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Cleavage of Si–C and Ge–C bonds with lithium aluminium hydride

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Abstract

Lithium aluminium hydride can cleave Si–C and Ge–C bonds, providing a useful means for substituting furyl, dihydrofuryl and tetrahydrofuryl groups. Spectra are described of compounds prepared by this means.

Nucleophilic substitution of halogen, alkoxy and amino groups by hydride ion in silanes and germanes is one of the principal reactions involved in the synthesis of hydrosilanes and hydrogermanes.

According to our findings, $LiAlH_4$ can be used in some cases to break the Si–C and Ge–C bonds in organosilanes and -germanes. For instance, hydride ion can substitute the furyl, dihydrofuryl and tetrahydrofuryl groups in bis-heterylsilanes Ia–Ic and the dihydrofuryl group in bis-heterylgermane * Id to afford readily (25–80 °C) and in good yield (60–100%) (2-furyl)dimethylsilane (IIa), [2-(4,5-dihydrofuryl)]dimethylsilane (IIc) and earlier unknown [2-(4,5-dihydrofuryl)]dimethylgermane (IId), which are otherwise difficult to obtain.

In diethyl ether the reaction occurs selectively to give exclusively heterylhydrosilanes (germanes) IIa–IId. In the more polar solvent tetrahydrofuran the reaction proceeds more rapidly and extensively to give dimethylsilane IIIa or dimethylgermane IIId as the sole product.

It should be pointed out that the cleavage of Si–C_{sp^2} occurs more readily than that of Si–C_{sp^3}, substitution of the dihydrofuryl group in Ib, in its turn, proceeds more easily than in the case of conjugated furyl bond in Ia. The latter fact is consistent with the mass spectrometric evidence suggesting that the Si–C_{furyl} bond is stronger than the Si–$C_{dihydrofuryl}$ bond in bis-furyl and bis(dihydrofuryl)silanes [1,2]. In addition, substitution of the dihydrofuryl group in germane Id occurs much

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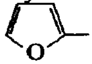
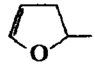
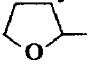
* The names heterylsilanes and heterylgermanes were used by us to denote respectively silanes and germanes containing a heterocyclic substituent, in our case ,  and  groups.

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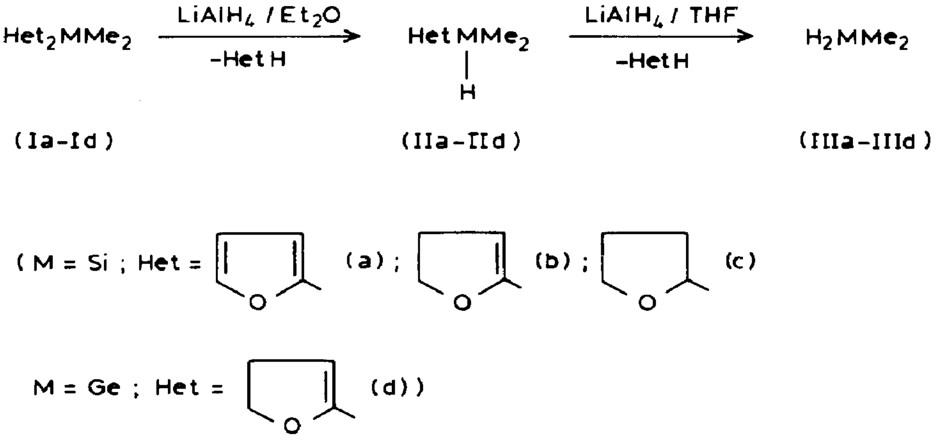
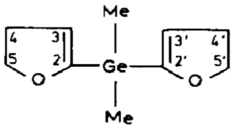


slower than in the silyl counterpart Ia, the latter reacting with $LiAlH_4$ even under the mild conditions of phase-transfer catalysis [3,4] (0.1 *M* solution in benzene, [Ib]/[$LiAlH_4$] 1/2, 80 ° C, 18-crown-6); IIb yield after 15 h is 20%.

