Journal of Organometallic Chemistry, 77 (1974) 177–181

THE CLEAVAGE OF SOME BIS(PERHALOARYL)METHYLSILANES AND TRIS(PERHALOARYL)SILANES BY ORGANOLITHIUM COMPOUNDS

R.D. HOWELLS and H. GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)
(Received March 11th, 1974)

Summary

Bis(perhaloaryl)methylsilanes and tris(perhaloaryl)silanes (halo = Cl, F) undergo reaction with methyl- and butyllithium under mild conditions to produce perhaloaryllithium derivatives in generally high yields.

Introduction

Previous work has shown that some perhaloaryldiphenylsilanes [1, 2] and perhaloaryldimethylsilanes [3—5] were cleaved by alkyllithium compounds forming a perhaloaryllithium compound, and the corresponding silane resulting from nucleophilic attack on silicon. Recently the cleavage of bis(pentafluorophenyl)-methylsilane with methyl- and n-butyllithium was reported [6].

The bis(perhaloaryl)methylsilanes and tris(perhaloaryl)silanes were prepared via reaction of a perhaloaryl metallic species with methyldichlorosilane and trichlorosilane, respectively. These chlorosilanes are more accessible than dimethylchlorosilane used in formation of (perhaloaryl)dimethylsilanes.

Results and discussion

Cleavage of the Si—C bond in the title compounds was effected under mild conditions (see Table 1) in diethyl ether. Very pure perhaloarylcarboxylic acids were obtained, from cleavage by methyllithium, upon derivatization with carbon dioxide. The perchloroarylcarboxylic acids derived from cleavage by n-butyllithium were recrystallized from chloroform to remove acid resulting from Li—Cl exchange on the starting perchloroarylsilane. In the absence of a Si—H moiety, Li—Cl exchange was the exclusive or nearly exclusive reaction path when perchloroaryl-substituted silanes are treated with n-butyllithium under mild conditions [2, 4, 7]. Even with the strong electron withdrawal from silicon provided by the three trichloro-2-thienyl groups in tris(trichloro-2-thienyl)methylsilane (I), Li—Cl exchange predominated as evidenced by a 59% isolated yield of the known [8]

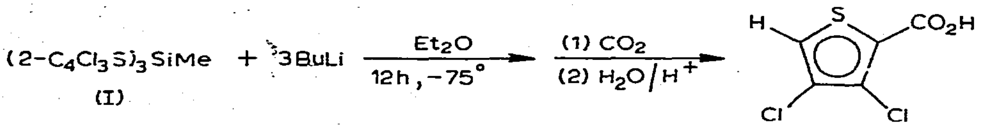
TABLE 1

REACTION OF BIS(PERHALOARYL)METHYLSILANES AND TRIS(PERHALOARYL)SILANES WITH n-BuLi OR MeLi IN Et_2O

Silane (mole)	RLi [a] (mole)	Temp. (°C)	Time (h)	Yield Ar_xCO_2H (%) [b]
$(2\text{-}C_4Cl_3S)_2SiMeH$ (0.005)	n-BuLi (0.010)	−75	1	72
$(2\text{-}C_4Cl_3S)_2SiMeH$ [c] (0.005)	n-BuLi (0.010)	−75	3	67
$(2\text{-}C_4Cl_3S)_2SiMeH$ (0.010)	MeLi (0.020)	−75	6	76
$(2\text{-}C_4Cl_3S)_2SiMeH$ (0.010)	MeLi (0.021)	−50	1	89
$(4\text{-}C_5Cl_4N)_2SiMeH$ (0.005)	n-BuLi (0.010)	−75	2	52
$(4\text{-}C_5Cl_4N)_2SiMeH$ [d] (0.005)	n-BuLi (0.0105)	−75	3/4	65
$(4\text{-}C_5Cl_4N)_2SiMeH$ (0.010)	MeLi (0.021)	−50	1	76
$(4\text{-}C_5Cl_4N)_2SiMeH$ (0.010)	MeLi (0.021)	−30	1	78
$(C_6Cl_5)_2SiMeH$ (0.005)	MeLi (0.010)	−30	2	65
$(2\text{-}C_4Cl_3S)_3SiH$ [e] (0.005)	MeLi (0.015)	−50	1	92
$(C_6F_5)_3SiH$ (0.005)	MeLi (0.015)	−50	1	90

[a] n-BuLi (1.65 *M* in hexane) or MeLi (1.72 *M* in ether) was added to the silane in ether. [b] Based on cleavage of all perhaloaryl groups. [c] Corresponding reaction in THF gave 54%. [d] Corresponding reaction in THF gave 56%. [e] Corresponding reaction in THF gave 66%.

