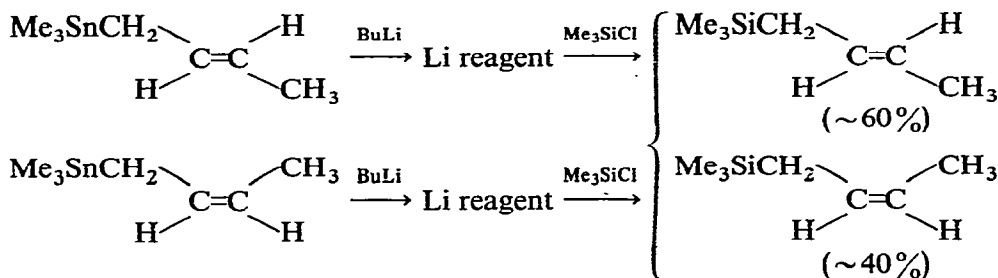


PRELIMINARY NOTES

cis-trans-Isomerization of crotyllithium and crotyltrimethyltin

In previous studies we had shown that the transmetalation occurring between *cis*- and *trans*-propenyltin compounds and organolithium reagents generated propenyllithium reagents without change in geometric configuration¹. We report here concerning studies of similar *trans*-metalation reactions involving crotyltin compounds and organolithium reagents.

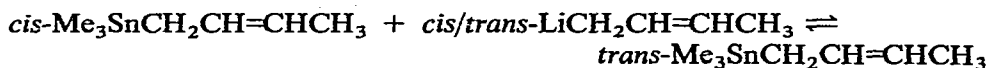
The reaction of 25.4 mmoles of *n*-butyllithium in 17 ml of *n*-hexane with 25.6 mmoles of *trans*-crotyltrimethyltin² (containing 4% of the *cis*-isomer) in 20 ml of ether produced a clear, yellow solution. Addition of 25.4 mmoles of trimethylchlorosilane discharged the color and resulted in precipitation of white solid. Hydrolysis was followed by gas-liquid partition chromatography (GE XF-1150 on Chromosorb P at 70° and 10 psi helium) of the organic layer. Crotyltrimethylsilane (a 3 : 2 mixture of isomers) had been formed in 94% yield. The more abundant isomer was eluted first from a silver nitrate GLPC column and had $\nu(\text{C}=\text{C})$ (w) at 1655 cm^{-1} . The other isomer had $\nu(\text{C}=\text{C})$ (m) at 1645 cm^{-1} . According to Muhs and Weiss³, the *cis*-isomer of an olefin has a longer retention time than the *trans*-isomer on a silver nitrate column. Furthermore, the C=C stretching frequency generally is less intense for the *trans*-isomer than for the corresponding *cis*-isomer and occurs at lower frequency for the latter⁴. On this basis, the crotyltrimethylsilane produced contains the *trans*- and *cis*-isomers in 3 : 2 ratio. Identical results were obtained when the reaction mixture from 13 mmoles each of *n*-butyllithium and 99% *cis*-crotyltrimethyltin² in hexane-ether was quenched with trimethylchlorosilane.



Previous NMR studies⁵ of allyllithium in ether showed that it, as is the allyl Grignard reagent⁶, is best described in terms of a rapid, dynamic equilibrium, $\text{Li}^*\text{C}^-\text{H}_2\text{CH}=\text{CH}_2 \rightleftharpoons \text{C}^*\text{H}_2=\text{CHCH}_2\text{Li}^*$. The fact that the lithium reagents prepared

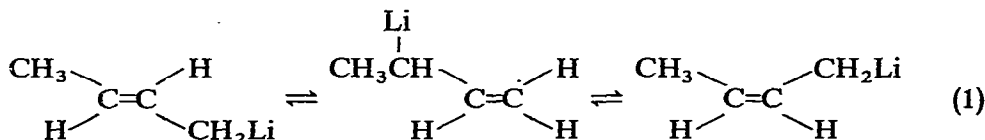
* Writing this equilibrium in this manner merely serves to indicate that an AX_4 NMR spectrum is observed. By what path the methylene protons in allyllithium become equivalent is not known precisely at present. A very rapid intramolecular process without C-Li bond ionization is a possibility, but we favor a very rapid exchange mechanism in which the ionized species, $\text{Li}^+[\text{CH}_2=\text{CH}-\text{CH}_2^-]$ and $\text{Li}^+[:\text{CH}_2-\text{CH}=\text{CH}_2^-]$, are in dynamic equilibrium with the covalent forms. Note the recent discussion of allylalkali metal derivatives by Grovenstein *et al.*⁷ in this connection. It seems reasonable that the relative importance

