# **1344.** *Compounds of Silicon. Part V.*[1] *Octaisopropylsilsesquioxane, its Bromination, and* $^1$H *Nuclear Magnetic Resonance Spectroscopy*

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The factors influencing the formation of octaisopropylsilsesquioxane have been investigated. This compound can be brominated by means of *N*-bromosuccinimide. Chemical evidence and $^1$H n.m.r. spectroscopy show the bromination to occur in the $\alpha$-position of the isopropyl groups.

VARIOUS yields of discrete oligomers $(RSiO_{1\cdot5})_n$ (where $n = 4, 6, 8, \ldots$, R = alkyl or aryl) have been obtained by the controlled hydrolysis of trifunctional organosilicon compounds or by the pyrolysis of suitable higher polymers obtained from these.[2-12] These oligomers consist of highly symmetrical three-dimensional molecules built up of trifunctional siloxane units which form cage-like structures, similar to that of adamantane, and of a number of inorganic compounds, such as phosphorus pentoxide, $P_4O_{10}$ (see ref. 13 for a review).

The octameric ($T_8$) species are the best known, and the structures of some members of this group have been determined by *X*-ray crystallography.[14] (For nomenclature see refs. 6—8.)

The reactions of the organic groups, R, in these compounds have been little investigated. The lack of reactivity of octaethyl-$T_8$, $(EtSiO_{1\cdot5})_8$, has been noted [3] and the nitration and

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bromination of various octa-aryl-$T_8$ compounds in all their aryl side-chains have been reported.[4] Up to now unsymmetrical cage-like compounds, with only some of the organic side-chains substituted, have not been described.

Numerous attempts at repeating the preparation of tetraisopropyl-$T_4$ failed.[12] Attention was therefore turned to octaisopropyl-$T_8$, a stable compound of known structure.[14] Using Olsson's method,[3] octaisopropyl-$T_8$ was prepared by heating under reflux a dilute solution of the hydrolysate of isopropyltrichlorosilane in strong methanolic hydrogen chloride. The product precipitated from the boiling solution; a small amount of waxy material was also obtained on cooling. After 3—4 days under reflux, the formation of octaisopropyl-$T_8$ practically ceased. However, if hydrogen chloride was passed into the cooled, filtered solution until a cloudiness appeared, further octaisopropyl-$T_8$ formed on refluxing. Repetition of this process gave octaisopropyl-$T_8$, accompanied by increasing proportions of waxy materials, which eventually became the sole product. Concentration of the reaction mixture did not result in the formation of further octaisopropyl-$T_8$. The yield of 30% (compared with the 17% obtained by Olsson) appears to be the maximum attainable by this method.

The hydrogen chloride is probably not just a catalyst since, for this, such high concentrations would hardly be necessary. It probably also aids the precipitation (and hence the formation) of the octamer by reducing its solubility, effectively removing methanol by solvation. Loss of hydrogen chloride from the boiling solution causes the solubility of the product to rise to its equilibrium concentration and thus its precipitation ceases. The importance of solubility factors is demonstrated by the fact that very little octaisopropyl-$T_8$ is obtained if its solubility in the reaction mixture is increased by replacing half the methanol by tetrahydrofuran, in which the cage compound is more soluble. Pure octaisopropyl-$T_8$ is disrupted by methanolic hydrogen chloride in the presence of acetone, another good solvent for this compound, showing that in solution its formation and decomposition are, at least in part, reversible.

Addition of the waxy by-product obtained in octamer preparations to a fresh reaction mixture increased the speed of formation of octaisopropyl-$T_8$, but not its overall yield, suggesting that the by-product itself did not contain significant amounts of the precursors of the cage compound. Little octaisopropyl-$T_8$ could be obtained from the by-product under a variety of conditions. This confirms the views of Sprung and Guenther [9] that the precursors of $T_8$ compounds under acid conditions have specific structures and can condense to cage-like molecules.

Octaisopropyl-$T_8$ was brominated readily by *N*-bromosuccinimide in the presence of benzoyl peroxide and ultraviolet light. Products containing up to about nine bromine atoms per molecule were obtained. Increasing degrees of bromination were accompanied by decreasing solubilities and volatilities of the materials. Their infrared spectra showed that the siloxane cage was still intact, and progressive changes with increasing bromination showed the structural similarities of the materials. Their chemical inertness suggested that bromination had occurred in the $\alpha$-position of the isopropyl groups as $\beta$-halogenoalkyl groups are usually very readily cleaved from silicon.[15]

Clear evidence that the bromine atoms are substituted on the $\alpha$-carbon atoms of the isopropyl groups is provided by $^1H$ n.m.r. spectroscopy. Two materials, corresponding stoicheiometrically to $(C_3H_6Br)(C_3H_7)_7(SiO_{1\cdot5})_8$ and $(C_3H_6Br)_2(C_3H_7)_6(SiO_{1\cdot5})_8$, were examined. The n.m.r. spectrum of octaisopropyl-$T_8$ showed a band at $\tau$ 8·95 with a shoulder at 8·93. A C–Me group is in general less shielded than an Si–Me, and the same can be anticipated for C–CH and Si–CH; hence, little chemical shift is to be expected between the methyl and methine protons of Si–CHMe$_2$. The brominated material analysing for $(C_3H_6Br)(C_3H_7)_7(SiO_{1\cdot5})_8$ gave a spectrum with bands at $\tau$ 8·98 and 8·20. The half-height band-widths were approximately equal, and thus the ratio of band heights, 1 : 0·1, gave

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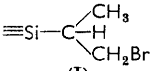
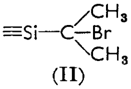
an approximate measure of the relative intensities. If the bromine atom were in a β-position, as in (I), a doublet at *ca.* τ 7·0 [16a] would be expected for the methylene protons


(I)


(II)

and the intensity ratios of the doublet to the remainder of the absorption should be 2 : 53. However, for the alternative structure (II), we should predict [16b] two absorption peaks at τ 8·14 and 8·95 in intensity ratio 6 : 49. Clearly, both the intensities and the chemical shifts favour structure (II). The spectrum of the material analysing as $(C_3H_6Br)_2(C_3H_7)_6(SiO_{1\cdot5})_8$ again showed two peaks, at τ 8·95 and 8·20, with heights in the ratio 1 : 0·36, so that bromination is again in the α-position (the predicted intensity ratio here is 42 : 12).

