISOMERS THEORETICALLY OBTAINABLE BY CHLORINATION OF BTC[11]

BTC isomer	*cis* addition (ea or ae)	*trans* addition	
		ee	aa
α(eeaa)	γ,η	α	$1/\alpha^a$
β(aeea $\rightleftarrows$ eaae)	η	α,ϵ	$1/\alpha,1/\epsilon^a$
γ(eeea)	α,θ	δ	γ
δ(eeee)	δ	β	α
ϵ(eeae)	ϵ,θ	δ	η
ζ(eaea)^b	$\iota,^b\eta$	θ	η

^{a} Non-separable ring conversion forms. ^{b} Not known.

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[1] Presented at the 121st Meeting of the American Chemical Society, March 24, 1952; Abstracts, p. 5K.

[2] O. Hassel, *Research*, **3**, 504 (1950), a review.

[3] (a) O. Bastiansen, Ø. Ellefsen and O. Hassel, *ibid.*, **2**, 248 (1949); (b) *Acta Chem. Scand.*, **3**, 918 (1949).

[4] O. Hassel, *Tids. Kjemi Bergvesen Met.*, **3**, 32 (1943).

[5] (a) O. Hassel, and B. Ottar, *Acta Chem. Scand.*, **1**, 521 (1947); (b) J. M. Bijvöet, *Rec. trav. chim.*, **67**, 777 (1948).

[6] S. J. Cristol, THIS JOURNAL, **71**, 1894 (1949).

[7] (a) D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Science*, **119**, 49 (1954); *Nature*, **172**, 1096 (1953). (b) On the basis of the older planar formulation, the *cis–trans* relationships of the chlorine substituents in the BHC isomers are: α(1,2,4/3,5,6), β(1,3,5/2,4,6), γ(1,2,4,5/3,6), δ(1,2,3,5/4,6), ϵ(1,2,3/4,5,6), η(1,2,3,4/5,6), θ(1,2,3,4,5/6) and ϵ(1,2,3,4,5,6). Those of the benzene tetrachlorides (Table I) are: α(1,4/2,3), β(1,2/3,4), γ(1,3,4/2), δ(1,3/2,4), ϵ(1,2,3/4) and ζ(1,2,3,4).

[8] O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 683 (1947).

[9] Ø. Ellefsen, O. Hassel and E. W. Lund, *ibid.*, **4**, 1145 (1950); G. Calingaert, A. J. Kolka and H. D. Orloff, THIS JOURNAL, **73**, 2359 (1951); R. Riemschneider, *Z. Naturforsch.*, **6b**, 48, 339 (1951).

[10] (a) G. Calingaert, M. E. Griffing, E. R. Kerr, A. J. Kolka and H. D. Orloff, THIS JOURNAL, **73**, 5224 (1951); (b) H. D. Orloff, A. J. Kolka, G. Calingaert, M. E. Griffing and E. R. Kerr, *ibid.*, **75**, 4243 (1953); (c) R. Riemschneider, O. Mater and P. Schmidt, *Monatsh. Chem.*, **84**, 1234 (1953).

[11] In the original presentation of the results of this investigation[1] and in subsequent communications dealing with the new isomers of BHC (10b, 12), the latter have been designated as η and θ. This notation, suggested by Dr. E. J. Crane, Editor, *Chemical Abstracts*, was proposed previously (XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., Sept. 13, 1951) in order to avoid confusion in the literature with the so-called "ζ-hexachlorocyclohexane," m.p. 145°. Subsequently, Riemschneider, *et.al.*,[13] have reported the isolation of one of the new isomers, m.p. 88–89°, by partition chromatography of a BHC isomeric mixture and have employed the designation ζ for it. Bastiansen and Hassel[14] concur in the use of the latter Greek letter.

[12] R. C. Back, *Contrib. Boyce Thompson Inst.*, **16**, 451 (1952).

[13] R. Riemschneider, M. Spät, W. Rausch and E. Böttger, *Monatsh. Chem.*, **84**, 1068 (1953).

[14] O. Bastiansen and O. Hassel, *ibid.*, **85**, 303 (1954).

the chlorination products of β-, γ- and ε-BTC suggested the possible presence of hitherto unknown BHC isomers. Since, of the new hexachlorides, only η(aeaaee) can be formed from α- and β-BTC, and only θ(aeaeee) from γ-BTC (Table II), it should not only be possible to prepare them but also to establish their structures. Both of these objectives have been achieved.

