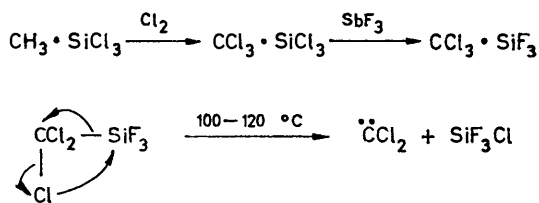


Carbene Chemistry. Part V.¹ A Route to Dichlorocarbene in the Vapour Phase²

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The thermal decomposition of trifluoro(trichloromethyl)silane in the vapour phase at 140 °C in the presence of the olefins cyclohexene, CMe₂:CMe₂, CMe₂:CHMe, CMe₂:CH₂, CH₂:CH₂, CH₂:CF₂, and CCl₂:CCl₂ leads to high yields (>85% in most cases) of the corresponding *gem*-dichlorocyclopropanes. The reaction is stereospecific with *cis*- and *trans*-but-2-ene, and an almost quantitative breakdown of the silane into dichlorocarbene and chlorotrifluorosilane is inferred.

SEVERAL reactions leading to the generation of dichlorocarbene have been reported in recent years, and the use of these for the synthesis of *gem*-dichlorocyclopropanes is well established.³ Many of the methods for dichlorocarbene generation in solution necessitate the presence of a strong base, which may destroy the carbene before its reaction with a comparatively unreactive or volatile substrate can take place. The thermal⁴ or iodide-ion catalysed⁵ decomposition of trihalogenomethylmercury compounds in solution has provided a source of dichlorocarbene under conditions where its reaction with olefins deactivated towards electrophilic attack (*e.g.* tetrachloroethylene) gives good yields of cyclopropanes. An alternative convenient source of dichlorocarbene in the gas phase, or in solution, at moderate temperatures is now described.



The thermal decomposition of trichloro(trichloromethyl)silane provides dichlorocarbene in good yield,^{1,2} but the low volatility of the silane (m.p. 116 °C; b.p. 156 °C) and its high decomposition temperature¹ (>230 °C) restrict its use for gas-phase carbene generation. Halogen exchange with antimony trifluoride yields trifluoro(trichloromethyl)silane,⁶ b.p. 43.5 °C; thermal decomposition of this readily accessible trifluorosilane in the gas phase begins at about 100 °C, and is complete after 24 h at 120 °C. Increase in the electron-deficiency of the silicon due to the attached fluorine atoms has clearly made it more susceptible to intramolecular nucleophilic attack by a neighbouring halogen atom (*cf.* refs. 1 and 2).

¹ Part IV, W. I. Bevan and R. N. Haszeldine, *J.C.S. Dalton*, in the press.

² Preliminary publication, W. I. Bevan, J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, 'Organic Reaction Mechanisms,' *Chem. Soc. Special Publ.* No. 19, 1965, p. 174; see also R. N. Haszeldine, 'Polyfluoroalkyl Silicon Compounds,' in 'New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 115.

³ E. Chinoporos, *Chem. Rev.*, 1963, **63**, 235; W. Kirmse, 'Carbene Chemistry,' Academic Press, London, 1964; T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes and Arynes,' Nelson, London, 1969.

Reactions with Olefins.—The thermal decomposition of trifluoro(trichloromethyl)silane vapour at 140 °C in the presence of a six-molar excess of cyclohexene, 2,3-dimethylbut-2-ene, 2-methylbut-2-ene, isobutene, ethylene, or 1,1-difluoroethylene, at a total pressure of about 1 atm, gives 85–95% yields of the corresponding *gem*-dichlorocyclopropane. Under identical conditions, tetrachloroethylene gives hexachlorocyclopropane in 69% yield. Stereospecific addition to *cis*- or *trans*-but-2-ene gives the corresponding *cis*- or *trans*-1,1-dichloro-2,3-dimethylcyclopropane in >90% yield with no trace of isomerisation products; this implies generation of singlet state dichlorocarbene. Chlorotrifluorosilane is the main volatile product, and traces of silicon tetrafluoride and dichlorodifluorosilane are doubtless formed by disproportionation. The cyclopropanes formed are identical with samples obtained by the reaction of the parent olefins with chloroform and potassium *t*-butoxide; the stereospecific character of the latter process is well established,^{7,8} but the yields of adducts obtained are usually much lower.