3,4-dichlorothiophene-2-carboxylic acid which resulted from Li—Cl exchange followed by hydrolytic cleavage of the Si—C bonds after carbonation.



That the Si—H moiety allows preferential Si—C cleavage by RLi may be due to a combination of lesser steric hindrance to the approach of a nucleophile to silicon, and lesser inductive electron release to silicon than in the corresponding Si—Me compounds.

It should be noted, however, that cleavage of the Si—C bond has been shown to occur in the reaction of n-butyllithium with 2,5-bis(trimethylsilyl)-thiophene [9] where Li—Cl exchange is not possible.

Hydride, which may be cleaved from silicon [10], resists cleavage by an alkyllithium if a better leaving group such as Ar_x is present [4, 6].

An interesting side-reaction was noted in the preparation of bis(trichloro-2-thienyl)methylsilane (II) via the slow addition of methyldichlorosilane to trichloro-2-thienyllithium.

$$2\text{-}C_4Cl_3SLi + Cl_2SiMeH \rightarrow \underset{(I)}{(2\text{-}C_4Cl_3S)_3SiMe} + \underset{(II)}{(2\text{-}C_4Cl_3S)_2SiMeH} + \underset{(III)}{(2\text{-}C_4Cl_3S)SiMeH_2}$$

Tris(trichloro-2-thienyl)methylsilane (I) could arise from nucleophilic attack of trichloro-2-thienyllithium on silicon in II followed by loss of hydride. Hydride reduction of either methyldichlorosilane or the possible intermediate [(2-C_4Cl_3S)-Si(Cl)MeH] would result in formation of III. A redistribution reaction may also be involved [11].

Inverse addition of trichloro-2-thienyllithium to methyldichlorosilane resulted in the isolation of II in 91.5% yield. This mode of addition was also the method of choice for the preparation of tris(trichloro-2-thienyl)silane and tris(pentafluorophenyl)silane. The isolated yield of the latter (83%) was higher than that reported [12].

Experimental

All reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware which was assembled while hot and flushed with dry nitrogen prior to addition of reagents. Isolation of all bis(perhaloaryl)methylsilanes and tris(perhaloaryl)silanes was done under anhydrous conditions to avoid hydrolytic cleavage of the Si—C bond. Ether and THF were distilled from $LiAlH_4$. The molarity of alkyllithium reagents (Foote Mineral Company) was determined by the double-titration method [13]. The cleavage reactions were carried out by adding the alkyllithium solutions via syringe to the perhaloarylsilanes under a nitrogen atmosphere according to the conditions given in Table 1. Silane co-products from the cleavage reactions were not quantitatively determined but isolated samples had identical properties to the known compounds. Carbonations were accomplished by pouring the reaction mixture over a large excess of freshly crushed Dry-Ice. All melting and boiling points are uncorrected. Molecular weights were determined by mass spectrometry. Values given represent the parent ion and the most intense peak(s) of the molecular ion cluster.

Preparation of bis(trichloro-2-thienyl)methylsilane (II)

Bis(trichloro-2-thienyl)methylsilane (II) was prepared by the inverse addition of trichloro-2-thienyllithium to methyldichlorosilane (Method A), and by the normal mode of addition (Method B).

Method A. To a solution of 5.75 g (0.05 mole) of methyldichlorosilane in 25 ml of ether was added trichloro-2-thienyllithium [14] (0.10 mole) in 250 ml of ether at ca. —30°. The reaction mixture was stirred for 1 h (Color Test I [15] was negative after 1/2 h) and then filtered while cold to remove LiCl. Distillation of the filtrate under reduced pressure gave 19.1 g (91.5%) of II, b.p. 164—165°/0.05 mm, m.p. 55—56.5°. The ^1H NMR spectrum (CCl_4) showed a doublet (Si—Me) at δ 0.79 and a quartet (Si—H) at δ 5.08 ($J(CH_3, H)$ 3.9 Hz) integrating for 3 and 1 protons, respectively. The IR spectrum (Nujol) showed Si—H (2175 cm^{-1}), C_4Cl_3S (1405, 1315, 1005 cm^{-1}), and Si—Me (1260 cm^{-1}). Parent ion: *m/e* 414 (calcd.: 414): most intense M^+: *m/e* 416 (calcd.: 416). (Found: C, 25.99; H, 0.99; Cl, 50.95; S, 15.51. $C_9H_4Cl_6S_2Si$ calcd.: C, 25.92; H, 0.96; Cl, 51.01; S, 15.37%.)