TABLE II

POSSIBLE SYNTHESIS OF η- AND θ-BHC

BTC isomer	New BHC expected *via cis* addition	 *via trans* addition
α	η	..
β	η	..
γ	θ	..
ε	θ	η

In addition to the known hexachlorides expected, the infrared spectra of the chlorination products of β-, and particularly of γ- and ε-BTC, showed[10b] the presence of identified bands which might be attributed to heptachlorocyclohexanes or to hitherto unknown BHC isomers. To facilitate their identification, the reaction products were separated by partition chromatography (Figs. 1–3). Known BHC and unreacted BTC isomers were identified spectrophotometrically, and unidentified components were characterized, wherever possible, by melting point, chlorine analysis and the results of alkaline dehydrochlorination.

η-BHC, m.p. 89.8–90.6° (cor.), was obtained in pure form from both β- and ε-BTC (Figs. 1 and 3, respectively). Its characterization as a benzene hexachloride was confirmed by chemical analysis and by dehydrochlorination with ethanolic alkali to trichlorobenzene. Since this isomer was formed by the chlorination of β-BTC but could not be detected in the reaction product of γ-BTC, its structure can only be aeaaee (Table II). The validity of this conclusion has been confirmed by X-ray[15] and dipole moment[16] investigations and by chemical evidence based on further chlorination to hepta- and octachlorocyclohexane.[13]

In the course of other work dealing with the separation of known hexachloride isomers by partition chromatography of commercial BHC, a fraction eluted between γ- and ε-BHC was found by infrared spectrophotometry to be predominantly η-BHC. Upon rechromatographing the concentrate, a pure sample of the η-isomer was obtained. Because the isomeric mixture used in the separation represented a composite of residues from various solvent extractions, it was not possible to estimate the amount of η-BHC in the original commercial material.

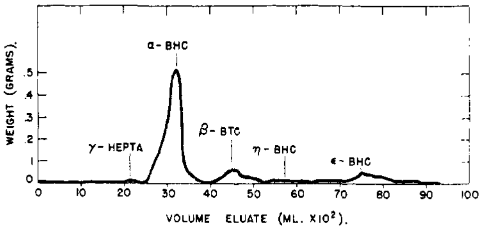

Fig. 1.—Chromatogram of the chlorination products of β-BHC.

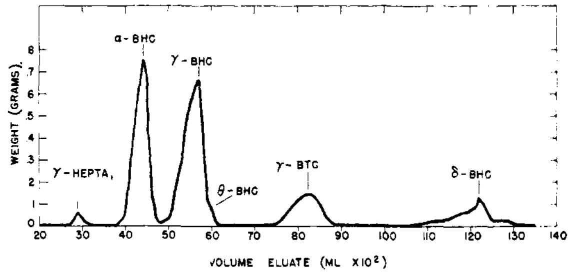

Fig. 2.—Chromatogram of the chlorination products of γ-BHC.

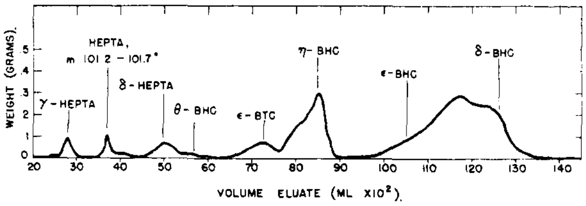

Fig. 3.—Chromatogram of the chlorination products of ε-BHC.

Evidence for the formation of the seventh isomer (θ) of BHC has been obtained from the results of chlorination of γ- and ε-BTC. Its separation in pure form, however, has not been accomplished. As expected, chlorination of γ-BTC gave rise to the three known hexachlorides, α, γ and δ (Fig. 2). Unknown spectral bands in the tailings of the γ-BHC zone indicated the presence of an unknown hexa- or heptachlorocyclohexane in addition to γ-BHC which constituted 50% of its weight. Following alkaline dehydrohalogenation, approximately 90% of the product was found to be trichlorobenzene. The remaining 10%, tetrachlorobenzene, indicated the presence of a corresponding concentration of heptachlorocyclohexane in the original chlorination product. These results strongly suggested the presence of θ-BHC to the extent of 40% in the dehydrochlorinated fraction.

