

Carbene Chemistry. Part IX.¹ Some C-H Insertion Reactions of Dichlorocarbene in the Gas Phase

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Dichlorocarbene, from the thermal decomposition of trifluoro(trichloromethyl)silane at 140–180 °C in the gas phase, gives good yields of α -C-H insertion products with ethylbenzene, cumene, diethyl ether, 2-methoxypropane, and tetrahydrofuran. The tertiary C-H bond of isobutane is 70 times more reactive than a C-H bond of cyclohexane at 140 °C, and no products of insertion into primary C-H bonds have been identified with certainty. Dichlorocarbene reacts with cyclopentadiene at 180 °C to give chlorobenzene (58%) and with indene to give 2-chloronaphthalene (69%).

THE unique value of trifluoro(trichloromethyl)silane as a source of dichlorocarbene in the gas phase has been described in relation to its decomposition at *ca.* 140 °C in the presence of olefins,² and kinetic evidence for the rate-determining formation of the free carbene has also been advanced.¹ The use of the silane for the first study of gas-phase C-H insertions by dichlorocarbene is now reported. Previous studies of such insertion reactions under mild conditions have been confined to the liquid phase and, with the notable exception of the work on

trihalogenomethylmercurials,^{3,4} have given only low yields of insertion products.^{5,6}

Reactions with Hydrocarbons.—In these reactions, trifluoro(trichloromethyl)silane was heated with a four- to six-fold excess of the hydrocarbon under conditions where both reactants were completely vaporised at the reaction temperature (180 °C; 1.2–1.5 atm total pressure). Under these conditions, ethylbenzene and cumene give the products of benzylic insertion of dichlorocarbene (PhCHMe·CHCl₂ and PhCMe₂·CHCl₂, respectively) in yields (32 and 57%) very similar to those obtained with (bromodichloromethyl)phenylmercury at 80 °C in the

¹ Part VIII, F. Anderson, J. M. Birchall, R. N. Haszeldine, and B. J. Tyler, *J.C.S. Perkin II*, 1975, 1051.

² R. N. Haszeldine in 'New Pathways in Inorganic Chemistry,' eds. E. A. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge Press, Cambridge, 1968; J. M. Birchall, G. N. Gilmore, and R. N. Haszeldine, *J.C.S. Perkin I*, 1974, 2530.

³ D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, 1963, **85**, 2667; D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne, and C. J. Attridge, *J. Org. Chem.*, 1970, **35**, 1989; D. Seyferth and Y.-M. Cheng, *Synthesis*, 1974, 114; D. Seyferth and X. M. Cheng, *J. Amer. Chem. Soc.*, 1971, **93**, 4072; 1973, **95**, 6763.

⁴ D. Seyferth, V. A. Mai, and M. E. Gordon, *J. Org. Chem.*, 1970, **35**, 1993.

⁵ E. K. Fields, *J. Amer. Chem. Soc.*, 1962, **84**, 1744; E. V. Dehmlow, *Tetrahedron*, 1971, **27**, 4071; M. Makosza and M. Fedorynski, *Roczniki Chem.*, 1972, **46**, 311 (*Chem. Abs.*, 1972, **76**, 153 254e).

⁶ J. C. Anderson and C. B. Reese, *Chem. and Ind.*, 1963, 575; J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 1964, 4874.

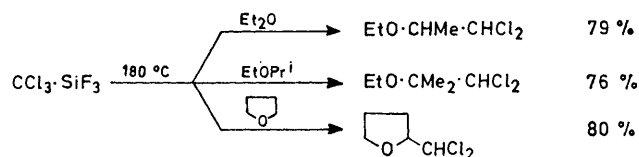
liquid phase.³ No products derived from insertion into the primary C-H bonds in the β -positions of these substrates were detected.

An attempt to effect the previously unreported insertion of dichlorocarbene into the benzylic C-H bonds of toluene under the same conditions was less successful. A fraction of b.p. corresponding to that of 1,1-dichloro-2-phenylethane was obtained in low yield (<8%), but contamination with hexachlorobutadiene (a decomposition product of the silane) prevented purification on the scale employed, and identification of the insertion product rests solely on mass spectrometry. It is, however, improbable that the product of molecular formula $C_8H_8Cl_2$ arose from insertion into the aromatic C-H bonds.

