Experimental

Ferrocenylmethyl methyl sulfide. To a stirred suspension of 2.0 g (0.053 mole) lithium aluminum hydride in 100 ml ether there was added slowly a solution containing 6.0 g (0.045 mole) aluminum chloride in 75 ml ether. The reaction mixture was stirred at reflux for ½ h to insure complete reaction, followed by dropwise addition of a solution of 2.0 g (0.0077 mole) methyl thiolferrocenoate in 50 ml ether. The reaction mixture was stirred for 2 h at reflux then hydrolyzed by careful addition of wet ether followed by water and finally dilute hydrochloric acid. Evaporation of the ether phase provided a light orange oil which was taken up in hexane and chromatographed on activity grade III alumina (Alcoa F-20) using hexane as eluent.

Evaporation of the eluate containing the first yellow band provided 0.4 g (26 %) of methylferrocene identified by its infrared and NMR spectra. Evaporation of the hexane containing the second band provided 1.3 g (69 %) of yellow crystals m.p. 39–41°. (Found: C, 58.72; H, 5.84; S, 12.90. $C_{12}H_{14}FeS$ calcd.: C, 58.65; H, 5.73; S, 13.02 %.) Similar reduction of ethyl, n-propyl, isopropyl, n-butyl, and n-octyl thiolferrocenoate provided the corresponding alkyl ferrocenylmethyl sulfide.

When the reduction of methyl thiolferrocenoate was carried out using only excess lithium aluminum hydride, the products were ferrocenylmethanol (88 %) and bis(ferrocenylmethyl) ether (10 %), in addition to methyl mercaptan.

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Organogermanium compounds

VII.* Hydrogen-exchange in germanium- and silicon-substituted acetylenes

To obtain further information about electronic effects of trialkylsilyl and trialkylgermyl groups we have measured the rates of detritiation at 25° in a mixture of

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* For Part VI see ref. 1.

methanol (1 vol.) and an aqueous buffer solution (pH, 8.05) (4 vol.) of some $XC{\equiv}C^3H$ compounds in which $X = R_3M$ or R_3MCH_2, with $M = C$, Si and Ge. The rate-determining step in such reactions is the abstraction of the alkynyl proton by hydroxide ion, and the transition state is believed to lie close to the products, the carbanion $XC{\equiv}C^-$ and water[2]. Steric effects of substituents must be effectively absent, and electron supply by X lowers and electron withdrawal by X raises the rate[3].

TABLE 1

RATES OF DETRITIATION OF $XC{\equiv}C^3H$ COMPOUNDS IN BUFFERED 20% METHANOL/WATER (pH ~ 8.05) AT 25°

X	*10^4k (min^{-1})*	*X*	*10^4k (min^{-1})*
Me_3Si	65.9	Me_3CCH_2	6.97
Et_3Si	35.7	Me_3SiCH_2	3.58
Et_3Ge	31.9	Et_3SiCH_2	2.40
Me_3C	8.93	Et_3GeCH_2	1.65

The results, shown in Table 1 as observed pseudo first-order rate constants, have the following features.

(*a*) The compound with $X = Me_3SiCH_2$ is less reactive than that with $X = Me_3CCH_2$. Since the order must be very predominantly or exclusively determined by inductive effects, it is consistent with the view that the $+I$ effect of the trimethylsilyl is greater than of the tert-butyl group[4].

When the reactivities of the Et_3MCH_2 compounds are also taken into account, the reactivity order of R_3MCH_2 compounds accords with the view that $Alkyl_3Si$ and $Alkyl_3Ge$ groups show very similar electron release towards an attached saturated carbon atom[5]. While the difference is small, the results provide yet another example of the behaviour in which such electron release is less for silicon than germanium, and thus, in this special sense, the electropositivity of silicon is slightly less than that of germanium, and markedly greater than that of carbon (*cf.* refs. 4 and 5).

(*b*) The compounds with $X = Me_3Si$, Et_3Si, and Et_3Ge are all several times as reactive as that with $X = Me_3C$, whereas if only inductive effects operated the Me_3C compound would be the most reactive. The high reactivity of the silicon- and germanium-containing compounds is to be attributed to p_π–d_π interaction between the alkynyl group and the metalloid atom[6], an electron-withdrawing effect which stabilizes the negatively-charged transition state more than the initial state.

