Preliminary Note

The isomeric 1-propenyllithium reagents: their NMR spectra and the stereochemistry of their formation by the direct reaction and by the transmetalation reaction

Several groups of workers have studied the formation of the isomeric propenyllithium reagents, $CH_3CH{=}CHLi$, from 1-halopropenes and subsequent reactions of these lithium reagents[1-3]. In all of these studies the reaction sequences:

$$\textit{cis}\text{-}CH_3CH{=}CHX \xrightarrow[(1)]{Li} \text{Li reagent} \xrightarrow[(2)]{} \textit{cis}\text{-}CH_3CH{=}CH\text{-derivative}$$

and

$$\textit{trans}\text{-}CH_3CH{=}CHX \xrightarrow[(1)]{Li} \text{Li reagent} \xrightarrow[(2)]{} \textit{trans}\text{-}CH_3CH{=}CH\text{-derivative},$$

were observed. This overall stereospecificity, together with the reasonable (but unproven) assumption that there is no change in geometric configuration of the propenyl group in reaction (2), was taken as proof that reaction (1), the generation of the lithium reagent, also proceeds with retention of the *cis*- or *trans*-propenyl configuration of the starting halide. Nesmeyanov and Borisov[3] applied their "method of odd and even cycles" in an attempt to obtain further information concerning this question, but this approach has been criticized*[4]. That the question of the stereochemistry of formation of the propenyllithium compounds had not been resolved satisfactorily was recognized by Allinger and Hermann[4], who sought direct confirmation of the structures of the lithium reagents by an examination of their infrared spectra. Unfortunately, this work does not appear to give the unambiguous answer claimed for it. In assigning structures to the *cis*- and *trans*-propenyllithium isomers, bands at 1035 and 1045 cm^{-1} respectively were assumed to be due to C–Li stretching vibrations. A further band at 1030 cm^{-1} in the infrared spectrum of the presumed trans isomer was believed indicative of the trans configuration; this band was absent in the spectrum of the other isomer. Later work has shown that absorption in the infrared spectra of organolithium compounds in the region around 1050 cm^{-1} is not due to the C–Li bond, and the only bands which involve the motion of lithium atoms occur between 350 and 570 cm^{-1} (see ref. 5). Absorption near 1050 cm^{-1} appears to be due to oxidation products of the lithium reagent[6]. Thus the assignments of Allinger and

---

* See footnote (9) in ref. 2.

Hermann do not provide the required evidence concerning the stereochemistry of propenyllithium formation.

We have used nuclear magnetic resonance spectroscopy to investigate this long-standing question and report results which confirm experimentally the assumptions of the previous workers cited.

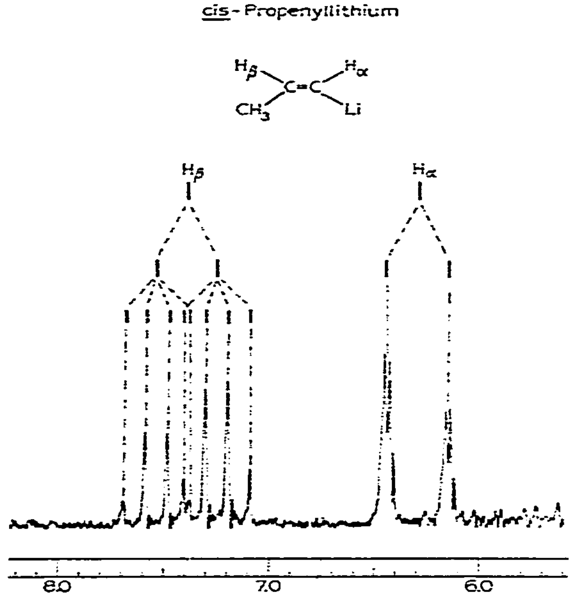


Fig. 1. NMR spectrum of *cis*-propenyllithium. Chemical shifts are recorded in p.p.m. downfield from tetramethylsilane. Positions of Hα and Hβ indicated at center of gravity of AB system.

cis-Propenyllithium was prepared by the reaction of *cis*-1-bromopropene with metallic lithium in ether[1]. The NMR spectrum (Fig. 1) of this reagent (2*M* in diethyl ether) showed the α proton as a doublet (J = 17.4 c.p.s.) with its midpoint at 6.30 p.p.m. downfield from tetramethylsilane. The β proton occurred as two slightly overlapping quartets (J = 6.0 c.p.s.) at 7.23 and 7.52 p.p.m. respectively, the methyl group as a doublet (J = 6.0 c.p.s.) at 1.88 p.p.m. The reaction of this isomer with trimethylchlorosilane gave *cis*-propenyltrimethylsilane, a known compound, whose geometric configuration had been assigned on the basis of its NMR and infrared spectra[7].

trans-Propenyllithium was obtained by the reaction of *trans*-1-chloropropene with lithium metal which contained *ca.* 1 % sodium. Its NMR spectrum (Fig. 2) (3.2*M* in ether) was that of an extreme ABX$_3$ system. The α proton occurred as a doublet (J = 22.2 c.p.s.) with its midpoint at 6.70 p.p.m. The β proton appeared as two quartets (J = 4.2 c.p.s.) at 6.42 and 6.05 p.p.m., the methyl group as a doublet (J = 4.2 c.p.s.) at 1.78 p.p.m. The solution containing this reagent subsequently was treated with trimethylchlorosilane to give *trans*-propenyltrimethylsilane, also a known compound[7].