A total of eight bromine atoms can be introduced into α-positions. It is rather unlikely that the bromination of one isopropyl group will substantially affect the reactivity of the others, because of the distance by which they are separated in a formally saturated system. The material analysing for, say, a dibromo-derivative is likely to be a mixture of isomers and/or compounds of varying degrees of substitution.

We experienced initially considerable difficulties in trying to separate and characterise individual molecular species. Melting point and mixed melting point determinations were of very limited value. Attempts to separate the compounds by vacuum fractional sublimation or gas–liquid chromatography were unsuccessful. Column adsorption chromatography was of only limited value as the compounds eluted very rapidly under all experimental conditions tried. Thin-layer chromatography, however, indicated that materials analysing for a given degree of bromination were in fact mixtures of at least four compounds.

Some chemical studies were carried out with brominated products separated from non-octameric impurities. The compounds were found to be uniformly unreactive. Dehydrobromination by pyridine could be brought about at 200°, but attempted halogen exchange with sodium iodide or with sodium thiocyanate, even at 250°, failed, although in the latter case some dehydrobromination occurred. No reaction was observed with methylmagnesium iodide in ether or tetrahydrofuran, or with n-butylmagnesium bromide in ether. Aniline, n-butylamine, or ammonia brought about dehydrobromination but did not yield substituted amino-derivatives. Brominated products of the octaethyl-$T_8$ compound also dehydrobrominated thermally, as well as in the presence of pyridine.

## EXPERIMENTAL

Isopropyltrichlorosilane was prepared by the method of Booth and Spessard.[17] Attempted preparation of tetraisopropyl-$T_4$ by the method of Wiberg and Simmler [12] was unsuccessful. Variation of the temperature and time of reaction, and of the method of working-up, still gave only intractable mixtures.

*The Synthesis of Octaisopropyl-*$T_8$.—*The effect of hydrogen chloride.* Octaisopropyl-$T_8$ was prepared by Olsson's method [3] using methanol (2300 ml.), isopropyltrichlorosilane (120 ml.), saturated methanolic hydrogen chloride (1450 ml.), and concentrated hydrochloric acid (110 ml.). After 3 days under reflux a white solid was obtained on filtration. The octameric product was freed from waxy material by recrystallisation from ethyl acetate in which the latter was much more soluble. Hydrogen chloride was passed into the filtrate until a cloudiness appeared, and the mixture was heated under reflux for a further 3 days. This process was repeated until no more octaisopropyl-$T_8$ was obtained (total reflux time 700 hr.). Three recrystallisations from ethyl acetate were necessary to remove the large proportion of waxy material from the last batch of product. Total yield, 20 g. (30%), m. p. 314—316° (lit.,[3] 300°) (Found: C, 37·6; H, 7·6; Si, 29·2. Calc. for $C_{24}H_{56}O_{12}Si_8$: C, 37·9; H, 7·4; Si, 29·5%).

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[16] L. M. Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, London, 1959, (*a*) p. 59; (*b*) p. 53.

[17] H. S. Booth and D. B. Spessard, *J. Amer. Chem. Soc.*, 1946, **68**, 2660.

*Bromination of Octaisopropyl*-$T_8$ *and Octaethyl*-$T_8$.—Octaisopropyl-$T_8$ was readily brominated by *N*-bromosuccinimide in refluxing carbon tetrachloride in the presence of ultraviolet light and a trace of benzoyl peroxide. The degree of bromination depended on the amount of *N*-bromosuccinimide used, 50% being the maximum amount of bromine which could be introduced by this method. For example, reaction with one equivalent of *N*-bromosuccinimide yielded a material analysing for a *monobromo-derivative*, m. p. 324—326° (Found: C, 34·9; H, 6·8; Br, 8·7. $C_{24}H_{55}BrO_8Si_{12}$ requires C, 34·3; H, 6·6; Br, 9·5%). Octaethyl-$T_8$ reacted less readily. Bromination with elemental bromine also proceeded readily, but only 24% bromine could be introduced by this method.

*Dehydrobromination of Brominated Octaisopropyl*-$T_8$ *and Octaethyl*-$T_8$.—The brominated octaisopropyl-$T_8$ materials were dehydrobrominated by heating to $>200°$ with pure, dry pyridine in Carius tubes. The infrared spectra and m. p.s showed differences from those of the starting materials, the products forming rhombic crystals and, like octaisopropyl-$T_8$, they were easily purified by recrystallisation from ethyl acetate. For example, a material analysing for a monobromo-derivative gave eventually a bromine-free product, m. p. 306—310° (Found: C, 38·3; H, 7·8; Si, 30·1. Calc. for $C_{24}H_{54}O_{12}Si_8$: C, 38·0; H, 7·2; Si, 29·6%).

*Infrared and* $^1$H *N.m.r. Spectra* [A. R. K.].—Infrared spectra were obtained in potassium bromide discs using a Perkin-Elmer Infracord spectrophotometer. $^1$H N.m.r. spectra were obtained in carbon tetrachloride solution using a Perkin-Elmer permanent-magnet spectrometer operating at 40 Mc./sec.

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