Journal of Organometallic Chemistry, 284 (1985) C31—C32
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REDUCTION OF ALKOXYSILANES, HALO-SILANES AND -GERMANES WITH LITHIUM ALUMINIUM HYDRIDE UNDER PHASE-TRANSFER CONDITIONS

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(Received November 27th, 1984)

Summary

In the presence of phase-transfer catalysts, silicon and germanium organohydrides were obtained in high yield by reduction of the corresponding halo and alkoxy derivatives with lithium aluminium hydride in the solid $LiAlH_4$/hydrocarbon two-phase system.

The preparation of highly reactive hydro-silanes and -germanes by reduction of various silicon- and germanium-functional compounds with $LiAlH_4$ in ether or THF is often complicated by difficulties of their isolation, since the subsequent destruction by excessive lithium aluminium hydride with water or ethyl acetate considerably decreases the yield of the reaction due to dehydrocondensation in side reactions. For this reason, it seems more suitable to obtain organo-silanes and -germanes by heterogeneous reduction of the corresponding halo and alkoxy derivatives of silicon and germanium. In the literature the heterogeneous reduction of halo, alkoxy and amino derivatives of the Group IVB elements to the respective hydrides in hydrocarbon solvents upon ultrasonic (US) irradiation of the reaction mixture [1] and the reduction of aryl halides in hexane with $LiAlH_4$ supported by finely dispersed silica gel [2] are reported.

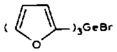
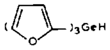
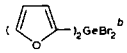
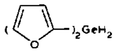
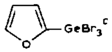
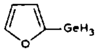
A more convenient preparative procedure has been recently proposed for the reduction of ketones, alkyl and aryl halides, nitriles, and amides with $LiAlH_4$ in non-polar solvents under phase-transfer conditions [3]. The present study was undertaken to explore a possibility of synthesizing silicon and germanium organohydrides under similar conditions.

As a result of their reduction in the solid $LiAlH_4$/hydrocarbon two-phase

0022-328X/85/$03.30

TABLE 1

SYNTHESIS OF ORGANO-SILANES AND -GERMANES IN THE SOLID $LiAlH_4$/HYDROCARBON SYSTEM (0.1 *M* solution, 5 *M* % of catalyst with respect to substrate [substrate]/[$LiAlH_4$] 1/2)

Substrate	Product	Catalyst	Solvent	*T* (°C)	Time (h)	Yield[a] (%)
$PhMe_2SiOMe$	$PhMe_2SiH$	—	hexane	25	6	—
				60	3	12
		15-Crown-5	hexane	25	6	45
				60	3	83
		Oct_4NBr	hexane	25	6	18
				60	3	92
Et_3SiCl	Et_3SiH	—	toluene	25	6	3
				60	3	11
		15-Crown-5	toluene	25	6	60
				60	1	84
		$Et_3(PhCH_2)NCl$	toluene	25	6	>95
				60	1	>95
Et_3GeCl	Et_3GeH	—	benzene	25	1	3
		15-Crown-5	benzene	25	1	82
		$Et_3(PhCH_2)NCl$	benzene	25	1	>95
		$Et_3(PhCH_2)NCl$	benzene	25	1	>95
		$Et_3(PhCH_2)NCl$	benzene	25	6	>95
				80	1	>95
		$Et_3(PhCH_2)NCl$	benzene	25	6	70
				80	1	81

[a] GLC data. [b] [substrate]/[$LiAlH_4$] 1/4. [c] [substrate]/[$LiAlH_4$] 1/6.

system in the presence of phase-transfer catalysts the halo- and alkoxysilanes, and halogermanes gave the corresponding hydrides (see Table 1).

A convincing example illustrating the advantages of this phase-transfer method is the preparation of earlier unknown furylhydrogermanes which could not be obtained in ether due to Ge—C_{furyl} bond cleavage by lithium aluminium hydride. This reaction was uneffective in hydro carbons upon ultrasonic irradiation of the reaction mixture because of low yield and slowness of the synthetic procedure. Hence, the reduction of halo-silanes and -germanes with lithium aluminium hydride in the solid $LiAlH_4$/hydrocarbon two-phase catalytic system is an effective and convenient method for preparation of hydro-silanes and -germanes.

References

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