In the chlorination of ε-BTC, a number of unknown components were formed (Fig. 3), of which three were characterized as heptachlorocyclohexanes. Infrared examination of the tailings of the δ-heptachlorocyclohexane zone failed to reveal the presence of a known BHC but did show the presence of an unknown component whose spectral bands were strikingly similar to those of the "θ" component in the preceding experiment. Dehydrohalogenation of the composite containing the unknown compound together with some of the δ-heptachlorocyclohexane yielded tri- and tetrachlorobenzene in the ratio of 3:1. The formation of such an appreciable amount of trichlorobenzene cannot be attributed to a known benzene hexachloride since the presence of the latter would have been detected at a very much lower concentration. Fractional microsublimation of the mixtures containing the unknown from both γ- and ε-BTC, yielded traces of crystals melting at 124–125°, a value which does not correspond to any reported for known hexa- or heptachlorocyclohexanes. These results provide strong

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(15) O. Hassel, XIIIth International Congress of Pure and Applied Chemistry, Stockholm, Sweden, July–August, 1953.

(16) R. G. Schneider and H. Heuer, *Z. Naturforsch.*, **8b**, 695 (1953).

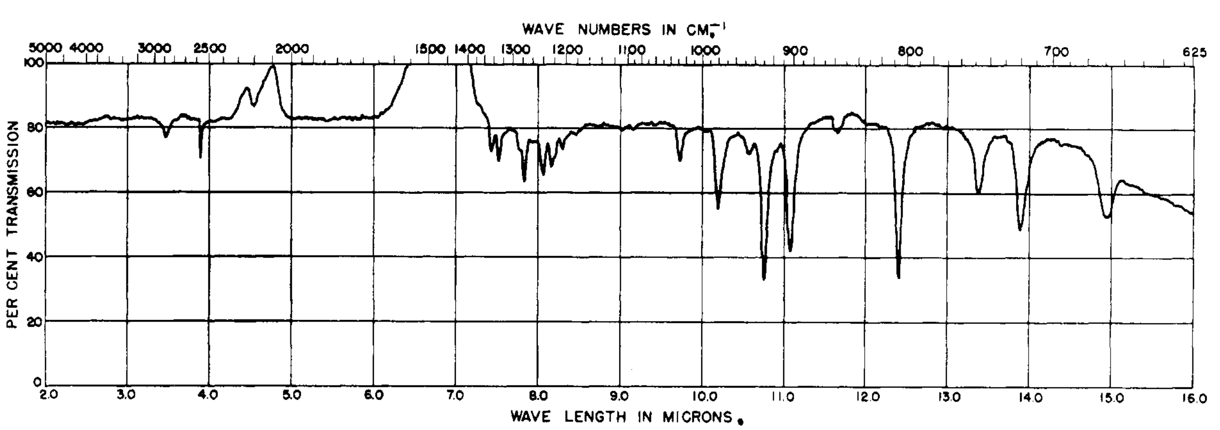

Fig. 4.—Infrared absorption spectrum of η-BHC; concentration 0.1323 g. in 10 ml. in CS_2.

evidence for the presence of the seventh isomer, θ(aeaeee), of BHC in both chlorination products.

The identification of four different benzene hexachlorides in the chlorination products of both γ- and ε-BTC provides conclusive evidence that chlorine addition to a cycloölefin proceeding by a free radical process[10] can take place by two *cis* and two *trans* mechanisms. The chlorine substituents introduced by *cis* addition are oriented ae and ea, those by *trans* addition, ee and aa.

η-BHC showed little or no insecticidal properties[12,13] as compared with the γ-isomer. These results indicate that the activity of γ-BHC is not associated with the presence of a strained *meta* axial orientation, as the latter structure is also present in the η-isomer.

Experimental

Chlorination of BHC Isomers.—The preparation of BHC for the separation of η- and θ-BHC was performed by the photochlorination of purified samples of BTC isomers in carbon tetrachloride.[10a] Approximately 93–96% yields, calculated as BHC, were obtained from 2.5 g. of β-BTC, 7.0 g. of γ-BTC and 6.5 g. of ε-BTC.

Partition Chromatography.—The separation of the chlorination products was effected by partition chromatography in three silicic acid-packed columns (Table III) according to the procedure previously employed.[10b] The eluate from each column was removed in 100-ml. fractions, evaporated to dryness and the residue weights plotted in Figs. 1–3 as a function of eluate volume.