Small amounts of chloroform (2 and 7%), produced during the reactions with the but-2-enes, may arise from trichloromethyl radicals produced by homolysis of the carbon-silicon bond in the silane, but the reaction of dichlorocarbene with hydrogen chloride, produced in small amounts in the system *via* hydrogen-abstraction by chlorine atoms, seems a more likely route.⁹

EXPERIMENTAL

G.l.c. analysis was carried out on a Perkin-Elmer 154B or 116 instrument; columns (2 m × 4 mm int. diam.) were packed with 30% (w/w) stationary phase on 80-mesh Celite. The instrument was calibrated with standard mixtures of the pure components for each analysis. I.r. spectra were recorded on a Perkin-Elmer 21 spectrophotometer, and molecular weights were determined by Regnault's method unless otherwise stated.

Trifluoro(trichloromethyl)silane.—Trichloro(trichloromethyl)silane was obtained in *ca.* 90% yield by chlorination

⁴ D. Seyferth, R. J. Minasz, A. J. H. Treiber, J. M. Burlitch, and S. R. Dowd, *J. Org. Chem.*, 1963, **28**, 1163.

⁵ D. Seyferth, M. Gordon, J. Yick-Pui Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1967, **89**, 959.

⁶ R. Mueller, S. Reichel, and C. Dathe, *Chem. Ber.*, 1964, **97**, 1673.

⁷ W. E. Doering and W. A. Henderson, *J. Amer. Chem. Soc.*, 1958, **80**, 5274.

⁸ R. A. Moss and R. Gersth, *J. Org. Chem.*, 1967, **32**, 2268.

⁹ F. Anderson, J. M. Birchall, R. N. Haszeldine, and B. J. Tyler, unpublished observations.

of methyltrichlorosilane;¹⁰ sublimation *in vacuo* gave material of m.p. 115.5–161 °C (lit.,¹⁰ 116 °C), but the highly purified material was often difficult to fluorinate and omission of the sublimation usually gave better results. Although fluorination in xylene has been reported to give excellent yields,⁶ we have found the following procedure more dependable.

The reaction between trichloro(trichloromethyl)silane (27.4 g, 0.109 mol), antimony trifluoride (39.0 g, 0.218 mol), and antimony pentachloride (3 drops) was initiated by gentle warming, which was continued only when the initial reaction had subsided. Heating under reflux (condenser at –78 °C) was continued for a further 10 min, and the volatile products were then distilled off under reduced pressure. Fractionation in a high-vacuum apparatus gave trifluoro(trichloromethyl)silane (9.8 g, 45%) (Found: C, 6.1; Cl, 52.4; ionisable F, 27.9%; *M*, 204. Calc. for CCl₃F₃Si: C, 5.9; Cl, 52.4; F, 28.0%; *M*, 204), b.p. (isoteniscope) 43.5 °C at 760 mmHg (lit.,⁶ b.p. 45 °C).

Reactions with Olefins.—In each of these experiments, trifluoro(trichloromethyl)silane and the olefin, in the molar ratio 1 : 6, were sealed *in vacuo* in a Pyrex flask (2350 ml) fitted with a 'cold-finger' to facilitate loading. The flask was placed in an electric oven, the temperature of which was raised to 140 °C during *ca.* 3 h, so that liquid olefins were completely vaporised before the silane began to decompose. The initial total pressure in each case was about 1.2 atm at 140 °C, and this temperature was maintained for 24 h. The volatile products were transferred directly to a high-vacuum apparatus and separated by fractional condensation.

(a) *Cyclohexene*. The silane (2.41 g) and this olefin (5.80 g) gave 7,7-dichloronorcarane (1.74 g, 89%) (g.l.c. *via* Silicone MS 550; 204 °C) and chlorotrifluorosilane (1.37 g) (Found: *M*, 114. Calc. for SiClF₃: *M*, 120.5) containing (g.l.c.; dinonyl phthalate; 20 °C) silicon tetrafluoride and dichlorodifluorosilane.

(b) *2,3-Dimethylbut-2-ene*. The silane (2.13 g) and this olefin (5.30 g) gave 1,1-dichloro-2,2,3,3-tetramethylcyclopropane (1.54 g, 88%) (Found: C, 50.1; H, 7.0; Cl, 42.5. Calc. for C₇H₁₂Cl₂: C, 50.3; H, 7.2; Cl, 42.5%), m.p. 50 °C (lit.,⁷ 49.8–50.5 °C), showing no C=C i.r. absorption.

