Tetrahedron Letters No. 45, pp 3969 - 3972, 1977. Pergamon Press. Printed in Great Britain.

CONFIGURATIONAL ISOMERIZATION OF α-ARYL-VINYLLITHIUM: KINETICS, MECHANISM, AND STERIC ACCELERATION

Rudolf Knorr* and Ernst Lattke

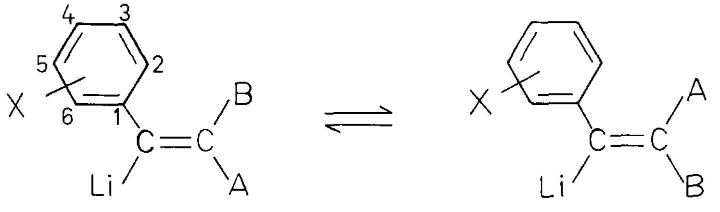
Institut für Organische Chemie der Universität München
Karlstr. 23, D-8000 München 2, Germany

(Received in UK 15 August 1977; accepted for publication 22 September 1977)

The configurational lability **1** ⇌ **2** of α-aryl-vinyllithium in ethereal solvents as studied by Curtin et al.[1,2] has never been subjected to kinetic scrutiny.[3] We report here that a quantified study reveals the kinetic importance of de-aggregation of **1**, provides an explanation of solvent participation, and discloses large structural effects on reactivity.

We prepare the vinyllithium compounds **1** from α-aryl-bromoethylenes and n-butyllithium in pentane/hexane below -70°C. Colourless precipitates of **1** formed in most cases on stirring at room temperature were washed with pentane. The liquid compounds **1b** and **1c** were dried at 0.01 Torr below 25°C. All operations had to be performed under purified nitrogen gas in order to prevent explosions. Appropriate solvents were then added below -20°C and the formal concentrations of **1** determined by ^{1}H nmr integration against calibrated capillaries ($ClCH_2CN$) or solvent signals; all samples contained some lithium bromide ($AgNO_3$ titration). The purity of **1** was checked by comparing olefinic and aromatic nmr integrals and also by computer simulation of the aromatic part of the nmr spectra. Structural proofs relied on derivatization.

(E/Z)-Equilibrium mixtures **1a-c** ⇌ **2a-c** are well suited for kinetic measurements, using full ^{1}H nmr lineshape analyses of the olefinic signals with



1 **2**

1	**a**	**b**	**c**	**d**	**e**
A	H	H	H	CH_3	$2\text{-}C_6H_4CH_3$
B	D	D	D	CH_3	$2\text{-}C_6H_4CH_3$
X	H	$2\text{-}CH(CH_3)_2$	$2,6\text{-}(CH_3)_2$	H	H

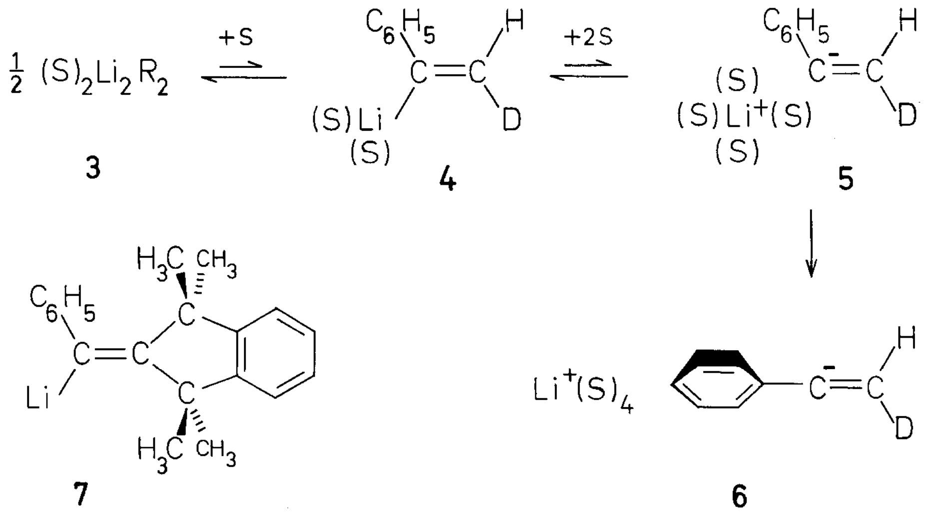
deuterium decoupling. Rate constants k_ψ were practically the same for **1** and their non-deuterated analogs, with isotope effects well below the error limits. The singlet resonances of **1a**-**c** offer the additional advantage of applying the saturation transfer technique.[4] Since a 110° change of temperature was covered by these two methods, the parameters of activation given in Table I should be reliable. No rate changes were noted if a sample was run again after several months or after addition of the naphthalene anion-radical in tetrahydrofuran (THF); induction of E/Z isomerization by a radical mechanism is therefore improbable.