Saturated hydrocarbons often display low reactivity towards dichlorocarbene in the liquid phase,³ but decomposition of trifluoro(trichloromethyl)silane at 140 °C in an excess of cyclohexane vapour gives (dichloromethyl)cyclohexane in 57% yield (cf. 32% in the liquid-phase reaction) together with traces of chlorocyclohexane, chloroform, and tetrachloroethylene. The related reactions between the silane and isobutane or propane proceed similarly to give the products of tertiary ($Me_3C \cdot CHCl_2$) and secondary ($Me_2CH \cdot CHCl_2$) C-H insertion, respectively (57 and 29% yield), again with traces of monochloroalkanes and tetrachloroethylene and significant amounts of chloroform (5 and 21%, respectively). No products of reaction at the primary C-H bonds in these substrates have been detected, and competition experiments with mixtures of isobutane and cyclohexane reveal reactivity ratios for tertiary : secondary insertion of 70 : 1 at 140 and 49 : 1 at 180 °C. Reaction of the silane with ethane gives chloroethane in low yield (5%), and no insertion product is detected.

Although traces of a product which may have arisen from C-H insertion are formed during the reaction of cyclopentadiene with the silane at 180 °C, the major product is chlorobenzene (58% yield).⁷ A related reaction with indene gives 2-chloronaphthalene (69%).

Reactions with Ethers.—The activating influence of an α -oxygen atom on the liquid-phase C-H insertions of dichlorocarbene is established,^{4,6} and very high yields of α -insertion products are obtained in the gas phase from trifluoro(trichloromethyl)silane and the ethers shown. These reactions provide excellent preparative routes to α -dichloromethyl-substituted ethers, and no significant



side-reactions occur in these systems. The high reactivity of the α -C-H bond in ethers towards radical attack⁸ testifies to its very low dissociation energy, and probably accounts for the ease of the insertion reaction.

⁷ Cf. W. E. Parham, H. E. Reiff, and P. Swartzentruber, *J. Amer. Chem. Soc.*, 1956, **78**, 1437; A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.*, 1958, 283.

The formation of chlorinated hydrocarbons and of chloroform during the reactions described here may usually be attributed to a minor side-reaction involving chlorine atoms, followed by the reaction of dichlorocarbene with hydrogen chloride.² The part played by such processes increases as the reactivity of the substrate towards dichlorocarbene decreases or when, as in the cyclopentadiene reaction, hydrogen chloride may be generated in the system in another way.

EXPERIMENTAL

Except where otherwise stated, reactions were carried out *in vacuo* in a sealed 2.34 l Pyrex flask heated in an electric oven. Analysis by g.l.c. was carried out on a Perkin-Elmer 451 or 452 instrument, columns (4 mm internal diameter) being packed with 30% by weight of the stationary phase supported on 80 mesh Celite. Dichloromethylalkanes required for reference purposes were prepared from the corresponding aldehydes and phosphorus pentachloride.⁹

Reactions of Trifluoro(trichloromethyl)silane with Hydrocarbons.—(a) *Ethylbenzene.* The hydrocarbon (6.40 g, 61 mmol) and the silane (2.24 g, 11 mmol)² were heated at 180 °C for 18 h. Fractionation *in vacuo* gave a mixture of silicon halides (1.30 g),² and less volatile material (7.05 g) was distilled to give ethylbenzene (6.12 g) and 1,1-dichloro-2-phenylpropane (0.65 g, 31%) (Found: C, 57.4; H, 5.3; Cl, 37.3. Calc. for $C_9H_{10}Cl_2$; C, 57.2; H, 5.3; Cl, 37.5%), b.p. 86–88 °C at 4 mmHg, n_D^{20} 1.5360 (lit.,⁵ b.p. 57 °C at 0.4 mmHg, n_D^{20} 1.5351); g.l.c. (4 m Silicone MS550; 180 °C) showed that only one isomer had been formed.

(b) *Cumene.* Cumene (8.40 g, 70 mmol) and the silane (2.24 g, 11 mmol) were heated at 180 °C for 24 h, and fractionation *in vacuo* gave a mixture of silicon halides (1.32 g), chloroform (0.12 g, 9%), and tetrachloroethylene (0.02 g, 2%). Distillation of the higher-boiling material gave cumene (6.64 g) and chromatographically pure (2 m Silicone; 200 °C) 1,1-dichloro-2-methyl-2-phenylpropane (1.26 g, 57%), b.p. 60–62 °C at 1 mmHg, n_D^{20} 1.5381 (lit.,⁵ b.p. 68–70 °C at 3 mmHg, n_D^{20} 1.5400), showing i.r. and n.m.r. spectra identical with those described by Fields.⁵

(c) *Toluene.* Toluene (4.88 g, 53 mmol), and the silane (2.24 g, 11 mmol), heated at 180 °C for 18 h, gave a mixture of volatile silanes (1.30 g), toluene (4.30 g), and a fraction (0.16 g), b.p. 100–104 °C at 7 mmHg (lit. for 1,1-dichloro-2-phenylethane,¹⁰ b.p. 108 °C at 9 mmHg), shown by i.r. and mass spectrometry to contain a compound of molecular formula $C_8H_8Cl_2$ contaminated with hexachlorobutadiene.