Method B. To a solution of trichloro-2-thienyllithium (0.04 mole) in 200 ml of ether was slowly added 2.30 g (0.02 mole) of methyldichlorosilane in 25 ml ether at —50°. The reaction mixture was allowed to warm to —10° during 1 h, cooled to —50° and filtered. The filtrate was concentrated to near dryness under reduced pressure. The solid residue was washed with cold acetonitrile. Filtration provided 3.1 g (37.2%) of II, m.p. 55—56.5°.

Extraction of the first filtercake gave 2.5 g (20.8%) of tris(trichloro-2-thienyl)-methylsilane (I), m.p. 212—213°. The ^{1}H NMR spectrum (CCl_4) showed a singlet (Si—Me) at δ 1.17. The IR spectrum (Nujol) showed Si—H (2160 cm^{-1}) and C_4Cl_3S (1400, 1315, 1003 cm^{-1}). Parent ion: *m/e* 598 (calcd.: 598); most intense M^+: *m/e* 602 (calcd.: 602). (Found: C, 25.83; H, 0.63; S, 16.10. $C_{13}H_3Cl_9S_3Si$ calcd.: C, 25.91; H, 0.50; S, 15.96%.) An identical sample was prepared in 68% yield from reaction of methyltrichlorosilane with trichloro-2-thienyllithium.

Distillation of the acetonitrile solution gave 1.0 g (21.6%) of trichloro-2-thienylmethylsilane (III), b.p. 50°/0.2 mm. The ^{1}H NMR spectrum (neat) showed a triplet (Si—Me) at δ 0.44 and a quartet (H—Si—H) at δ 4.32 ($J(CH_3, H)$ 4.2 Hz) integrating for 3 and 2 protons, respectively. The IR spectrum (neat) showed Si—H (2175 cm^{-1}), C_4Cl_3S (1405, 1310, 1000 cm^{-1}) and Si—Me (1255 cm^{-1}). Parent ion: *m/e* 230 (calcd.: 230); most intense M^+: *m/e* 230, 232 (calcd.: 230, 232). Upon storage some decomposition of III was observed. A satisfactory elemental analysis was not obtained.

Preparation of tris(trichloro-2-thienyl)silane

To a solution of 9.5 g (0.07 mole) of trichlorosilane in 25 ml of ether was added trichloro-2-thienyllithium (0.21 mole) in 300 ml of ether at ca. 30°. After 1 h (Color Test I [15] was negative after 1/2 h) the reaction mixture was filtered while cold. Extraction and recrystallization of the crude solid from hexane provided 26.7 g (65%) of tris(trichloro-2-thienyl)silane, m.p. 133—134°. The ^{1}H NMR spectrum (CCl_4) showed a singlet at δ 5.84. The IR spectrum (Nujol) showed Si—H (2205 cm^{-1}), and C_4Cl_3S (1400, 1320, 1015 cm^{-1}). Parent ion: *m/e* 584 (calcd.: 584); most intense M^+: *m/e* 588 (calcd.: 588). (Found: C, 24.72; H, 0.22; S, 16.37. $C_{12}HCl_9S_3Si$ calcd.: C, 24.49; H, 0.17; S, 16.35%.)

Preparation of bis(tetrachloro-4-pyridyl)methylsilane

To a solution of tetrachloro-4-pyridylmagnesium chloride [16] (0.26 mole) in 800 ml of THF was added 14.95 g (0.13 mole) of methyldichlorosilane at —10°. The reaction mixture was stirred at —10° for 1 h and then was warmed to room temperature. The THF was removed under reduced pressure and the resulting dark-colored solid extracted with hot benzene. (Washing with cold acetonitrile prior to benzene extraction removes much of the dark-colored material and facilitates further work-up). From the benzene extracts there was obtained 32.1 g (52%) of bis(tetrachloro-4-pyridyl)methylsilane, m.p. 161—162.5°. The ^{1}H NMR spectrum (CCl_4) showed a doublet (Si—Me) at δ 0.99 and a quartet (Si—H) at δ 5.54 ($J(CH_3, H)$ 4.2 Hz) integrating for 3 and 1 protons, respectively. The IR spectrum (Nujol) showed Si—H (2235 cm^{-1}), C_5Cl_4N (1295, 1080 cm^{-1}) and Si—Me (1260 cm^{-1}). Parent ion: *m/e* 472 (calcd.: 472); most intense M^+: *m/e* 476 (calcd.: 476). (Found: C, 27.55; H, 0.99; Cl, 59.61; N, 6.08. $C_{13}H_4Cl_8N_2Si$ calcd.: C, 27.76; H, 0.84; Cl, 59.60; N, 5.87%.)

