Reaction of Group IV Hydrides with Di-iodoalkanes

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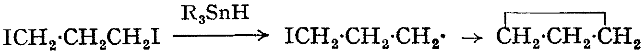
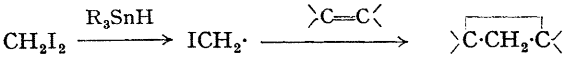
GROUP IV hydrides can be used as radical-generating and -trapping agents and also to effect some radical cyclization reactions.

Initially[1] reaction of organotin hydrides with organic halides was used to produce radicals tactically and clean. The method has one serious disadvantage, in that the life of the radical is determined by the rate of hydrogen abstraction from the tin hydride, and since this is a good radical trapping agent, [1d,h,2] the radical may be trapped before it can undergo the desired reaction. This prevented our observation of the reactions:



$$ICH_2{\cdot}CH_2CH_2I \xrightarrow{R_3SnH} ICH_2{\cdot}CH_2{\cdot}CH_2{\cdot} \rightarrow \overline{CH_2{\cdot}CH_2{\cdot}CH_2}$$

and



$$CH_2I_2 \xrightarrow{R_3SnH} ICH_2{\cdot} \xrightarrow{>C=C<} >\overline{C{\cdot}CH_2{\cdot}C}<$$

Instead, complete stepwise reduction of the dihalide occurred. Our solution to these[3a,b] and similar[3c-e] problems involved use of the reaction of a simple reactive radical (Me or Ph) with an organic iodide; however this method still has some of the disadvantages of the traditional methods.

Reactions similar to the stannane reductions occur with the corresponding silicon, germanium, and lead hydrides.[4] Although the free-radical chain nature of the silane reaction is fairly well established, the evidence for the radical nature of the mechanism of the germane and plumbane reactions is only qualitative and suggestive. In view of the apparent reactivity trends,[4] we believe that silicon, germanium, and lead hydrides, when used complementarily with the tin hydrides, will overcome the major difficulty found with last named compounds whilst retaining the advantages.[1c,d]

To illustrate this we treated Group IV hydrides with di-iodoalkanes. Results for the 1,3-di-iodopropane and methylene iodide–olefin[5] systems are summarized in Tables 1 and 2.

TABLE 1. *Reaction of Group* IV *hydrides with* 1,3-*di-iodopropane*[a]

Hydride	Temp.[b]	Cyclization : reduction ratio[c]
Ph_3SnH	Room temp.	0·000
Ph_3GeH	71°[e]	0·040
Ph_3GeH	99[e]	0·074
Ph_3GeH	134[f]	0·14
Ph_3GeH	189	0·36
Ph_3GeH	225	0·45
Ph_3SiH	189	1·8
Ph_3SiH	225	1·8
Ph_2SiH_2[d]	189	1·5
Ph_2SiH_2[d]	225	0·44

[a] Typically 0·055 and 0·11 mole fraction 1,3-di-iodopropane and hydride, respectively, in benzene as solvent. [b] 1,3-Di-iodopropane in benzene is thermally stable at all temperatures used except at 225° where reaction occurred to a very small extent in the absence of hydride. [c] These were the only detectable reaction paths. Yields were estimated by use of n.m.r. spectroscopy and g.l.c. analysis. [d] We recognize the possible uncertainty in the nature of the reducing agent(s). [e] AIBN-initiated; no reaction occurred in its absence. [f] $(Bu^tO)_2$-initiated; no reaction occurred in its absence.

TABLE 2. *Reaction of diphenylsilane with methylene iodide–olefins*[a,b]

Olefin	Conversion into cyclopropane, at 189° (%)
1-Octene	23
$PhCH{=}CH_2$	17
$Ph_2C{=}CH_2$	38
trans-Stilbene	37

[a] Typically, 0·050, 0·050, and 0·10 mole fraction CH_2I_2, olefin, and Ph_2SiH_2, respectively, in benzene as solvent. Although reaction in the absence of Ph_2SiH_2 yielded no cyclopropanes, $PhCH_2Me$, Ph_2CHMe, and $PhCH_2{\cdot}CH_2Ph$ were produced in yields of 55, 55, and 34%, respectively, from the corresponding olefins. The olefin + HI ⇌ alkane + iodine equilibrium and the reduction of olefins brought about by iodine are well known.

The reaction of 1,5-di-iodopentane with Ph_3GeH between

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71 and 225° resulted only in reduction (>99·5%). Its reaction with Ph_2SiH_2 at 225° and 255° resulted in cyclization : reduction ratios of 0·043 and 0·061, respectively.[6] The role, if any, of ω-iodo-alkyl silanes and germanes in all of these reactions is unknown.

These results and other considerations portend the general utility of the Group IV hydrides as selective radical trapping agents. By choice of one or a series of such hydrides it may be possible (*a*) kinetically to identify radicals along a reaction path and establish their intermediacy, (*b*) to study configurational and structural isomerization of radicals, (*c*) to intercept photochemical intermediates,[7] and (*d*) to produce optically active compounds from the corresponding racemic halides.[8]

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[5] Use of $CH_2{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$ led to complete destruction of the OEt group and the production of ethane. Although a silane-induced $R'CO_2R \rightarrow RH$ conversion is apparently unprecedented, the corresponding hydrostannolysis reaction has recently been reported [L. E. Khoo and H. H. Lee, *Tetrahedron Letters*, 1968, 4351.

[6] Reaction in the absence of Ph_2SiH_2 led initially to an extremely complex reaction mixture and then to the essentially exclusive presence of pentane in the solution component of the reaction mixture. (See footnote a to Table II).

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