Allyl-lithium: A Rapidly Equilibrating, Unsymmetrical Dimer in Tetrahydrofuran

William R. Winchester, Walter Bauer, and Paul von Ragué Schleyer*

Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

Cryoscopic measurements and variable temperature ^{13}C n.m.r. studies on isotopically perturbed samples show allyl-sodium and allyl-potassium to have symmetrical structures, but allyl-lithium to be an unsymmetrical dimer in tetrahydrofuran; this association explains the discrepancy between the observed rotational barrier (10.7 kcal/mol) and that calculated for the isolated allyl-lithium monomer (17.7 kcal/mol) (1 cal = 4.184 J).

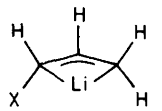
Even though the structures of allyl-metal compounds[1] are central to the question of metal-π bonding, the nature of allyl-lithium in solution is still not clear.[2–5] The results of ^{1}H and ^{13}C n.m.r. studies in tetrahydrofuran (THF) are consistent with a symmetrical or rapidly equilibrating species,[2] but isotopic perturbation experiments have not decided conclusively between these possibilities.[3]

The structure of allyl-lithium usually is discussed in terms of the symmetrical monomer (**1**) (the geometry favoured by theoretical calculations, with or without solvation),[5] or a pair of rapidly equilibrating alternatives (**2**). However, allyl-lithium is known to be associated in ether solvents[2a] and an *X*-ray structure shows the tetramethylethylenediamine complex to be an endless polymer.[4]† Discussions of allyl-lithium in solution have not considered the effect of aggregation adequately. In particular the suggested role of aggregation[5f] in the discrepancy between the calculated (17.7 kcal/mol)[5f] and observed ($\Delta G^{\ddagger}$ 10.7 ± 0.2 kcal/mol,[2d] E_a 10.5 ± 2 kcal/mol 2[a]) rotational barriers has not been accepted[2j] (1 cal = 4.184 J).

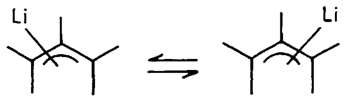
Saunders' isotopic perturbation method[6] has been applied by three research groups to allyl-lithium.[3] The results were the same but the interpretations differed. The observed 0.3 ± 0.1 p.p.m. separation per deuterium between the C(1) and C(3) ^{13}C signals of terminally deuteriated allyl-lithium is less than that expected if there is an equilibrium between two highly unsymmetrical structures. Consequently, two groups concluded that allyl-lithium was symmetrical.[3b,c] However, Schlosser and Stähle[3a] noted that the behaviour was intermediate between that of the rapidly equilibrating allyl-magnesium bromide and symmetrical allyl-potassium, and favoured rapidly equilibrating, slightly unsymmetrical structures (**2**).

To distinguish conclusively between symmetrical and unsymmetrical possibilities we have repeated the isotopic perturbation experiments on [1-^{2}H$_{1}$]allyl-lithium,[3b] [1-^{2}H$_{1}$]allyl-sodium,[2d] and [1-^{2}H$_{1}$]allyl-potassium,[2d] using high-field n.m.r. spectroscopy (400 MHz) and variable temperature ^{13}C n.m.r. measurements in tetrahydrofuran (THF). If such an allyl species were symmetrical, the chemical shift difference {Δδ[C(1) - C(3)]} for the 1-deuterio-derivative would be expected to be *temperature independent* because there would be only one minimum. Indeed, Δδ[C(1) - C(3)], as well as the chemical shift difference between C(3) of the deuteriated and undeuteriated [1-^{2}H$_{1}$]allyl-sodium and [1-^{2}H$_{1}$]allyl-potassium (*ca.* 0.2 p.p.m., Table 1) did not vary significantly with temperature. Furthermore, the signal for the deuteriated carbon, C(1), always appeared *upfield* from that for C(3), consistent with a single minimum.