Preparation of bis(pentachlorophenyl)methylsilane

To a solution of 5.75 g (0.05 mole) of methyldichlorosilane in 25 ml of THF was added pentachlorophenylmagnesium chloride [17] (0.10 mole) in 200 ml of THF at 0°. The reaction mixture was stirred for 12 h, cooled to —50° and filtered. The filtercake was extracted with hot benzene (3 × 100 ml). From the benzene extracts there was obtained 13.6 g (50.2%) of bis(pentachlorophenyl)methylsilane, m.p. 208—209°*. The ^{1}H NMR spectrum (CCl_4) showed a doublet (Si—Me) at δ 0.97 and a quartet (Si—H) at δ 5.62 ($J(CH_3, H)$ 4.2 Hz) integrating for 3 and 1 protons, respectively. The IR (nujol) showed Si—H (2215 cm^{-1}), C_6Cl_5 (1300, 1095, 873, 678 cm^{-1}) and Si—Me (1250 cm^{-1}). Parent ion: *m/e* 538 (calcd.: 538); most intense M^+: *m/e* 542 (calcd.: 542). (Found: C, 29.01; H, 0.89; Cl, 65.59. $C_{13}H_4Cl_{10}Si$ calcd.: C, 28.77; H, 0.74; Cl, 65.32%.)

Acknowledgment

This research was supported by the National Science Foundation (GP-34632). We are grateful to the Hooker and Olin Companies, and to Dr. F.J. Marshall for assistance.

References

1 P. Morris, F.W.G. Fearon and H. Gilman, J. Organometal. Chem., 9 (1967) 427.
2 F.W.G. Fearon and H. Gilman, J. Organometal. Chem., 10 (1967) 409.
3 K. Shiina, T. Brennan and H. Gilman, J. Organometal. Chem., 11 (1968) 471.
4 M.R. Smith, Jr. and H. Gilman, J. Organometal. Chem., 37 (1972) 35.
5 C. Tamborski and E.J. Soloski, J. Organometal. Chem., 20 (1969) 245.
6 D. Sethi, R.D. Howells and H. Gilman, J. Organometal. Chem., 69 (1974) 377.
7 P.J. Morris and H. Gilman, J. Organometal. Chem., 11 (1968) 463.
8 E. Profft and G. Solf, J. Prakt. Chem., 24 (1964) 38.
9 F.H. Pinkerton and S.F. Thames, J. Organometal. Chem., 29 (1971) C4.
10 C. Eaborn and R.W. Bott, in A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 1, Part 1, Dekker, New York, 1968, pp. 146—149.
11 K. Moedritzer, Organometal. Chem. Rev., 1 (1966) 179; K. Moedritzer, Advan. Organometal. Chem., 6 (1968) 171.
12 T. Brennan and H. Gilman, J. Organometal. Chem., 16 (1969) 63.
13 H. Gilman and F.K. Cartledge, J. Organometal. Chem., 2 (1964) 447.
14 G.B. Bachman and L.V. Heisey, J. Amer. Chem. Soc., 70 (1948) 2378; M.D. Rausch, T.R. Criswell and A.K. Ignatowicz, J. Organometal. Chem., 13 (1968) 419; M.R. Smith, Jr. and H. Gilman, Organometal. Chem. Syn., 1 (1971) 265.
15 H. Gilman and F. Schulze, J. Amer. Chem. Soc., 47 (1925) 2002.
16 S.S. Dua and H. Gilman, J. Organometal. Chem.,12 (1968) 234.
17 H.E. Ramsden, A.E. Balint, W.R. Whitford, J.J. Walburn and R. Cser, J. Org. Chem., 22 (1957) 1202; S.D. Rosenberg, J.J. Walburn and H.E. Ramsden, J. Org. Chem., 22 (1957) 1606; H. Gilman and S.Y. Sim, J. Organometal. Chem., 7 (1967) 249.

---

* On other occasions a possible dimorph was obtained with m.p. 227—228° and with identical ^{1}H NMR, IR and mass spectra. (Found: C, 28.66; H, 0.85; Cl, 65.54. $C_{13}H_4Cl_{10}Si$ calcd.: C, 28.77; H, 0.74; Cl, 65.32%.) Mixed m.p. of 50/50 mixture was over the range 207—227°.