(c) *2-Methylbut-2-ene*. The silane (2.21 g) and the olefin (4.55 g) gave chromatographically pure (Silicone MS 550; 120 °C) 1,1-dichloro-2,2,3-trimethylcyclopropane (1.50 g, 95%) (Found: C, 46.9; H, 6.7; Cl, 46.2. Calc. for C₈H₁₀Cl₂: C, 47.1; H, 6.5; Cl, 46.4%), b.p. (isoteniscope) 151 °C at 760 mmHg, 64.5 °C at 47 mmHg (lit.,⁷ 64.3–64.7 °C at 47 mmHg).

(d) *Isobutene*. Two distillations *in vacuo* of the product from the silane (2.42 g) and this olefin (3.99 g) gave pure 1,1-dichloro-2,2-dimethylcyclopropane (1.57 g, 95%) (Found: C, 43.0; H, 5.7. Calc. for C₆H₈Cl₂: C, 43.2; H, 5.8%), b.p. 119 °C at 760 mmHg (lit.,⁶ 119.5–120 °C).

(e) *Ethylene*. The silane (2.19 g) and the olefin (1.81 g) similarly yielded 1,1-dichlorocyclopropane (1.02 g, 86%) (Found: C, 32.2; H, 3.8; Cl, 63.8. Calc. for C₃H₄Cl₂: C, 32.4; H, 3.6; Cl, 64.0%), b.p. 75 °C at 760 mmHg (lit.,¹¹ 75 °C).

(f) *1,1-Difluoroethylene*. The silane (2.17 g) and 1,1-difluoroethylene (4.10 g) gave 1,1-dichloro-2,2-difluorocyclopropane (1.22 g, 85%) (Found: C, 24.4; H, 1.3; Cl, 48.6; F, 26.0%; *M*, 147. C₃H₂Cl₂F₂ requires C, 24.5; H, 1.3; Cl, 48.3; F, 25.9%; *M*, 147), b.p. (isoteniscope) 61 °C at 760 mmHg; λ_{max} (vapour) 6.39, 6.51, 6.70, 6.97, 7.40, 7.63, 7.89, 8.26, 8.40, 9.49, 9.74, 10.00, 10.48, 11.18, 11.53, 11.87, 12.30, and 12.73 μm.

(g) *Tetrachloroethylene*. The involatile (room temperature) residue from the reaction of the silane (2.33 g) with tetrachloroethylene (11.40 g) was removed from the flask with ether, sublimed *in vacuo*, and recrystallised twice from ethanol-ether, to give white needles of hexachlorocyclopropane (2.05 g, 69%) [Found: C, 14.2; Cl, 84.1%; *M* (vapour pressure osmometry), 250. Calc. for C₃Cl₆: C, 14.4; Cl, 85.5%; *M*, 249], m.p. 103–105 °C (lit.,¹² 103.5–104.5 °C).

(h) *trans-But-2-ene*. The silane (2.10 g) and *trans*-butene (3.47 g) gave 1,1-dichloro-*trans*-2,3-dimethylcyclopropane (1.32 g, 92%) and chloroform (0.09 g, 7%); there was no trace of the *cis*-cyclopropane (g.l.c.; trixylyl phosphate; 102 °C). The recovered *trans*-butene contained no *cis*-isomer. Identification of the *trans*-cyclopropane was facilitated by comparison with a pure specimen (Found: C, 43.3; H, 5.7; Cl, 50.7. Calc. for C₆H₈Cl₂: C, 43.2; H, 5.8; Cl, 51.0%), b.p. 120.5–121.5 °C, obtained in 35% yield from *trans*-butene, chloroform, and potassium *t*-butoxide.⁸

(i) *cis-But-2-ene*. The silane (2.16 g) and *cis*-butene (3.56 g) gave 1,1-dichloro-*cis*-2,3-dimethylcyclopropane (1.37 g, 93% yield) and chloroform (0.03 g, 2%); no *trans*-cyclopropane or *trans*-but-2-ene was detected. A specimen of the cyclopropane (Found: C, 43.0; H, 5.8; Cl, 50.8%), b.p. 128–129 °C, was obtained in 44% yield by the butoxide route.⁸

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