

Perchlorophenyl-silicon Compounds. Crystal and Molecular Structure of Perchlorotriphenylsilane

Luis Fajari,^a Luis Juliá,^{a*} Juan Riera,^a Carlos Miravittles,^b and Elies Molins^b

^a Departamento de Materiales Orgánicos Halogenados, Centro de Investigación y Desarrollo (C.S.I.C.), Jorge Girona Salgado, 18-26, 08034 Barcelona, Spain

^b Instituto de Ciencia de Materiales (C.S.I.C.), Martí i Franqués, s/n, 08028 Barcelona, Spain

The synthesis of tris(pentachlorophenyl)silane (**1**), perchlorotriphenylsilane (**2**), and bromotris(pentachlorophenyl)silane (**3**) are reported for the first time, the hydrolysis of (**2**) and (**3**) under neutral conditions giving tris(pentachlorophenyl)silanol (**4**); the structure of the silane (**2**) has been established by X-ray crystallography.

While tris(pentafluorophenyl)silane and corresponding halogenosilane derivatives have been extensively studied,¹ little is known about the corresponding pentachlorophenyl derivatives. Glidewell *et al.*² attempted to prepare perchlorotriphenylsilane (**2**) by use of the reagent BMC³ ($S_2Cl_2-AlCl_3-SO_2Cl_2$), but it was only obtained in traces. Gilman *et al.*⁴ were unable to prepare (**2**) *via* pentachlorophenylmagnesium chloride and silicon tetrachloride. We now report the synthesis of tris(pentachlorophenyl)silane (**1**), and of some of its derivatives by replacement of hydrogen by chlorine, bromine, and hydroxy groups, and the determination of the crystal structure of (**2**) by X-ray analysis (Figure 1).†

The silane (**1**) was synthesized (49% yield) from pentachlorophenylmagnesium chloride and trichlorosilane. The silane (**1**) is converted into the perchlorosilane (**2**) (100%) by u.v. irradiation in CCl_4 , as occurs for similar compounds.⁵ Bromination of (**1**) in CCl_4 gave bromotris(pentachlorophenyl)silane (**3**) (100%). In contrast with fluorotris(pentachlorophenyl)silane, which is readily hydrolysed under neutral conditions yielding pentachlorobenzene,⁴ we have been able to hydrolyse the silicon-halogen bond of (**2**) or (**3**) preferentially yielding tris(pentachlorophenyl)silanol (**4**). The

treatment of both (**2**) and (**3**) with NaOH in dimethyl sulphoxide gives pentachlorobenzene. All the new compounds have been characterized by elemental analysis and i.r. spectroscopy.

The crystal structure of (**2**) shows mean values of the Cl-C and C-C bond distances of 1.723(7) and 1.386(9) Å, respectively. The three Si-C bond distances are similar (*ca.* 1.91 Å) and Si-Cl is 2.053(6) Å, all slightly longer than average literature values.⁸ The Cl-Si-C bond angles are all *ca.* 105°, with C-Si-C *ca.* 114°. These values show distortion of the

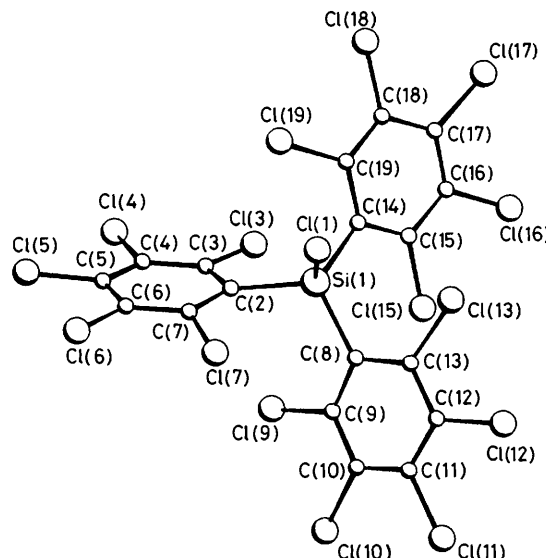
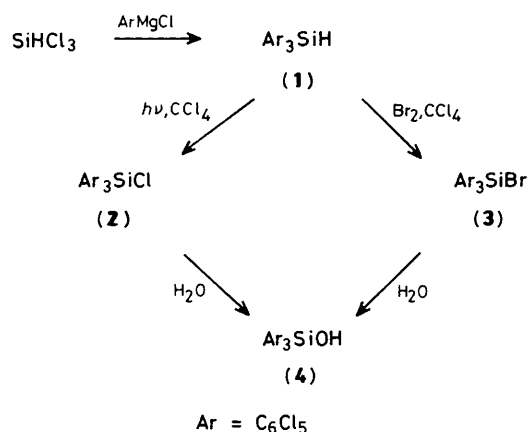


Figure 1. Perspective view of (**1**) with atom numbering. Selected distances: Si(1)-C(2) 1.910(6), Si(1)-C(8) 1.902(6), Si(1)-C(14) 1.915(6), Si(1)-Cl(1) 2.053(2) Å; selected angles: C(2)-Si(1)-Cl(1) 105.1(2), C(8)-Si(1)-Cl(1) 105.2(2), C(14)-Si(1)-Cl(1) 104.2(2), C(2)-Si(1)-C(8) 113.1(3), C(2)-Si(1)-C(14) 113.4(3), C(8)-Si(1)-C(14) 114.4(3)°.