(d) *Cyclohexane.* (i) *At ca. 1 atm.* Cyclohexane (5.80 g, 69 mmol) and the silane (2.24 g, 11 mmol), heated at 180 °C for 18 h, gave a mixture of silanes (1.32 g) and fractions shown by g.l.c. (4 m Silicone; 90 and 150 °C) to contain chloroform (0.06 g, 5%), cyclohexane (4.87 g), tetrachloroethylene (0.01 g, 1%), chlorocyclohexane (0.02 g, 2%), and dichloromethylcyclohexane (1.05 g, 57%). Distillation gave a specimen of the pure insertion product, b.p. 58 °C at 3 mmHg (lit.,³ 59–60 °C at 3 mmHg), identified by i.r. and n.m.r. spectroscopy.³

(ii) *At ca. 8 atm.* Cyclohexane (5.88 g, 70 mmol) and the silane (2.24 g, 11 mmol), heated at 140 °C in a sealed 330 ml tube for 24 h, gave a mixture of halogenosilanes (1.31 g) and

⁸ See, for example, H. Singh and J. M. Tedder, *J. Chem. Soc. (B)*, 1966, 612.

⁹ A. J. Hill and F. Tyson, *J. Amer. Chem. Soc.*, 1928, **50**, 172.

¹⁰ A. P. ter Borg and A. F. Bickel, *Rec. Trav. chim.*, 1961, **80**, 1217.

fractions shown by g.l.c. to contain chloroform (0.10 g, 8%), cyclohexane (5.00 g), tetrachloroethylene (0.04 g, 4%), chlorocyclohexane (trace), and dichloromethylcyclohexane (0.48 g, 26%). Tar (*ca.* 0.5 g) was also formed.

(e) *Isobutane.* Isobutane (4.06 g, 70 mmol) and the silane (2.24 g, 11 mmol) were heated at 140 °C for 24 h. Fractionation *in vacuo* gave a mixture of silanes (1.32 g), isobutane (3.24 g), and fractions shown by g.l.c. (4 m Silicone) and i.r. spectroscopy to contain *t*-butyl chloride (0.01 g, 1%), chloroform (0.06 g, 5%), carbon tetrachloride (0.07 g, 4%), tetrachloroethylene (0.04 g, 3%), and a component with a retention time corresponding to that of either 1,1-dichloro-2,2-dimethylpropane or 1,1-dichloro-3-methylbutane (0.88 g, 57%). Isolation of the last component by preparative g.l.c. gave pure 1,1-dichloro-2,2-dimethylpropane (Found: C, 42.5; H, 7.3; Cl, 50.3. $C_5H_{10}Cl_2$ requires C, 42.6; H, 7.1; Cl, 50.3%), b.p. 119–120 °C, identical with a specimen obtained in low yield from 2,2-dimethylpropanal and phosphorus pentachloride. Its n.m.r. spectrum shows singlets at τ 4.45 (1H) and 8.85 (9H) and its i.r. spectrum shows strong bands at 3.33, 6.75, 6.82, 7.29, 11.05, and 13.14 μ m. An experiment on the same scale at 180 °C gave the insertion product in 56% yield.

(f) *Isobutane and cyclohexane.* Isobutane (3.69 g, 64 mmol), cyclohexane (5.35 g, 64 mmol), and the silane (2.44 g, 12 mmol) were heated in a sealed 4.73 l flask at 140 °C for 18 h. Analysis of the liquid products by g.l.c. (4 m Silicone, 160 °C) showed them to contain 1,1-dichloro-2,2-dimethylpropane (0.85 g, 6.02 mmol) and dichloromethylcyclohexane (0.17 g, 1.03 mmol), revealing a reactivity ratio per hydrogen atom of 70 : 1. A similar experiment on the same scale at 180 °C for 18 h gave 1,1-dichloro-2,2-dimethylpropane (0.94 g, 6.67 mmol) and dichloromethylcyclohexane (0.27 g, 1.64 mmol) (reactivity ratio 49 : 1).

