

donor properties of highly electronegative atoms adjacent to silicon, such as oxygen or chlorine, have also been previously suggested^{8,9}.

By convention, groups which are more powerful electron attractors than the hydrogen atoms are said to exhibit negative ($-I$) effects, whereas those which are poorer electron attractors than hydrogen display positive inductive ($+I$) effects⁶. However, most polysilanes are substituted with organic groups rather than hydrogen as in carbon chemistry. The present series studied consists of an increasing number of dimethylsilylene units in which the polarity of the silicon-methyl bonds in the fully permethylated series are symmetrical or equivalent. Using this series for a relative value a $+I$ effect would be exhibited by a terminal hydrogen attached to silicon while a $-I$ effect would be displayed by chlorine. This observation would be based on the assumption that the molar absorptivity decreases with an increasing positive inductive effect of the substituent relative to a methyl group and increases with increasing negative inductive values relative to a methyl group. It would appear that further data from a variety of substituents precludes any formal assignment of the directive effects of the terminal substituents and their influence on the electron transitions involved in the ultraviolet excitations of the polysilane molecule. Further investigations are being made in this direction.

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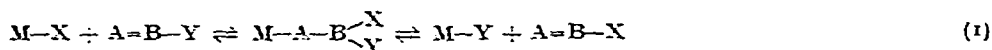
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A new route to trihalogenomethylmetallic compounds: tributyltrichloromethyltin.

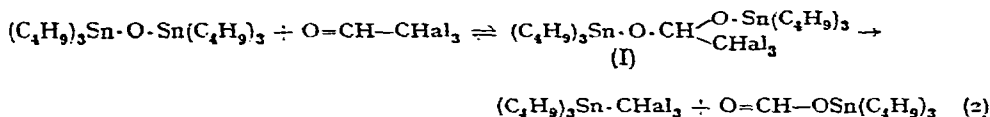
The exchange of groups X and Y between a metallic compound M-X and an acceptor molecule A=B-Y can be brought about by the addition-elimination process shown in equation 1.



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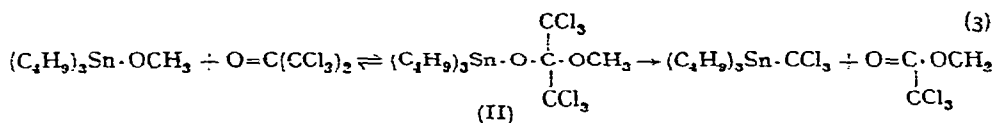
When Y is a trihalogenomethyl group, this provides a new route to trihalogenomethylmetallic compounds, which are of current interest as carbene-transfer reagents¹. This is illustrated by the reaction between trialkyltin oxides or alkoxides, and trihalogenomethyl aldehydes or ketones.

Bis(tributyl)tin oxide and chloral form a 1:1 adduct² (I; Hal = Cl) which decomposes at 150° to give tributyltin formate as one principal product.



The oxide-bromal adduct (I; Hal = Br) is much less stable. A 1 M solution in carbon tetrachloride decomposes in one day at room temperature to give again tributyltin formate, and now tributyltribromomethyltin which was identified by virtue of its reaction with methanol giving tributyltin methoxide and bromoform overnight.

Tributyltrichloromethyltin is isolated from the analogous reaction involving tributyltin methoxide and hexachloroacetone. The adduct (II) is formed exothermically. In 6 h at 55° it decomposes according to equation 3; the methyl trichloroacetate can be removed at room temperature under reduced pressure leaving tributyltrichloromethyltin as an oil (Found: C, 38.15; H, 6.55; Cl, 26.3. Required: C, 38.2; H, 6.65; Cl, 26.05 %), which reacts with ethereal hydrogen chloride giving chloroform in about 75 % yield during 10 days.



Analogous reactions occur when trichloroacetonitrile acts as the acceptor molecule, and when Sn-N bonded compounds (*e.g.* N-trialkylstannylformamides, -carbamates, or -ureas) act as the addenda³.

Reactions of this type are potentially capable of affording routes to a wide variety of electro-negatively substituted methylmetallic compounds.

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