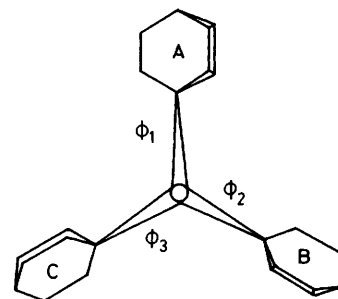


Figure 2. Conformational torsion angles.

† Crystal data, $C_{18}Cl_{16}Si$, $M = 811.3$, monoclinic, $a = 10.259(1)$, $b = 13.044(1)$, $c = 21.301(3)$ Å, $\beta = 92.25(1)^\circ$, $U = 2848.2$ Å³, $Z = 4$, $D_c = 1.89$ g cm⁻³, Mo-K α radiation (graphite monochromator), $\lambda = 0.71069$ Å, $\mu = 16.1$ cm⁻¹, space group $P2_1/n$. Well formed colourless crystals. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer in the range $1 < \theta < 25^\circ$. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN 11/84⁶ and refined by full-matrix least-squares technique with SHELX-76⁷ to $R = 0.052$ and $R_w = 0.054$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

tetrahedral environment around silicon due to steric repulsions between the perchlorophenyl groups.

The conformation of the three perchlorophenyl rings can be described by the torsion angles between the Cl–Si–C planes and the corresponding mean planes of the phenyl rings, ϕ_1 (50.0°), ϕ_2 (48.6°), and ϕ_3 (45.9°) (Figure 2), indicating an approximate CCC conformation belonging to the symmetry group $C_3(3)$.⁹ This conformation is determined by the shortest intramolecular Cl ··· Cl distances (apart from those within a particular C_6Cl_5 group), from which two types can be distinguished. The shortest distances involve Cl(1) [Cl(1) ··· Cl(7) 3.18, Cl(1) ··· Cl(13) 3.20, Cl(1) ··· Cl(19) 3.21 Å], and the others Cl(3), Cl(9), and Cl(15), with Cl ··· Cl distances ranging between 3.6 and 4.1 Å. Also, owing to strong steric repulsions, the phenyl rings are slightly twisted towards a boat conformation (r.m.s.d. of mean plane 0.02 Å) and some chlorine atoms [mainly Cl(3), Cl(7), Cl(9), Cl(13), Cl(15), and Cl(19)] lie significantly out of the mean plane of their phenyl ring.

The compact crystal packing indicated by a relatively high density is confirmed by numerous short Cl ··· Cl intermolecular distances, the shortest being Cl(16) ··· Cl(11)ⁱ (3.362 Å, $i = -1,0,0$). This high density is reflected in the hardness of the crystals and their high m.p. (304 °C).

We thank the C.S.I.C. and the Vallés Industrias Orgánicas S.A. for financial support of this work.

Received, 18th August 1986; Com. 1193

References

- 1 E. Hengge, E. Starz, and W. Strubert, *Monatsh. Chem.*, 1968, **99**, 1787; M. F. Lappert and J. Lynch, *Chem. Commun.*, 1968, 750; R. R. Schrieke and B. O. West, *Aust. J. Chem.*, 1969, **22**, 49; M. Weidenbruch and N. Wessal, *Chem. Ber.*, 1972, **105**, 173; G. Haegeler and M. Weidenbruch, *ibid.*, 1973, **106**, 460; C. Eaborn and I. D. Jenkins, *J. Organomet. Chem.*, 1974, **69**, 185; M. A. Lopatin, V. A. Kiznetsov, A. N. Egorochkin, and M. N. Bochkarev, *J. Gen. Chem. USSR*, 1979, **49**, 1983.
- 2 C. Glidewell and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1977, 915; A. F. Andrews, C. Glidewell, and J. C. Walton, *J. Chem. Res.*, 1978, (S), 294; (M) 3683.
- 3 M. Ballester, C. Molinet, and J. Castañer, *J. Am. Chem. Soc.*, 1960, **82**, 4254; M. Ballester and S. Olivella, in 'Polychloroaromatic Compounds,' ed. H. Suschitzky, Plenum Press, London and New York, 1974.
- 4 F. W. G. Fearon and H. Gilman, *J. Organomet. Chem.*, 1966, **6**, 577.
- 5 M. J. S. Gynane, M. F. Lappert, P. I. Riley, P. Riviere, and M. Riviere-Baudet, *J. Organomet. Chem.*, 1980, **202**, 5.
- 6 P. Main, G. Germain, and M. M. Woolfson, Multan 11/84. A System of computer programs for the automatic solution of crystal structures from X-ray diffraction data., Universities of York, England, and Louvain, Belgium, 1984.
- 7 G. M. Sheldrick, SHELX 76. Program for crystal structure determination. University of Cambridge, 1976.
- 8 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham (present distributor, D. Reidel, Dordrecht), 1974, pp. 257, 275.
- 9 J. D. Dunitz, in 'X-Ray Analysis and the Structure of Organic Molecules,' Cornell University Press, Ithaca and London, 1979, p. 466.