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Preliminary communication

THE SYMMETRICALLY BRIDGED STRUCTURE OF ALLYLLITHIUM

WOLFGANG NEUGEBAUER and PAUL VON RAGUE SCHLEYER*
Institut für Organische Chemie der Friedrich-Alexander-Universität, Erlangen-Nürnberg, D-8520 Erlangen (Federal Republic of Germany)

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Summary

The ^{13}C NMR spectrum of allyllithium-1-*d*, with superposed CHD and CH_2 carbon signals, excludes rapid equilibrating unsymmetrical structural alternatives from consideration. All evidence considered, a symmetrical bridged C_s structure for allyllithium is indicated.

What is the structure of allyllithium? Despite many experimental [1—4] and theoretical [5—8]investigations, this question has not been fully answered. NMR spectral evidence rules out a dynamic equilibrium between species with covalent C—Li character (eq. 1) which would have a low barrier to rotation around the C—CH_2Li bond. The ^1H NMR spectrum at low temperatures shows an AA′BB′C pattern; C(1) and C(3) are equivalent in the ^{13}C spectrum. Bridged or ion pair formulations with C_s symmetry (II) are generally concluded to represent the structure of allyllithium. However, the available experimental evidence does not rule out a dynamic equilibrium between unsymmetrical species in which lithium oscillates rapidly on an allyl face between C(1) and C(3) (eq. 3).

Distinction between symmetrical (II) and rapidly equilibrating alternatives, (I or III), can easily be made by applying Saunders' isotopic perturbation method, the effectiveness of which has been demonstrated in carbocations, conformational equilibria, and organometallic compounds [9,10.] Labelling C(1) in allyllithium with deuterium should perturb an equilibrium (eq. 1 or 3) sufficiently so that the two well separated ^{13}C signals for C(1) and C(3) should be observable in the ^{13}C NMR. The C_s bridged (or ionic) structure (II), however, should exhibit only perturbation of symmetry by such deuterium labelling; this should only result in separation of C(1) and C(3) signals by 0.2—0.4 ppm (intrinsic isotope effect) [9,10].

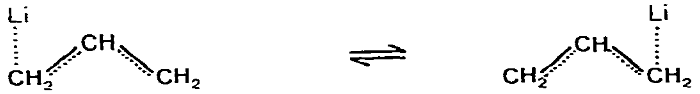
Because literature methods for the preparation of allyllithium [4,11—14] in our hands were either not suitable for the deuterated compound or yielded only impure material, we prepared allyllithium from tetraallyltin and lithium

(Ia) (Ib)

(1)

(IIa) (IIb)

(2)



(IIIa) (IIIb)

(3)

TABLE 1

^{13}C NMR CHEMICAL SHIFTS (vs. TMS) OF ALLYLLITHIUM IN TETRAHYDROFURAN

	C(1), C(3)	C(2)
This work	50.4	146.1
Ref. 3	51.2	147.2
Ref. 15	51.7 ± 0.5	147.1 ± 0.6

metal in benzene. Evaporation of the benzene, dissolving the product in tetrahydrofuran, and filtration yielded a brown solution of NMR-pure allyllithium. The ^{13}C NMR spectrum of the unlabelled compound at 25.2 MHz (two signals) agreed well with the literature [3,15] (see Table 1). Allyllithium-1-*d*, when measured with proton noise-decoupling at –60°C, gave the same ^{13}C spectrum; due to line-broadening the expected triplet for the CHD group was obscured. The CH_2 (triplet) and CHD (doublet) signals, however, are observable in the proton coupled spectrum (Fig. 1). The superposition of these two signals shows that the separation of ^{13}C chemical shifts between C(1) and C(3) must be very small, 0.3 ± 0.2 ppm (peak broadening makes accurate determination difficult).

The results rule out the dynamic equilibria (eq. 1 and eq. 3). The ionic formulation (II) seems unlikely considering the low rotational barrier (10.7 ± 0.2 kcal mol^{-1}) of the CH_2 groups in allyllithium [15] (participation of the metal in the rotation transition state), the higher barriers in allylpotassium (16.7 ± 0.2 kcal mol^{-1}) and allylcesium (18.0 ± 0.3 kcal mol^{-1}) (expected to have less covalent character) [15], and the even higher calculated barrier for the free allyl anion (ab initio MO estimates are 29 [16] or 27.6 kcal mol^{-1} [17]). The ionic formulation is also not consistent with the magnitude of observed ^{13}C—^{13}C coupling constants in alkyl-substituted allyllithium [18]. We conclude that allyllithium has a bridged structure with C_s symmetry (IIa) in tetrahydrofuran solution. The highest level theoretical

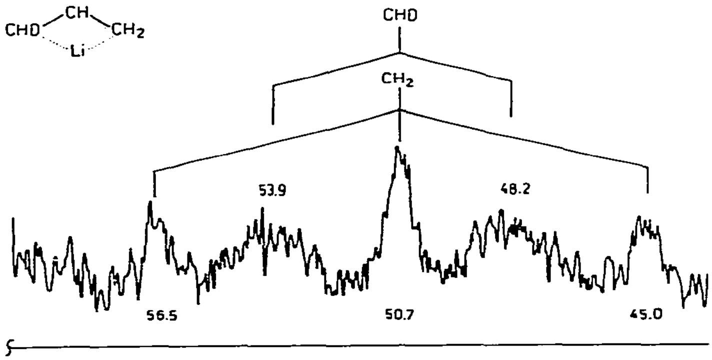


Fig. 1. ^{13}C-NMR spectrum of deuterated allyllithium in THF, proton coupled, at 25.2 MHz, −60°C. Internal lock and standard: C_6D_6. Chemical shifts are given vs. TMS.

calculations [8], which pertain to isolated species (e.g., monomers in the gas phase), also indicate the bridged structure IIa to be preferred. The calculated barrier to rotation around the CC bonds was calculated to be 15.7 kcal mol^{-1} (via the *syn* conformer corresponding to I), 5 kcal mol^{-1} higher that the value measured in THF solution [15]. This indicates that solvation favors the classical forms (e.g., I if these represent the rotation transition state) over the bridged structure, but not enough to overcome the natural preference for polyhapto bonding.

This work further demonstrates that Saunders' isotopic perturbation method will have a wide range of applicability.

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