The basis for these assignments of configuration is provided by the numerous studies[8–10] which have shown that coupling between trans protons in olefinic systems is greater than cis coupling. Thus the coupling constants observed, 17.4 and 22.2 c.p.s., could with confidence be assigned to the *cis*- and *trans*-propenyllithium structures respectively. Of particular interest and significance is the similarity of these values to the cis and trans coupling constants in the closely related vinyllithium: 19.3 and 23.9 c.p.s. respectively[11].

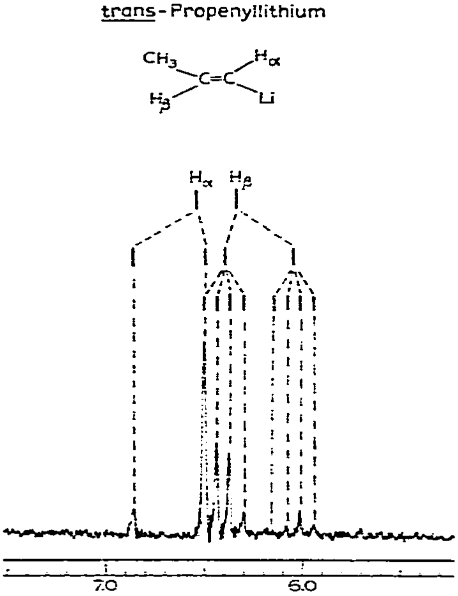
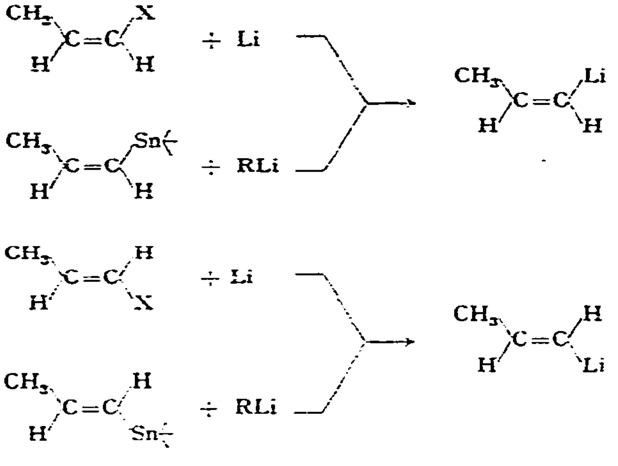


Fig. 2. NMR spectrum of *trans*-propenyllithium. Chemical shifts are recorded in p.p.m. downfield from tetramethylsilane. Positions of H_α and H_β indicated at center of gravity of AB system.

cis-Propenyllithium was prepared *via* the transmetalation route by the reaction of 0.48 mmole of *cis*-propenyltrimethyltin[7] with 0.3 ml of 1.73*M* methyllithium (0.52 mmole) in ether. The NMR spectrum of the reagent prepared in this manner was identical to that of *cis*-propenyllithium obtained from *cis*-1-bromopropene. Moderate background bands due to unconverted *cis*-propenyltrimethyltin were present. *trans*-Propenyllithium was prepared in a similar manner by the reaction of 0.88 mmole of *trans*-propenyltrimethyltin[7] in 1.0 ml of ether with 0.6 ml of 1.50*M* *n*-butyllithium (0.90 mmole) in ether. The NMR spectrum of this reagent was identical to that of *trans*-propenyllithium as described above, as was the NMR spectrum of an ether solution prepared from solid *trans*-propenyllithium obtained by the reaction of 5.1 mmoles of tetra-*trans*-propenyltin[7] with 12.0 mmoles of *n*-butyllithium in pentane followed by partial evaporation of the reaction mixture. Thus the preparation of *cis*- and *trans*-propenyllithium from propenyltin compounds by transmetalation involves retention of the geometric configuration of the propenyl groups in the organotin precursor.

The results of this study may be summarized by the following equations:



Complete details concerning this work, including a more detailed study of the transmetalation reactions leading to propenyllithium reagents and selected reactions of the latter will be given at a later date.

The authors are grateful to the National Science Foundation for support of this work under Grant NSF G-21051.

Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Mass. (U.S.A.)

DIETMAR SEYFERTH*
LAWRENCE G. VAUGHAN**

1 E. A. Braude and J. A. Coles, *J. Chem. Soc.*, (1951) 2078, 2085.
2 D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, 80 (1958) 1922.
3 A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, 1 (1957) 158;
A. N. Nesmeyanov, A. E. Borisov and N. V. Novikova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* (1959) 1216.
4 N. L. Allinger and R. B. Hermann, *J. Org. Chem.*, 26 (1961) 1040.
5 R. West and W. Glaze, *J. Am. Chem. Soc.*, 83 (1961) 3580.
6 T. L. Brown, D. W. Dickerhoof and D. A. Bafus, *J. Am. Chem. Soc.*, 84 (1962) 1371.
7 D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, 1 (1963) 138.
8 L. M. Jackman, *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, London, 1959, pp. 89–90.
9 J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, p. 54.
10 D. W. Moore and J. A. Happe, *J. Phys. Chem.*, 65 (1961) 224.
11 C. S. Johnson, Jr., M. A. Weiner, J. S. Waugh and D. Seyferth, *J. Am. Chem. Soc.*, 83 (1961) 1306.

Received June 4th, 1963

---

[*] Alfred P. Sloan Research Fellow.
[**] National Science Foundation Cooperative Graduate Fellow, 1961–3.