TABLE III

PARTITION CHROMATOGRAPHY OF BTC CHLORINATION PRODUCTS

Chlorination product charged Obtd. from	Wt., g.	Column dimen., cm.	Silicic acid, g.	Results plotted in
β-BTC	3.02	4.5 × 185	1000	Fig. 1
γ-BTC	8.13	5.1 × 195	1500	Fig. 2
ε-BTC	7.94	4.5 × 240	1400	Fig. 3

Identification of Components.—Infrared spectra of samples taken from the beginning and end of each distinct zone were recorded. A middle fraction from each of the larger zones was checked to ascertain homogeneity. Known BHC isomers as well as unreacted BTC were identified readily by this method. Where quantities permitted, unknown components were recrystallized and characterized by melting point, infrared spectrum and alkaline dehydrochlorination.

(1) **η-BHC.**—A composite (2.21 g.) of the fractions eluted between 7700 and 8900 ml. in the chromatography of the chlorination product of ε-BTC (Fig. 3) was dissolved in hexane, slurried at 25° with 0.2 g. of Norit A and filtered. On partial evaporation of the filtrate, 0.90 g. of material, m.p. 89.8–90.6° (cor.), separated as colorless crystals. *Anal.* Calcd. for $C_6H_6Cl_6$: Cl, 73.13. Found: Cl, 73.76. A sample (0.10 g.) was refluxed with 10 ml. of 10% ethanolic KOH for 6 hours, diluted with water and the organic product extracted with carbon disulfide. Infrared examination of the carbon disulfide solution indicated the presence only of trichlorobenzenes, primarily the 1,2,4-isomer (93%) and a smaller amount of the 1,2,3-isomer (7%). These results established the compound as a new isomer of BHC which is designated as η. The infrared spectrum (Fig. 4) of η-BHC, which had been isolated from the chlorination product of ε-BTC, was found to be identical with that of a fraction (5400–6200 ml., Fig. 1) in the chromatogram of the chlorination products of β-BTC. Since β- and ε-BTC, but not γ-BTC, theoretically may form a BHC isomer of structure aeaaee, the configuration of η-BHC is established.

(2) **θ-BHC.**—Partition chromatography (Fig. 2) of the chlorination product of γ-BTC resulted in the separation of the three known hexachlorides, α, γ and δ, as well as some unreacted γ-BTC. These components were identified spectrophotometrically. Two unknown fractions were detected. The first (zone peak 2900 ml.) was subsequently shown to be γ-heptachlorocyclohexane. The second was not separated in pure form. Its presence was indicated by unknown spectral bands which were obtained from the last two eluate fractions (6000–6100 ml.) of the γ-BHC zone. A composite of the two fractions, which contained 0.02 g. of γ-BHC, approximately 50% of the total weight, was dehydrochlorinated with 10% ethanolic KOH to establish whether the unidentified constituent was a hexa- or heptachlorocyclohexane. Approximately 90% of the product from the latter reaction was found by infrared analysis to be trichlorobenzene, chiefly the 1,2,4-isomer; a trace (0.002 g. or 10% of the product) was tetrachlorobenzene, primarily the 1,2,3,4-isomer, which indicated the presence of a corresponding concentration of heptachlorocyclohexane in the original chlorination product. These results strongly suggest the presence of θ-BHC as a major component of the composite.

In the chlorination product of ε-BTC, a number of unknown products were formed (Fig. 3). Three of the latter were characterized as heptachlorocyclohexanes. The spectrum of the fraction eluted at 5500–6000 ml. possessed bands in common with that of the unknown present in the tailings of the γ-BHC zone from the chlorination of γ-BTC and thought to be θ-BHC. Since all other detectable components formed by the chlorination of γ-BTC had been identified, this remaining material was suspected to be the seventh (θ) hexachloride. No bands attributable to other BHC isomers could be detected in the spectrum of the composite, 5500–6000 ml. (Fig. 3). Furthermore, this fraction was well separated by an intervening heptachlorocyclohexane and unreacted ε-BTC from other BHC isomers. Because the unidentified material was contaminated with δ-heptachlorocyclohexane (zone peak 5000 ml.), m.p. 142–143°, alkaline dehydrochlorination of the composite was expected to yield tetrachlorobenzene (from the heptachlorocyclohexane) and, if the unknown were indeed θ-BHC, trichlorobenzene. Infrared analysis showed that both tetra- and trichlorobenzenes were formed in the ratio of 3:1. This result confirms that the unknown product was a BHC isomer. It was possible by microsublimation to effect some 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).

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[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]

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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).