The physico-chemical constants of synthesized bis-heterylsilanes Ia [5], Ib, Ic [6] and hydrosilanes IIa [7], IIb, IIc obtained in reactions with $LiAlH_4$ [6] correspond to published data.

Bis(dihydrofuryl)germane



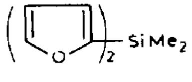
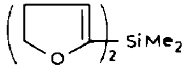
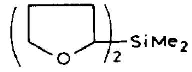
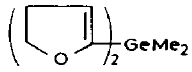
(Id)

(Id) was prepared similarly to the silicon counterpart Ib [6]. Id: ^{1}H NMR ($CDCl_3$, δ, ppm.): 0.44 (C, 6H, Ge–CH_3), 2.57 (d.t. 4H, 5 4,4'-CH_2, J_{4-3} 2.2 Hz, J_{4-5} 9.6 Hz), 4.29 (t. 4H, 5,5'-CH_2, J 9.6 Hz), 5.15 (t. 2H, 3,3'-CH, J 2.2 Hz); mass spectrum, *m/e* (rel. intensity, %): 244 (8), 242 (41), 241 (8), 240 (30), 238 (22), 227 (11), 199 (22), 197 (48), 196 (11), 195 (37), 193 (22), 184 (11), 173 (14), 171 (25), 169 (37), 167 (55), 166 (12), 165 (37), 163 (23), 145 (27), 143 (100), 142 (27), 141 (77), 139 (57), 138 (17), 137 (10), 115 (19), 113 (37), 112 (11), 111 (31), 110 (35), 109 (29) ,107 (10), 105 (19), 104 (25), 103 (17), 102 (17), 101 (16), 100 (15), 93 (12), 97 (16), 91 (43), 89 (85), 88 (21), 87 (66), 85 (45), 79 (19), 75 (11), 74 (11), 73 (10), 68 (25), 55 (15), 53 (15), 42 (10), 41 (99); IR (cm^{-1}): 1660 (ν(C=C)).

IId: ^{1}H NMR ($CDCl_3$, δ, ppm.): 0.36 (d, 6H, Ge-CH_3, J 2.6 Hz), 2.42-2.71 (m, 2H, 4-CH_2), 4.16 (m, 1H, Ge-H), 4.27 (t, 2H, 5-CH_2, J 9.3 Hz), 5.11 (t, 1H, 3-CH, J 2.5 Hz); mass spectrum, *m/e* (rel. intensity, %): 174 (33), 173 (11), 172 (25), 170 (19), 159 (37), 158 (12), 157 (30), 155 (24), 144 (26), 143 (22), 142 (22), 141 (13), 140 (14), 131 (18), 129 (43), 128 (10), 127 (33), 125 (21), 113 (18), 111 (14), 107 (14), 106 (13), 105 (62), 104 (60), 103 (57), 102 (36), 101 (40), 100 (28), 91 (31), 89 (100), 88 (27), 87 (76), 85 (54), 74 (11), 69 (27), 41 (12), 39 (12); IR (cm^{-1}): 2050 (ν(Ge-H)), 1602 (ν(C=C)).

Table 1

Reaction between heterylsilanes I and $LiAlH_4$ (0.1 M solution, $[I]:[LiAlH_4] = 1:2$)

Substrate	Solvent	T (°C)	Time (h)	Yield [b] (%)	
				II	III
 (Ia)	Et_2O	80 [a]	200	60	–
	THF	25	6	57	40
			24	–	100
 (Ib)	Et_2O	25	6	100	–
	THF	25	6	–	100
 (Ic)	Et_2O	80 [a]	6	18	–
	THF	25	100	25	10
		80	3	42	25
 (Id)	Et_2O	25	180	100	–
	THF	25	24	80	15
			72	–	100

[a] Reaction was carried out in Pierce reaction-vials. [b] GLC data.

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