In contrast, if the allyl derivative were unsymmetrical and rapidly equilibrating, Δδ[C(1) − C(3)] of the deuteriated species would be *temperature dependent* since the two minima would no longer be of equal energy. This behaviour is exhibited by allyl-lithium (Table 1). The Δδ[C(1) − C(3)] values vary from 0.08 to 0.60 p.p.m. In addition, the C(1) chemical shift of [1-^{2}H$_{1}$]allyl-lithium at 298 K is 0.18 p.p.m. *upfield* relative to the value for C(1) of undeuteriated allyl-lithium. On cooling to 176 K, this Δδ[(**1a**),C(1) − (**1b**),C(1)] order is reversed; the C(1) signal of the deuteriated compound is 0.07 p.p.m. *downfield* relative to the C(1) signal of the undeuteriated reference. The C(3) chemical shifts show the opposite behaviour, at room temperature the signal for the deuteriated compound is 0.26 p.p.m. upfield of that for the



(**1**) a; X = H
b; X = D



(**2**)

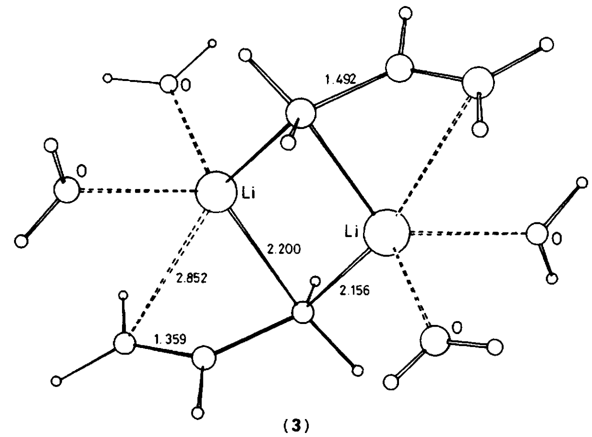
---

† A recent *X*-ray structure shows allyl-lithium to be a monomer when complexed by the tridentate ligand, pentamethyldiethylenediamine (U. Schumann, E. Weiss, H. Dietrich, and W. Mahdi, *J. Organomet. Chem.*, in the press).

Table 1. Temperature effects on the chemical shifts of allyl- and [1-$^2H_1$]allyl-lithium contrasted with -sodium and -potassium derivatives.[a]

		[1-$^2H_1$]Allyl (**1b**)			$\Delta\delta$	Allyl (**1a**)	$\Delta\delta$	$\Delta\delta$
Temp./K	Metal	C(1)	C(2)	C(3)	[C(1) – C(3)]	C(1)	[(**1a**), C(1) – (**1b**), C(1)]	[(**1a**), C(1) – (**1b**), C(3)]
298	Li	51.04	146.98	50.96	0.08	51.22	0.18	0.26
258	Li	51.19	146.95	51.03	0.16	51.33	0.14	0.30
218	Li	51.37	147.05	51.05	0.32	51.44	0.07	0.39
202	Li	51.47	147.19	51.03	0.44	51.47	0.00	0.44
176	Li	51.68	{147.45 {147.35	51.08 51.01	0.60} 0.67}	51.61	−0.07	0.56
288	Na	48.40	145.28	48.45	−0.05	48.65	0.25	0.20
176	Na	48.32	143.57	48.32	0.00	48.57	0.25	0.25
263	K	52.27	143.91	52.42	−0.15	52.57	0.30	0.15
212	K	52.28	143.36	52.44	−0.16	52.62	0.34	0.18

[a] All values are in p.p.m. from $SiMe_4$. Spectra were recorded at 100.5 MHz in [$^2H_8$]THF. When two values are reported, these correspond to the *syn-* and *anti*-conformers which interconvert slowly on the n.m.r. time-scale.



(**3**)

Figure 1. MNDO Lowest energy structure (**3**) for allyl-lithium dimer, with distances in Å.

undeuteriated compound {$\Delta\delta$[(**1a**),C(**1**) – (**1b**),C(3)]}; on cooling to 176 K this difference increases to 0.56 p.p.m. Hence, we conclude that allyl-lithium possesses an unsymmetrical structure with a low barrier to interconversion, whereas allyl-sodium and allyl-potassium are symmetrically bridged.