by the reaction of crotyltriphenyltin and phenyllithium on one hand and α -methylallyltriphenyltin and phenyllithium on the other had identical electronic spectra⁸ suggested that here also such an equilibrium is operative: $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Li} \rightleftharpoons \text{CH}_3\text{CH}(\text{Li})\text{CH}=\text{CH}_2$. Such an equilibrium would destroy the *cis*- and *trans*-geometry of the reagents initially generated from *cis*- and *trans*-crotyltrimethyltin and would serve to explain the results cited above. Since such *trans*-metalation reactions are equilibrium processes^{1,9}, it was predicted that small amounts of an organolithium reagent in ether added to pure *cis*- or *trans*-crotyltrimethyltin should cause isomerization of these compounds, *i.e.*



This was found to be the case. Addition of 10 mole % of *n*-butyllithium to either *cis*- or *trans*-crotyltrimethyltin, followed by hydrolysis after 30 min, gave recovered crotyltrimethyltin which now contained the *trans*- and *cis*-isomers in *ca.* 3:2 ratio. Thus a new mode of isomerization of alkenyltin compounds is added to the photochemical and lithium-induced (radical anion) isomerization procedures we described earlier for propenyltin compounds^{10,11}.

The fact that *trans*- and *cis*-crotyltrimethylsilane were formed in 3:2 ratio in these experiments *cannot* be taken to indicate that the organolithium reagent solution from which they were obtained contains *trans*- and *cis*-crotyllithium in this ratio and none of the α -methylallyl isomer*, since the rate at which equilibrium (1) is attained undoubtedly is very rapid and since the product ratio then will depend on



the relative rates at which each isomer reacts with trimethylchlorosilane and not necessarily on the amounts of each isomer present at equilibrium.

An attempt has been made to obtain information concerning the nature of equilibrium (1) in solution by NMR spectroscopy. The reaction of crotyltrimethyltin with methyllithium in ether did not go to completion when a 1:1 reagent ratio was used, but the crotyltin compound was consumed when two equivalents of methyllithium were added. However, uncertainties existed about the effect of excess methyllithium on the nature of the crotyl/ α -methylallyllithium species in solution. The reaction of two equivalents of *n*-butyllithium with one of tetracrotyltin in pentane gave a solid precipitate, but NMR analysis of its dimethyl ether solution as well as a trimethylchlorosilane quench followed by product analysis showed it to contain crotyllithium and *n*-butyllithium in *ca.* 1:1 ratio. Finally, the reaction of ethyllithium

of ionized and covalent species in such dynamic equilibria will be affected by the solvent medium and by the nature of the substituents on the allyl moiety. We write the crotyllithium equilibria discussed in this communication in terms of covalent species only for the sake of convenience; it should be understood that in these equilibria ionized species most likely are also involved.

* It should be mentioned that *cis*- and *trans*-crotyltrimethylsilane were configurationally stable in the presence of ethereal *n*-butyllithium.

in benzene and tetracrotlytin in 1:1 ratio precipitated a solid lithium compound which showed no absorption due to ethyllithium or crotyltin compounds in the NMR spectrum of its dimethyl ether solution.

The NMR spectrum (Varian A60) of the organolithium product from the EtLi + tetracrotlytin reaction is shown in Fig. 1. The crotyllithium solution prepared

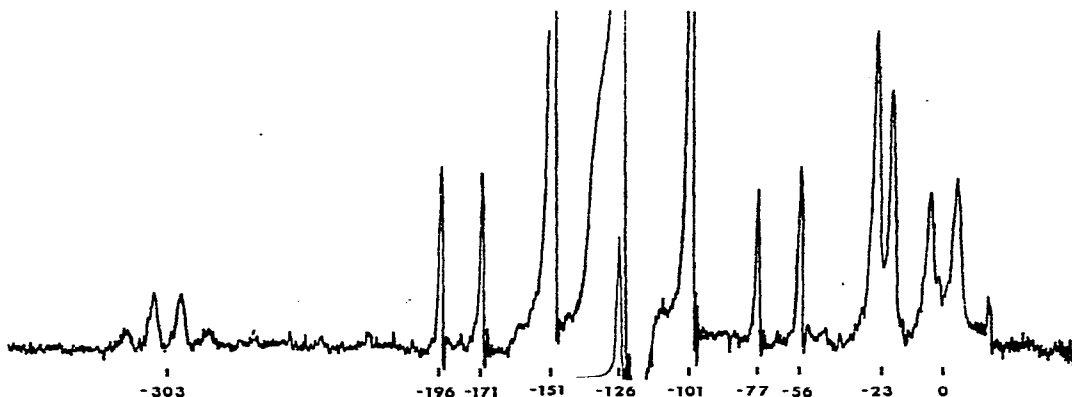
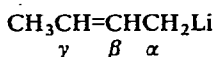


