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Preliminary communication

ALKALI METAL HYDRIDES: NEW METALLATING REAGENTS FOR GERMANIUM AND TIN

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Summary

New procedures for the preparation of organogermyl- and stannyl-sodium or -potassium, which undergo coupling reactions with alkyl, allyl, and benzyl halides and α-enones, are reported.

We previously described a new route for the preparation of silyl anions and especially for R_3Si^- [1]. We found that Si—H and Si—Si bonds are quantitatively cleaved by alkali metal hydrides, e.g. reactions 1, 2:

$$R_3SiH \xrightarrow{KH} R_3SiK \qquad (1)$$

$$Me_3Si{-}SiMe_3 \xrightarrow{KH/NaH} Me_3SiK/Na + Me_3SiH \qquad (2)$$

We have now found that Ge—H, Sn—H and Sn—Sn bonds are also quantitatively cleaved by alkali metal hydrides, e.g. reactions 3—5.

$$R_3GeH \xrightarrow{KH/NaH} R_3GeK/Na \qquad (3)$$

(R = n-Bu and Ph)

$$R_3SnH \xrightarrow{KH/NaH} R_3SnK/Na \qquad (4)$$

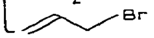
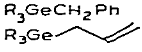
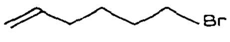
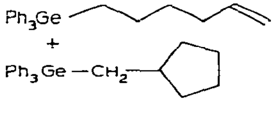
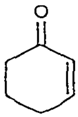
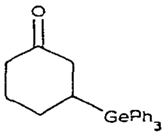
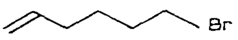
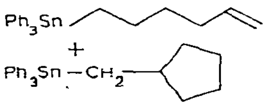
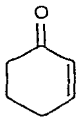
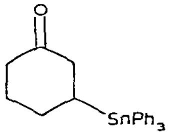
(R = n-Bu and Ph)

$$Ph_3Sn{-}SnPh_3 \xrightarrow{KH/NaH} 2\ Ph_3SnK/Na \qquad (5)$$

Reaction 3 was carried out in dimethoxyethane (DME) at room temperature for 1 h with KH or at 40°C for 4 h with NaH. Reaction 4 was carried out at room temperature using Et_2O, tetrahydrofuran or DME as solvent: quantitative cleavage of the Sn—H bond was obtained in 30 min. Reaction 5 was carried

TABLE 1

REACTIONS OF TRIALKYL-GERMYL AND -STANNYL ANIONS WITH VARIOUS SUBSTRATES

Germyl or stannyl anion (solvent)	Electrophile	Temp.(°C)	Product	Yield (%)
R_3GeK/Na (Et_2O, DME; R = n-Bu, Ph)	EtI $PhCH_2Cl$ 	Room temp. Room temp. Room temp.	R_3GeEt R_3GeCH_2Ph 	70—80
Ph_3GeK (DME)		Room temp.		80 (75)^a (25)^a
Ph_3GeK (DME)		−78		70
R_3SnK (Et_2O,THF,DME; R = Ph, n-Bu)	EtI $PhCH_2Cl$	0 0	R_3SnEt R_3SnCH_2Ph	60—70
Ph_3SnK (DME)		Room temp.		70 (70)^a (30)^a
Ph_3SnK (THF)		−78		75

[a] Ratio of the two isomers.

out in DME at room temperature using two equivalents of alkali metal hydrides. For instance, Ph_3GeH (20 mmol) was slowly added to a stirred suspension of the alkali metal hydride NaH or KH (2.2 mol) in DME. A clear yellow-green solution of Ph_3GeK or Ph_3GeNa was rapidly obtained. When the reaction was complete, the excess of hydride was eliminated by centrifugation to give a clear solution of Ph_3GeM.

Although several procedures are available for the preparation of organogermyl- [2] and organostannyl- [3] alkali metal compounds, our route has advantages in some cases. For instance, the preparation of R_3GeLi (R = alkyl) by hydrogen—metal exchange with organolithium reagents gives varying results: e.g., metallation of triethylgermane with PhLi or n-BuLi in ethereal solvents gives triethylgermyllithium in less than 10% yield [2]. Another advantage is that reagents are obtained free of alkali halides.

The reactions of the anions with various substrates were examined, and the results are summarized in Table 1. Organic halides give substitution products in good yields. The 1-bromohex-5-ene gives predominant S_N2-like substitution products either with Ph_3Ge^- or Ph_3Sn^- in DME, but a competitive radical process is shown by the formation of cyclic products. (This aspect will be considered in more detail in the full paper). Finally, 1,4-addition to cyclohexenone was observed for Ph_3Ge^- and Ph_3Sn^- in DME: CuI was not necessary.

References

1 R. Corriu and C. Guérin, J. Chem. Soc. Chem. Commun., (1980) 168.

2 M. Lesbre, P. Mazerolles and J. Satgé, The Organic Compounds of Germanium, Interscience Publishers John Wiley and Sons Ltd., New York, 1971, p. 646.

3 For instance: (a) W.P. Neumann, The Organic Chemistry of Tin, John Wiley, New York, 1970, p. 120; (b) M.J. Newlands, in A.K. Sawyer (Ed.), Organotin Compounds, Marcel Dekker, New York, Vol. 3, 1972, p. 881; (c) R.C. Poller, The Chemistry of Organotin Compounds, Logos Press, London, 1970, p. 145; (d) N.S. Vyazankin, C.A. Razuvaev and O.A. Kruglaya, Organometal. Chem. Rev. A, 3 (1968) 323; (e) J.P. Quintard and M. Pereyre, Bull. Soc. Chim. Belg., in press.