(*c*) The Et_3Si group is less electron-withdrawing than the Me_3Si group and the Et_3SiCH_2 slightly more electron-supplying than the Me_3SiCH_2 group. Both results can be attributed to the greater electron-supplying inductive effect of ethyl than of methyl groups.

Experimental

Preparation of acetylene compounds. tert-Butyl-[7], neopentyl-[8] and trimethylsilylacetylene[9] were prepared by published methods. Other acetylenes were prepared from the appropriate trialkyl-germyl or -silyl halide and propargylmagnesium bromide in ether[10] or ethynylmagnesium bromide in tetrahydrofuran[11].

Preparation of tritiated acetylenes ($XC{\equiv}C^3H$). The alkynylmagnesium bromides, prepared by metallating the acetylenes with ethylmagnesium bromide in ether or tetrahydrofuran, were treated with tritiated water (3–50 mc/ml) followed by an excess of ordinary water. The usual working-up culminating in fractionatal distillation, gave the tritiated acetylenes with the properties listed in Table 2.

TABLE 2

PHYSICAL PROPERTIES OF $XC{\equiv}CH$ COMPOUNDS

X	*Observed*		*Literature values*		*Ref.*
	B.p.	n_D^{20}	*B.p.*	n_D^{20}	
Me_3Si	52–53°	1.3870[a]	53.5°	1.3892	12
Et_3Si	65–68/50 mm	1.4318	138	1.4302	13
Et_3Ge	70–71/65 mm	1.4450[a]	70–71/65 mm	1.4485	14
Me_3C	38	1.3740	38–39	1.3773[b]	15
Me_3CCH_2	73	1.3934	73–75	1.4028	8
Me_3SiCH_2	89–90	1.4130	89–91		16
Et_3GeCH_2	100/60 mm	1.4664	76–77/18 mm	1.4669	14
Et_3SiCH_2[c]	85/22 mm	1.4446			

[a] At 25°. [b] At 15°. [c] Analysis found: C, 70.1; H, 11.9. $C_9H_{18}Si$ calcd.: C, 70.0; H, 11.9%.

Rate measurements. The technique has been described elsewhere[17]. The medium used was a mixture of methanol (1 vol.) and aqueous buffer solution (pH, 8.05 ± 0.02) (4 vol.)[17].

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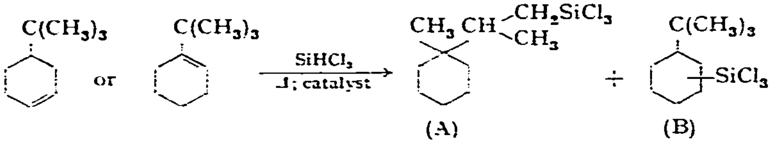
PRELIMINARY NOTE

Skeletal rearrangements in the reaction of trichlorosilane with t-butylcyclohexenes

It is well established that when trichlorosilane is added to either internal or terminal olefins under catalysis by chloroplatinic acid, there is a marked tendency for the formation of a terminally substituted trichlorosilylalkane. Thus, both 1- and 2-pentene add trichlorosilane in the presence of chloroplatinic acid to form n-amyltrichlorosilane almost exclusively[1].

Since it has been shown[1] that the trichlorosilyl group does not migrate under the reaction conditions, it is believed that the olefin substrate must undergo isomerization to a terminal alkene before introduction of the silane. While various cyclic and acyclic olefins have been shown[2–6] to undergo double bond migration during the process of adding trichlorosilane, no evidence of skeletal rearrangements accompanying the formation of a terminally substituted product from an internal olefin (or *vice versa*) has been reported. We are hereby reporting just such an isomerization phenomenon involving the addition of trichlorosilane to 1- and 4-t-butylcyclohexene catalyzed by dichlorobis(ethylene)-μ,μ'-dichlorodiplatinum(II)[7].



(1)

Treatment of *either* 1- or 4-t-butylcyclohexene with trichlorosilane and the aforementioned platinum complex resulted in the formation of the terminal adduct, (A), 1-trichlorosilyl-2-(1-methylcyclohexyl)propane and compound B, which we have identified as a ring adduct*. The structure of A was established by a comparison

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* The NMR and infrared spectra of this compound indicate that the tert-butyl group is present. Elemental analyses also check for a ring adduct. The exact ring isomer which this species represents has not yet been determined.