Fig. 1. Nuclear magnetic resonance spectrum of "crotyllithium" in dimethyl ether at room temperature (60 Mc), with the chemical shifts referred to the center of the α -CH₂ doublet of the lithium reagent. The CH₃ doublet is at -23 cps and the γ -CH quartet at -303 cps. The intense resonance at -126 cps is due to solvent, while the lines at -77, -101, -151 and -171 cps were shown to be spinning side bands. The two lines at -56 and -196 cps are ¹³C proton satellite resonances of the solvent.



via the reaction of crotyltrimethyltin with two equivalents of methyllithium in (C₂D₅)₂O showed the identical NMR spectrum (except that the γ -CH multiplet is visible since it is not obscured by solvent absorption) (Fig. 2). This suggests that excess methyllithium does not affect equilibrium (1).

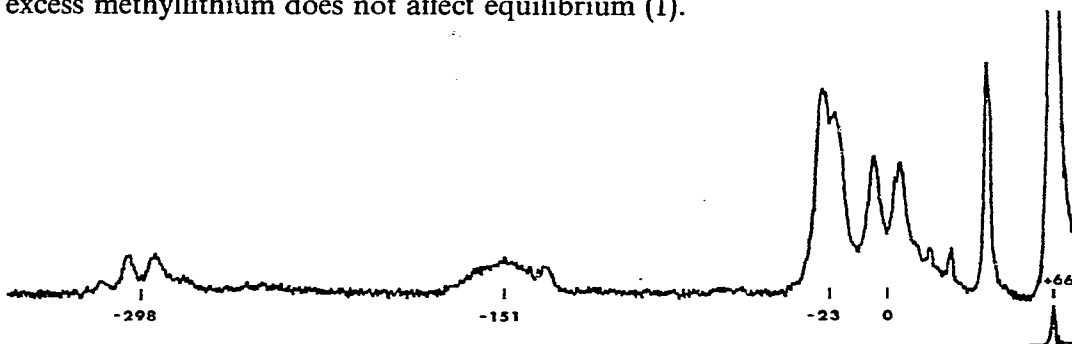
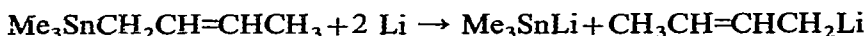


Fig. 2. Nuclear magnetic resonance spectrum of "crotyllithium" in diethyl ether-*d*₁₀ at room temperature at 60 Mc. with the chemical shifts referred to the center of the α -CH₂ doublet. The CH₃ doublet occurs at -23 cps; the γ -CH resonance is at -151 cps, and the β -CH quartet at -298 cps. The intense peak at +66 cps is the tetramethyltin resonance with one of the pair of the ¹¹⁷Sn, ¹¹⁹Sn satellite resonances at about +40 cps.

These spectra are quite similar to that of the crotyl Grignard reagent¹². If the species formed in the (crotyl)₄Sn + EtLi reaction existed predominantly as MeCHLiCH=CH₂, the CH₂ resonance would appear in the vinyl region. Since this

resonance actually appears closer to that in allyllithium, the primary form must predominate. However, the chemical shift of the CH_2 resonance is at somewhat lower field (20–40 cps) than estimated for a static primary form, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Li}$, and this suggests that the secondary isomer does make some contribution to the spectrum, but a quantitative estimate cannot be made. The CH_2 doublet is consistent with the presence of two equivalent protons on a carbon atom bonded to a carbon carrying a single proton, which rules out a configurationally stable allylic π -complex of the type reported for crotylcobalt tricarbonyl¹³. The involvement of the crotyl/ α -methylallyl anions in these equilibria is neither confirmed nor ruled out by these experiments. It is hoped that a study of the temperature dependence of the NMR spectrum of crotyl/ α -methylallyllithium solutions will provide more useful information concerning details of equilibrium (1).

Finally, it was found that small amounts of metallic lithium (containing 2% sodium) in 9:1 ether/DME at room temperature caused isomerization of *cis*- and *trans*-crotyltrimethyltin isomers to the 3:2 *trans/cis*-mixture mentioned above. Since the pure crotyltrimethylsilane isomers were not isomerized under these conditions, it is likely that a metal displacement mechanism is operative, in which small amounts of crotyllithium are formed which can then equilibrate with crotyltrimethyltin.



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