Since aggregation is important not only for the structures[7] but also for reactivities of organolithium compounds,[8] we determined the degree of association cryoscopically.[9] The measurements show conclusively that allyl-lithium is a *dimer* in THF at 165 K: $n = 2.1 \pm 0.1$, in a relatively low concentration, $C_{\text{formal}} = 97$ mmol dm^{-3}. West, *et al.* found from colligative property measurements that allyl-lithium has an apparent degree of aggregation of about 1.3 in THF from 0.1 to 0.7 mol dm^{-3} at 25 °C.[2a]

The aggregation of organolithium compounds in THF tends to *increase* at higher temperatures (because of the entropy gain due to solvent loss).[10] Furthermore, equilibria between different aggregates are frozen out at low temperatures;[8,10] *e.g.*, distinct n.m.r. peaks for butyl-lithium dimer and tetramer are seen. In contrast, we observe only a single allyl-lithium species at 176 K. The concentration dependence of allyl-lithium has been studied extensively by Thompson and Ford.[2d] Variations of 0.2 to 2 mol dm^{-3} in concentration and 189 to 336 K in temperature as well as addition of tetramethylethylenediamine to the THF solution produced no alterations of the ^{13}C chemical shifts within a narrow range. Our measurements agree with these values. McDonald and Bywater[2j] have measured the rotational barrier of neopentylallyl-lithium in dilute (0.01 mol dm^{-3}) concentration in THF by observing changes in u.v. intensities. The estimated n.m.r. coalescence temperature (about 228 K) is very close to that (*ca.* 223 K) reported for allyl-lithium at much higher concentrations (*ca.* 1 mol dm^{-3}).[2a,d]

All this evidence shows rather conclusively that allyl-lithium is a *dimer* in THF over a wide range of conditions. Higher aggregation is possible (although we find no evidence for this), but monomers (which should have been favoured under our cryoscopy conditions) can be *excluded.* This contradicts earlier conclusions.[2a,d]

Calculations on organometallic compounds usually are in good agreement with experimental results.[11] Thus, the *ab initio* rotational barrier computed for isolated allyl-sodium (11.5 kcal/mol)[5f] is the same as the experimentally observed value,[3c] even though the latter must refer to a solvated species. Our MNDO calculations on allyl-lithium structures indicate that little change in the barrier due to solvation is to be expected.‡ Hence, we attribute the discrepancy between the *ab initio* calculated barrier for isolated allyl-lithium (17.7 kcal/mol) and the experimental value in THF solution (10.7 kcal/mol) to dimerization.

While *ab initio* methods will be necessary to compute the rotational barrier of the associated species accurately, we have used model MNDO calculations to study many possible symmetrical and unsymmetrical dimer structures, both unsolvated and solvated with two water molecules per lithium.†[12] Of the various geometries examined for the allyl dimers, structure (**3**) (Figure 1; the unsolvated structure is similar), which has a favourable charge distribution and bridging lithiums [but closer to C(1) than C(3)], was lowest in energy.‡ This unsymmetrical structure is consistent with the n.m.r. results. The C–C bond lengths in (**3**) differ significantly, 1.492 and 1.359 Å, but their average value is identical to that calculated for (**1**) (1.426 Å). Rather similar dimeric structures have been found for two allenyl-lithium derivatives.[7]

In summary, while allyl-sodium and allyl-potassium favour symmetrical (presumably monomeric)[13] structures (**1**), allyl-lithium is an unsymmetrical rapidly equilibrating dimer in THF. The dimer has a lower rotational barrier than that expected for the monomer.

This work was supported by the Deutsche Forschungsge-

---

‡ Further computational details are available from the authors on request and will be presented in the full report. Structure (**3**) has C_i symmetry; the C_2 form is only slightly less stable.

meinschaft and the Fonds der Chemischen Industrie and by NATO under a Grant awarded in 1985 to W. R. W. We also thank T. Clark for discussions and the referees for suggestions.

Received, 14th July 1986; Com. 980

References

1 (a) K. Vrieze in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, ch. 11, pp. 441ff; (b) 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, Oxford, 1982.

