Alkyl Groups Migration from Tetra-alkyl-silanes, -germanes, and -stannanes to Carbenium Ions, effected by Lewis Acids: a Novel Method for Synthesising Hydrocarbons with a Quaternary Carbon Atom

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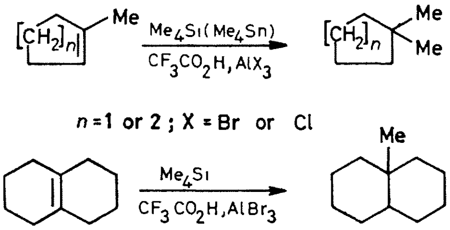
Summary Hydrocarbons with a quaternary carbon atom have been obtained by alkyl group transfer from group 4 tetra-alkyl derivatives to tertiary carbenium ions in the presence of Lewis acids

ORGANOSILICON hydrides in CF_3CO_2H are widely used as hydrogenation agents, particularly in the ionic hydrogenation of olefins [1] On the other hand tetra-alkyl- and tetra-aryl-silanes do not react with olefins in CF_3CO_2H,[2] presumably because of the higher stability of the Si–C bond towards the action of electrophilic reagents compared with that of the Si–H bond

We have found that addition of a methyl group from tetramethylsilane or tetramethylstannane, and a proton from the acid, to the C=C bond proceeds when $AlBr_3$ or $AlCl_3$ are added to the mixture of olefin and CF_3CO_2H in CH_2Cl_2 Thus, tri- and tetra-substituted ethylenes (1-methylcyclohexene, 1-methylcyclopentene, $\Delta^{9,10}$-octalin), which form tertiary carbenium ions upon protonation, undergo hydroalkylation to the saturated hydrocarbons containing a quaternary carbon atom In this reaction $AlBr_3$ is more active than $AlCl_3$ Under optimal reaction conditions (molar ratio of olefin : Me_4Si : CF_3CO_2H : $AlBr_3$ = 1 : 10 : 1·5 : 1·5, 20 °C, CH_2Cl_2) the yields of hydromethylation products reach *ca* 50% in 15 min

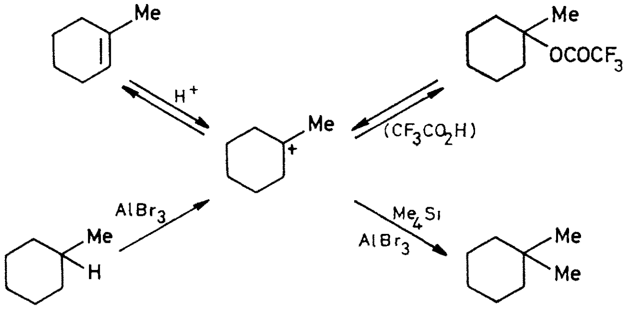


Cyclohexene, forming an unstable secondary carbenium ion upon protonation, affords only 4% of the hydroalkylation product (methylcyclohexane) along with 8% of cyclohexane and traces of 1,1-dimethylcyclohexane, methylcyclopentane, and 1,1-dimethylcyclopentane Since trifluoroacetates of tertiary alcohols can easily generate tertiary carbenium ions, they also react with Me_4Si in the presence of Lewis acids Thus, the trifluoroacetates of 1-methylcyclohexanol and 1-methylcyclopentanol yield *ca* 75% of 1,1-dimethylcyclohexane and 1,1-dimethylcyclopentane (trifluoroacetate : Me_4Si : $AlBr_3$ = 1 : 5 : 1·5, 20 °C, CH_2Cl_2) Under similar conditions the trifluoroacetate of a secondary alcohol (cyclohexanol) gives the same products as cyclohexane

Unlike Me_4Si, however, Me_3SiBu, Me_3SiCl, and $Me_3SiOSiMe_3$ do not add a methyl group to tertiary carbenium ions Methyl derivatives of germanium and tin (Me_4Ge, Me_4Sn, and Me_3SnCl) react with the trifluoroacetate of 1-methylcyclohexanol in the presence of $AlBr_3$ affording 1,1-dimethylcyclohexane in 40—75% yields The catalytic activity of Lewis acids in reactions with Me_4Sn increases in the series $MoCl_5 < WCl_6 < VOCl_3 < ZrCl_4 < AlCl_3 < TiCl_4 < AlBr_3$ It is also possible to transfer the propyl group from Pr_4Ge and Pr_4Sn and the butyl group from Bu_4Sn and Bu_4Si in the presence of $AlBr_3$

The ability of saturated hydrocarbons to form tertiary carbenium ions on abstraction of hydride ion with electrophilic reagents has been employed in the methylation of methylcyclohexane and decalin by Me_4Si in the presence of $AlBr_3$ [3] In this case, the hydrogen on the tertiary carbon atom is replaced by the methyl group yielding 1,1-dimethylcyclohexane (50%) and 9-methyldecalin (35%), respectively (hydrocarbon : Me_4Si : $AlBr_3$ = 1 : 10 : 3, 50 °C, 3—5 h, CH_2Cl_2) The role of the Lewis acid is probably associated with both increase of the medium acidity and activation of the alkylation agent

A typical reaction, involving Me_4Si and derivatives of methylcyclohexane, is shown in the Scheme



SCHEME

The reactions developed could be used for the synthesis of hydrocarbons with a quaternary carbon atom from olefins, esters, and tertiary hydrocarbons

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[1] D N. Kursanov, Z N Parnes, and N M Loim, *Synthesis*, 1974, **9**, 201

[2] D N. Kursanov, Z N Parnes, G D Kolomnikova, and I I Tyulyaev, *Izv Akad Nauk SSSR, Ser Khim* , 1972, 678.

[3] D. N. Kursanov, G I Bolestova, V A Kataev, and Z N Parnes, *Izv Akad Nauk SSSR, Ser Khim* , 1979, 1919.