

ULTRASOUND-INDUCED HETEROGENEOUS REDUCTION OF HALO,
ALKOXY AND AMINO DERIVATIVES OF GROUP IVB ELEMENTS
WITH LITHIUM ALUMINIUM HYDRIDE

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Abstract: Hydrides of group IVB elements have been prepared in high yield by heterogeneous reduction of the corresponding halo, alkoxy and amino derivatives using lithium aluminium hydride in non-polar solvents under ultrasonic irradiation.

The reduction of halo, alkoxy and amino derivatives of group IVB elements is a commonly-used method for the preparation of the corresponding hydrides¹⁻⁴.





Recently, a possibility of heterogeneous reduction of carbonyl compounds in non-polar solvents (hexane, benzene) by silica supported lithium aluminium hydride has been demonstrated⁵. On the other hand, there are numerous examples of successful heterogeneous reactions induced or accelerated by ultrasound (see, e.g.,^{6,7} and references therein). It has been shown, e.g., that ultrasonic irradiation enhances the reduction of aryl halides by LiAlH_4 in dimethoxyethane^{7c}. The aforesaid prompted us to study the possibility of using ultrasound for heterogeneous reduction of halo, alkoxy and amino derivatives of group IVB elements with lithium aluminium hydride in non-polar solvents.

We have found that LiAlH_4 suspended in a hydrocarbon solvent under ultrasonic irradiation is capable of reducing chloro, methoxy and diethylaminosilanes, chlorogermane and chlorostannane into the corresponding hydrides (Table). Under the same conditions, but in the absence of ultrasound the compounds under study were not reduced.

When the reduction by LiAlH_4 or LiAlD_4 must be carried out in deuterated solvents, hexane-d or cyclohexane-d₁₂ may be used instead of the expensive tetrahydrofuran-d₈.

Heterogeneous reduction with LiAlH_4 of derivatives of group IVB elements under ultrasonic irradiation ^{a, b}

Table

Substrate ^c	Solvent	Reaction time, h	Temperature, °C	Hydride ^d	Yield, % (by GLC)
Me_3SiCl	hexane	3	40	Me_3SiH	80 ^e
Ph_2SiHCl	hexane	2	40	Ph_2SiH_2	>95
Et_3GeCl	pentane	4,5	40	Et_3GeH	>95
Me_3SnCl	cyclohexane	2,5	25	Me_3SnH	>95
$\text{Me}_3\text{SiNEt}_2$	hexane	3	40	Me_3SiH	70 ^e
 Si(OMe)Me_2	pentane	3	25	 SiHMe_2	100
 Si(OMe)Me_2 ^f	cyclohexane- d_{12}	2	25	 SiDMe_2	100

a all reactions were carried out using a laboratory ultrasonic cleaner (Branson[®] B-220, 100 W)

b LiAlH_4 : Substrate molar ratio in all cases was 3:1

c 0,2 M solutions

d ¹H NMR and mass-spectra of the products were in compliance with those of a authentic samples

e isolated yield

f LiAlD_4 was used as a reducing agent

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(Received in UK 12 January 1984)