(g) *Propane.* (i) *At ca. 1 atm.* Propane (2.90 g, 66 mmol) and the silane (2.24 g, 11 mmol), heated at 140 °C for 18 h, gave a mixture of halogenosilanes and propane (3.82 g) and fractions shown by g.l.c. (4 m Silicone) to contain 2-chloropropane (0.03 g, 3%), dichloromethane (0.01 g, 1%), chloroform (0.27 g, 21%), carbon tetrachloride (0.08 g, 5%), tetrachloroethylene (0.08 g, 6%), 1,1-dichloro-2-methylpropane (0.40 g, 29%), and an unidentified product (*ca.* 0.05 g). The presence of 1,1-dichloro-2-methylpropane was confirmed by i.r. spectroscopy, and the retention time of the unidentified product did not correspond with that of 1,1-dichlorobutane.

(ii) *At ca. 20 atm.* Propane (3.06 g, 70 mmol) and the silane (2.04 g, 10 mmol), heated in a 100 ml autoclave for 16 h at 220 °C gave mainly halogenosilanes, chloroform, and tar.

(h) *Ethane.* Ethane (1.42 g, 47 mmol) and the silane (3.26

g, 16 mmol), heated at 140 °C for 18 h, gave halogenosilanes, butane (trace), chloroethane (*ca.* 0.05 g, 5%), dichloromethane (*ca.* 0.03 g, 2%), chloroform (*ca.* 0.48 g, 25%), carbon tetrachloride (*ca.* 0.04 g, 2%), tetrachloroethylene (0.15 g, 12%), and a number of unidentified components. One of the unidentified compounds showed a retention time corresponding to that of 1,1-dichloropropane, but the yield was insufficient for complete identification.

(i) *Cyclopentadiene.* The diene (4.15 g, 63 mmol) and the silane (2.24 g, 11 mmol), heated at 180 °C for 18 h, gave a mixture of halogenosilanes (1.37 g). The liquid products were shown by g.l.c. (2 m Silicone; 150 °C) and by i.r. spectroscopy to contain chloroform (0.19 g, 14%), chlorobenzene (0.75 g, 58%), and at least two unidentified components.

(j) *Indene.* The liquid products from the reaction of indene (4.88 g, 41 mmol) with the silane (2.24 g, 11 mmol) at 180 °C for 18 h were distilled and yielded indene (3.80 g) and 2-chloronaphthalene (1.24 g, 69%), b.p. 136 °C at 20 mmHg, m.p. 54–56 °C (lit.,¹¹ b.p. 121–122 °C at 12 mmHg, m.p. 56 °C), identified by i.r. spectroscopy.

Reactions of Trifluoro(trichloromethyl)silane with Ethers.—(a) *Diethyl ether.* The ether (4.30 g, 59 mmol) and the silane (1.77 g, 9 mmol) were heated at 180 °C for 18 h. Volatile products were identified as a mixture of halogenosilanes (1.01 g), ether (3.66 g), and chloroform (0.12 g, 11%), and distillation of the higher-boiling material gave 1,1-dichloro-2-ethoxypropane (1.08 g, 79%) (Found: C, 38.5; H, 6.6; Cl, 45.1. Calc. for $C_5H_{10}Cl_2O$: C, 38.3; H, 6.4; Cl, 45.2%), b.p. 49–50 °C at 16 mmHg (lit.,⁶ 42–43 °C at 14 mmHg). The n.m.r. spectrum was identical with that reported by Anderson *et al.*,⁶ and the i.r. spectrum was fully consistent with the proposed structure.

(b) *2-Methoxypropane.* The ether (3.50 g, 49 mmol) and the silane (2.04 g, 10 mmol), heated at 180 °C for 18 h, gave a mixture of halogenosilanes (1.18 g) and a fraction containing chloroform (0.06 g, 5%) and 2-methoxypropane (2.78 g). Distillation of the higher-boiling material gave 2-dichloromethyl-2-methoxypropane (1.18 g, 76%), b.p. 58 °C at 19 mmHg (lit.,⁶ 60–61 °C at 14 mmHg,) identified by i.r. and n.m.r. spectroscopy.⁶

(c) *Tetrahydrofuran.* Tetrahydrofuran (4.55 g, 63 mmol) and the silane (2.24 g, 11 mmol) were heated in a sealed 350 ml tube at 180 °C for 16 h. Fractionation *in vacuo* gave the usual mixture of silanes (1.30 g) and traces of chloroform and tetrahydrofuran. Distillation of the remaining liquid yielded tetrahydrofuran (3.44 g) and 2-dichloromethyltetrahydrofuran (1.37 g, 80%), b.p. 72–74 °C at 16 mmHg (lit.,⁶ 70–71 °C at 18 mmHg), identified by i.r. and n.m.r. spectroscopy.⁶

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¹¹ K. von Auers and A. Fruhling, *Annalen*, 1921, **422**, 194.