2 (a) P. West, J. I. Purmort, and S. V. McKinley, *J. Am. Chem. Soc.*, 1968, **90**, 797; 1970, **92**, 840; (b) D. H. O'Brien, A. J. Hart, and C. R. Russel, *ibid.*, 1975, **97**, 4410; (c) M. Schlosser and J. Hartman, *ibid.*, 1976, **98**, 4674; (d) T. B. Thompson and W. T. Ford, *ibid.*, 1979, **101**, 5459; (e) M. Schlosser and M. Stähle, *Angew. Chem.*, 1982, **94**, 142; (f) R. Benn and A. Rufinska, *J. Organomet. Chem.*, 1982, **239**, C19; (g) H. Ahlbrecht, K. Zimmermann, G. Boche, and G. Decher, *ibid.*, 1984, **262**, 1; (h) R. Benn and A. Rufinska, *Organometallics*, 1985, **4**, 209; (i) G. Fraenkel, H. F. Halasa, V. Mockel, R. Stumpe, and D. Tate, *J. Org. Chem.*, 1985, **50**, 4563; (j) R. T. McDonald and S. Bywater, *Organometallics*, 1986, **5**, 1529; (k) review: J. L. Wardell in ref. 1(b), vol. 1, pp. 97ff.

3 (a) M. Schlosser and M. Stähle, *Angew. Chem.*, 1980, **92**, 497; M. Stähle and M. Schlosser, *J. Organomet. Chem.*, 1981, **220**, 277; (b) W. Neugebauer and P. v. R. Schleyer, *ibid.*, 1980, **198**, C1–C3; (c) S. Brownstein, S. Bywater, and D. J. Worsfold, *ibid.*, 1980, **199**, 1.

4 H. Koester and E. Weiss, *Chem. Ber.*, 1982, **115**, 3422. Also see G. Boche, H. Etzrodt, M. Marsch, W. Massa, G. Baum, H. Dietrich, and W. Mahdi, *Angew. Chem.*, 1986, **98**, 84.

5 (a) E. R. Tidwell and B. R. Russell, *J. Organomet. Chem.*, 1974, **80**, 175; (b) J. B. Sebastian, J. R. Grunwell, and B. Hsu, *ibid.*, 1974, **78**, C1; (c) A. Bongini, G. Cainelli, G. Cardillo, P. Palmieri, and A. Umani-Ronchi, *ibid.*, 1976, **110**, 1; (d) T. Clark, E. D. Jemmis, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *ibid.*, 1978, **150**, 1; (e) G. Decher and G. Boche, *ibid.*, 1983, **259**, 31; (f) T. Clark, C. Rhode, and P. v. R. Schleyer, *Organometallics*, 1983, **2**, 1344; (g) R. J. Bushby and M. P. Tytko, *J. Organomet. Chem.*, 1984, **270**, 265; (h) G. B. Erusalinski and V. A. Kormer, *Zh. Org. Khim. (Russ.)*, 1984, **20**, 2028.

6 M. Saunders, L. Telkowski, and M. R. Kates, *J. Am. Chem. Soc.*, 1977, **99**, 8070; J. W. Faller, H. H. Murray, and M. Saunders, *ibid.*, 1980, **102**, 2306.

7 W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353. Also see C. Schade and P. v. R. Schleyer, *ibid.*, in the press. These reviews have extensive bibliographies of the organoalkali metal literature.

8 J. F. McGarrity, G. A. Ogle, Z. Brich, and H.-R. Loosli, *J. Am. Chem. Soc.*, 1985, **107**, 1810.

9 W. Bauer and D. Seebach, *Helv. Chim. Acta*, 1984, **67**, 1972.

10 (a) D. Seebach, R. Hässig, and J. Gabriel, *Helv. Chim. Acta*, 1983, **66**, 308; (b) J. Heinzer, J. F. M. Oth, and D. Seebach, *ibid.*, 1985, **68**, 1848; (c) J. F. McGarrity and C. A. Ogle, *J. Am. Chem. Soc.*, 1985, **107**, 1805; (d) G. Fraenkel, H. Hsu, and B. M. Su, in R. O. Bach, 'Lithium. Current Applications in Science, Technology, and Medicine,' Wiley, New York, 1985, ch. 19, pp. 273ff. Also see ref. 13.

11 P. v. R. Schleyer, *Pure Appl. Chem.*, 1984, **56**, 151; 1983, **55**, 383.

12 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899. Lithium parametrization: W. Thiel and T. Clark, Quantum Chemistry Program Exchange (QCPE), 1983, 438; QCPE News Letter, submitted.

13 Alkyl-sodium and alkyl-potassium derivatives are monomeric in THF: R. Pi, W. Bauer, B. Brix, C. Schade, and P. v. R. Schleyer, *J. Organomet. Chem.*, 1986, **306**, C1.