

STABLE CARBENOIDS XLIV¹ - PREPARATION, Silylation, AND LIGAND EXCHANGE

REACTIONS OF $(\text{CH}_3)_3\text{SiCBr}_2\text{Li}$ AND $[(\text{CH}_3)_3\text{Si}]_2\text{CBrLi}$

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(Received in UK 10 October 1970; accepted for publication 21 October 1970)

Summary: Compounds $[(\text{CH}_3)_3\text{Si}]_n\text{CBr}_{4-n}$ ($n=1,2,3$) have been prepared by silylation of the corresponding Li-carbenoids. $(\text{CH}_3)_3\text{SiCBr}_2\text{Li}$ and $(\text{CH}_3)_3\text{Si}_2\text{CBrLi}$ are stable at -100° . Rapid ligand exchanges are reported between the former and $(\text{CH}_3)_3\text{SiCBr}_3$ and between the latter and LiCBr_3 .

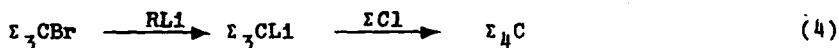
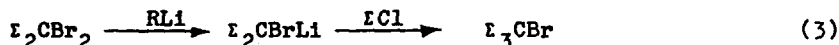
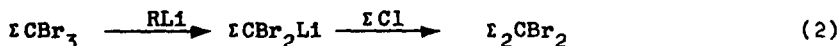
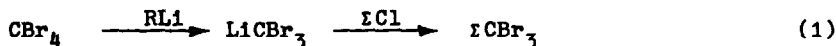
Previous papers in this series have shown that two reactions which were discovered in, and first published from, our laboratory, are of general utility: (1) the low-temperature metallation of halohydrocarbons in THF or Trapp mixture to form stable Li-carbenoids,^{2,3} and (2) the metathesis between these carbenoids and metal halides to give new α -haloorganometallic compounds.^{2c,3,4} A recent paper by Seyferth et al.,⁵ in which both procedures were used to prepare trimethylsilyl-dichloromethylithium and bis(trimethylsilyl)-chloromethylithium, prompts us to report some results of our work done since 1967 with trimethylsilyl-dibromomethylithium and bis(trimethylsilyl)-bromomethylithium.

Both of these carbenoids have been assumed as transient intermediates in a reaction sequence leading to tetrakis(trimethylsilyl)-methane from CBr_4 and Li-metal.⁶ Their thermal stability at -100° was demonstrated by the finding of Merkle,⁷ that a fourfold iteration of bromo-lithium exchange and silylation with trimethylchlorosilane ultimately also gave tetrakis(trimethylsilyl)-methane in moderate yield (eq. (1) - (4); the symbol Σ stands

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for $(\text{CH}_3)_3\text{Si}$).

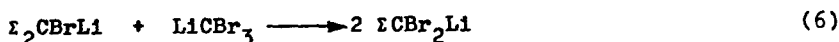


We have examined each reaction step in detail. Pure ECBr_3 (m.p. 201-203°, previously available in only 8% yield⁸) was obtained in 71% yield from LiCBr_3 ⁹ and EC1 (eq. (1)). ECBr_3 underwent very rapid Br/Li exchange with phenyllithium to give ECBr_2Li , silylation of which afforded E_2CBr_2 (eq. (2)). In the same way, E_3CBr (recently prepared in 35% yield from E_3CH and NBS¹⁰) was obtained in 79% yield, m.p. 197-198°, from E_2CBr_2 via E_2CBrLi (eq. (3)). Combination of procedures (2) - (4) gave 79% E_4C (based on ECBr_3 ; m.p. 408-410°, uncorr., from ethanol). All reactions were carried out in THF or Trapp mixture between -110° and -100°.

Although these reactions seem to be quite simple and straightforward, they are actually rather complex. Thus, a mixture of ECBr_2Li and ECBr_3 (as is present during the preparation of the former from the latter) will undergo extremely rapid ligand exchange (completed in less than 30 sec at -105°) to give E_2CBr_2 (yield, based on eq. (5), 70-81%; m.p. 70°, after sublimation; NMR (in CCl_4): τ 9,71) and LiCBr_3 (identified by carboxylation as tribromoacetic acid):

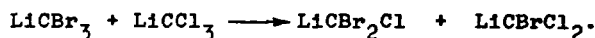


An equally rapid symproportionation was noted between the carbenoids E_2CBrLi and LiCBr_3 , to give ECBr_2Li (nicely evidenced, i.a., by mixing suspensions of the pure carbenoids at -110°):



Considering now, that I_2CBr_2 (from eq. (2)) is transformed into I_2CBrLi by phenyllithium under the conditions of the formation of ICBr_2Li from ICBr_3 , we meet the curious and unique situation, that at least a large portion of the carbenoid ICBr_2Li , which is finally silylated, according to eq. (2), has actually arisen via the transformations shown in eq. (5) and (6).

Displacements of halomethyl anions from "neutral" silanes, as outlined in reaction (5), are quite common, and are known to occur readily under basic conditions.¹¹ On the other hand, ligand exchanges between different carbenoids, as shown in the symproportionation (6), are rare and have only recently been reported by Köbrich and Fischer,¹² e.g.:



A third type of ligand exchange is described in the following paper.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

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