

Preliminary communication

SYNTHESIS OF 1,8-BIS(TRIMETHYLGERMYL)NAPHTHALENE

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Summary

Reaction of 1,8-dilithionaphthalene with trimethylchlorogermane yields the title compound. In contrast to the silicon analog, the extent of lithium transfer in this system is negligible.

Although reaction of 1,8-dilithionaphthalene (I) with trimethyltin chloride yields 1,8-bis(trimethylstannyl)naphthalene (II) [1], reaction of I with trimethylchlorosilane gives 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane (III) instead of the expected 1,8-bis(trimethylsilyl)naphthalene (IV) [2]. It therefore became of interest to explore the reaction of I with trimethylchlorogermane. We now report that this reaction affords 1,8-bis(trimethylgermyl)naphthalene (V) in excellent yields.

Reaction of I [3] with 2 eq of trimethylchlorogermane in ether at room temperature for 20 hr, followed by the usual workup, gave the reaction product in 80-90% yields as a colorless solid, mp 91-92°C, after recrystallization from methanol.** Anal. Found: C, 53.11; H, 6.71; Ge, 39.92. Calcd. for C₁₆H₂₄Ge₂: C, 53.15; H, 6.69; Ge, 40.16. The ¹H NMR spectrum (60 MHz, CDCl₃) featured signals at δ 0.45 (s, 18H, CH₃) and 7.10-7.75 ppm (complex m, 6H, aromatic H). The ¹³C {¹H} NMR spectrum

**The ¹H NMR spectrum of the mother liquors from the recrystallization of the reaction product contained signals indicative of the presence, in minor amounts, of 2-(1-naphthyl)-2,4,4-trimethyl-2,4-digermapentane (VI).

(25.2 MHz, CDCl_3 , $\text{Cr}(\text{acac})_3$) displayed a signal at δ 2.92 ppm due to the CH_3 carbons, three signals at δ 123.3, 129.4, and 134.9 ppm for the proton-bearing aromatic carbons, and three signals at δ 133.3, 140.8, and 141.8 ppm for the quaternary carbons. The mass spectral pattern was also consistent with the assigned structure.

The successful synthesis of II and V reveals that the course of the reaction of I with trimethylchlorosilane, to give III instead of IV, remains without parallel in this series. The formation of what appear to be minor quantities of VI along with V indicates that the lithium transfer reaction $\text{C}_{\text{sp}^2}\text{-Li} + \text{Z-CH}_3 \rightarrow \text{C}_{\text{sp}^2}\text{-H} + \text{Z-CH}_2\text{Li}$ decreases in importance in the series $\text{Z} = \text{Si} > \text{Ge} > \text{Sn}$. It remains to be determined which combination of factors is chiefly responsible for this behavior.

The present results suggest that in other cases where lithium transfer reactions have frustrated access to organosilanes (such as tetrakis(trimethylsilyl)ethylene [2]), the corresponding organogermane may also be more amenable to synthesis. Since steric parameters in organosilanes and -germanes are very similar ($\text{Si-H} = 1.48$, $\text{Ge-H} = 1.55$, $\text{Si-C} = 1.89$, $\text{Ge-C} = 1.98 \text{ \AA}$) [4], the latter represent good models for steric effects in the former.

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References

1. D. Seyferth and S. C. Vick, *J. Organometal. Chem.*, 141 (1977) 173.
2. R. J. Wroczynski, M. W. Baum, D. Kost, K. Mislow, S. C. Vick, and D. Seyferth, *J. Organometal. Chem.*, 170 (1979) C29.
3. R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, 27 (1962) 672.
4. "Organometallic Compounds of the Group IV Elements", ed. by A. G. MacDiarmid, Marcel Dekker, Inc., New York, Vol. I, Part I, pp 52-53 (1968).