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Preliminary communication

BIVALENT BEHAVIOUR OF TRIPHENYLSILYLLITHIUM IN REACTIONS WITH FUNCTIONAL ORGANOGERMANES

FRANCIS H. CARRE and ROBERT J.P. CORRIU*

Laboratoire des Organométalliques associé au C.N.R.S., No. 82, Université des Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34060 Montpellier Cédex (France)

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Summary

A study of the stereochemistry of nucleophilic substitution of asymmetric germanes, and chloro- and menthoxy-germanes has shown that with chlorogermanes, the expected triphenylsilylgermanes are produced in a low yield and with a weak optical activity, but that metallation occurs to some extent with menthoxygermanes, thus leading to *threo*-digermanes with excellent specific rotations; the stereochemistry is inversion at both centers.

In a previous paper [1] the reactions of triphenylgermyllithium and optically active germyllithiums with asymmetric chloro-, methoxy- and menthoxygermanes were reported. The germyllithium reagents were shown to retain their configuration whilst inversion occurs for the chloro- and alkoxy-germanes. We report here the behaviour of triphenylsilyllithium as reagent, along with the stereochemistry of substitution at asymmetric germanium.

Triphenylsilyllithium was prepared by a known method [2] and used in slight excess with the chloro- or menthoxy-germanes. Reaction products were chromatographed through a column packed with alumina. Elution with a mixture of light petroleum and benzene (9/1) allowed recovery of any unreacted germane. Then, elution with pure benzene gave the digermane or the triphenylsilylgermane. When a significant amount of hexaphenyldisilane was observed, this compound was eliminated by crystallisation and filtration before chromatography.

The results obtained are shown in Table 1.

It is noteworthy that the chlorogermane leads to the expected mixed organometallic compound whilst the menthoxygermanes give *threo*-digermanes. From previous work [1] we know that the sign of the specific rotation of these digermanes is evidence for inversion of configuration at both germanium atoms (Scheme 1).

In case of isopropylphenyl-1-naphthylmenthoxygermane, the specific rota-

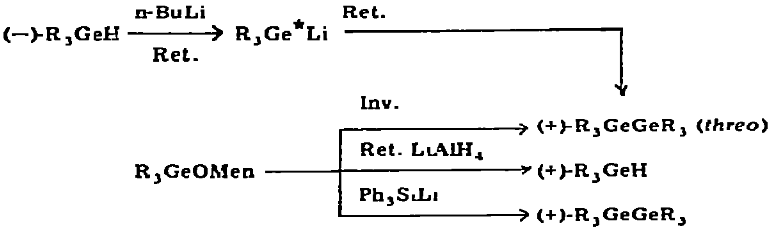
TABLE 1

REACTIONS OF Ph_3SiLi WITH GERMANES AT ROOM TEMPERATURE

Germanes	$[\alpha]_D^{25}$	Reaction time (h)	Product	Yield (%)	$[\alpha]_D^{25}$	Stereochemistry
(−)i-PrPhNpGeH	−0.85	20	(−)Ge*H	[100]	−0.81	Ret.
(+)i-PrPhNpGeCl	+5.0	0.5	(−)Ge*$SiPh_3$	6	−0.23	Inv.[a]
(−)i-PrPhNpGeOMen	−74.7	15	(−)Ge*H	22	−1.46	Inv.
			(+)Ge*Ge*	30	+20.9	Inv.
(−)MePhNpGeOMen	−49.0	1	(+)Ge*Ge*	14	+8.85	Inv.
Ph_3GeD		7	Ph_3GeH	28		

[a] In this case the stereochemistry is assumed.

SCHEME 1

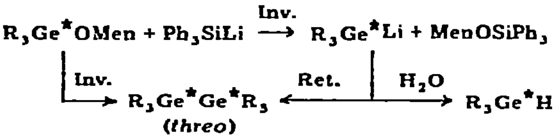


R_3 = i-Pr, Ph, 1-Np or Me, Ph, 1-Np

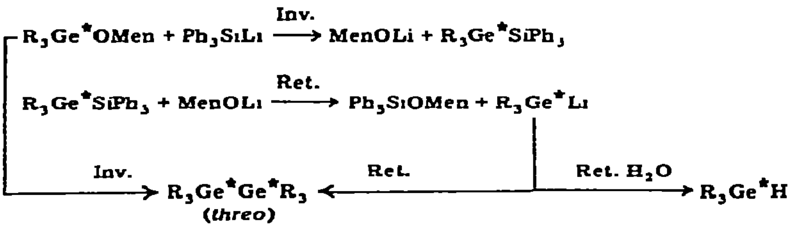
tion of the resulting digermane is higher than that previously reported for reaction with optically active germyllithiums [1].

The mechanism of the reaction of menthoxygermanes and triphenylsilyllithium probably involves either direct metallation of germanium (Scheme 2) or preliminary formation of a Ge—Si bond (Schemes 3 and 4). This type of bond seems extremely sensitive to cleavage by nucleophilic reagents, and Table 2 shows that such cleavages are complete within short times on treatment with lithium reagents or even sodium alkoxide, followed by hydrolysis of the reaction mixture.

SCHEME 2



SCHEME 3



SCHEME 4

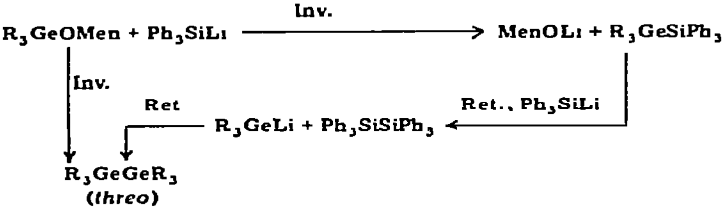


TABLE 2

CLEAVAGE OF *rac*-i-PrPhNpGeSiPh$_3$ BY NUCLEOPHILIC REAGENTS

Reagents	Results[a]
Ph_3SiLi	Colour of silyllithium disappears within 10 min, Si_2Ph_6 crystallises from the reaction mixture
RLi (R = CH_3, n-Pr)	i-PrPhNpGeH
CH_3ONa	i-PrPhNpGeH + starting material

[a] Possible traces of Ph_3SiH were investigated by IR spectroscopy in every case. None of this compound was detected in the crude reaction products. Reaction times were 12 h.

None of these routes can be finally rejected since all three explain the synthesis of the digermane and hexaphenyldisilane. However, we think Scheme 2 less probable since it involves metallation of germanium via inversion of configuration, whilst in Schemes 3 and 4 the stereochemistry assignments are consistent with known organogermanium chemistry. Furthermore, the first steps in Schemes 3 and 4 lead to the expected Si—Ge bonded compound, which is formed when chlorogermane is the starting material.

References

1 F. Carre et R. Corriu, J. Organometal. Chem., 65 (1974) 349.
2 L.H. Sommer and K.T. Rosborough, J. Amer. Chem. Soc., 91 (1969) 7067.