From the dependence of pseudo first-order rate constants k_ψ on the formal concentrations (0.3 - 0.7 M) in THF, we found the order of reaction to be 0.5 (±0.2) in **1a** or **1b**. As one example, k_ψ for **1b** at +88°C was 52 s^{-1} (0.3 M), 41 s^{-1} (0.55 M), 35 s^{-1} (0.65 M), and 19 s^{-1} (1.7 M). Therefore, a dissociative step must precede configurational isomerization.[5] However, dissociation to give lithium ions is very unfavourable in THF[6,7] and is <u>not</u> rate-controlling for **1a** since addition of lithium bromide causes no common ion rate depression.[8] In view of the persistence of lithium aggregation even in donor solvents,[5] we conclude that the 0.5 order of reaction is due to deaggregation into two sub-units. It is reasonable (albeit not compelling[9]) to suppose that **1a**-**c** is a dimer **3**; solvation presumably occurs with one THF (S) per lithium atom.[10,11] Partial dissociation produces the monomer or contact ion pair **4** which is expected to bind about two THF molecules.[6,12,13]

In order to arrive at a tentative interpretation of the activation parameters in Table I, we searched the literature for model reactions. Negative (rather than positive) entropies for <u>dissociation</u> reactions indicate extensive solvent immobilization. A pertinent model for **3** → **4** could be the formation of monomers[14] from $[LiN(SiMe_3)_2]_2$ with ΔH^o = -4 kcal/mol and ΔS^o = -17 eu in THF. However, comparison with $\Delta S^{\ddagger}$ = -36 eu for **1a** in Table I suggests the occurence of more strongly solvated intermediates. The solvent-separated ion pair **5** will presumably bind four THF molecules;[15] comparison of the step **4** → **5** with literature data[13,16] brings the balance for **3** → **5** to ΔH^o ca. -10 kcal/mol and ΔS^o ca. -37 eu. According to Table I, a transition

<u>Table I</u>. Parameters of activation for **1a**-**c** and pseudo first-order rate constants k_ψ of configurational inversion.

1	Formality	Solvent	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	k_ψ (s^{-1} at 27°C)
a	0.5 M	Ether	-	-	ca. 10^{-4}
a	0.7 M	1.1 M TMEDA/Ether	-	-	ca. 0.05
a	0.9 M	TMEDA	9.9 ± 0.7	-31 ± 3	0.062
a	0.9 M	2.5 M TMEDA/THF	7.3 ± 0.3	-38.4 ± 1	0.13
a	0.6 M	THF	7.8 ± 0.6	-36 ± 2	0.17
a	0.28 M	1.9 M HMPA/THF	5.4 ± 1.5	-24 ± 6	ca. 4040
b	1.7 M	$[D_8]$THF	11.1 ± 0.3	-22.4 ± 1	0.63
c	0.7 M	$[D_8]$THF	8.9 ± 0.2	-22.5 ± 0.6	24.1



state like 6 (ion-paired) can now be reached with an additional enthalpy of ca. +18 kcal/mol, in close agreement with the inversion of N-phenyl-imines[17] as a model for 5 ⟶ 6. (The exact magnitude of the barrier to anion inversion cannot be deduced from this analysis, of course.) Thus, our activation parameters of 1a lead to a thermodynamically consistent mechanistic rationalization and lend some support to Curtin's[1a] lateral-shift-mechanism which cannot operate in a contact ion pair like 4.

It must be stressed that monomeric ion pairs like 5 or 4 cannot be ground states because dissociation into free anions and free lithium ions was shown to be kinetically unimportant yet the order of reaction less than one. Hence, the kinetic behaviour of systems 1 which meet such conditions constitutes evidence for a more aggregated ground state like 3; it is, therefore, also an indicator for the integrity of the carbon-lithium bond in the sense that de-aggregation occurs on the way to the transition state 6. As discussed above, large negative entropies of activation support but do not prove this conclusion.

The donor dependence of k_ψ in Table I agrees with current notions,[1,3] except for 1,2-bis(dimethylamino)-ethane (TMEDA).[3] Moderate amounts of tris-(dimethylamino)-phosphinoxide (HMPA in Table I) cause an impressive rate enhancement. Roughly 2 - 3 HMPA are frozen for inversion via 5/6; unfortunately, the decomposition temperature of 1a drops from ca. +80° to below 0°C, precluding a more precise study.

Whereas 1d with β-CH$_3$ groups does not invert faster than 1a but rearranges irreversibly,[18] the E/Z topomerization of 1e is rapid in THF already at -25° C (k_ψ = 7.4 s^{-1} for CH$_3$ coalescence). For 7 with even bulkier tert.-alkyl β-substituents, nonequivalences were detected only in the ^{13}C nmr spectra with coalescences about -45°C (k_ψ = 50 s^{-1} in THF). Rate extrapolation by the activation parameters for 1a (k_{rel} = 1) in Table I permits a direct comparison with 1e (k_{rel} = 820) and with 7 (k_{rel} = 24200). This tremendous steric acce-

leration is possibly due to prevalent de-aggregation[19] such that the analog of **4** becomes the ground state. Interestingly, the chemical reactivity of **7** is also greatly enhanced.[18]

ACKNOWLEDGMENT. Thanks are due to Dr. J. Firl, Technical University of Munich, for taking ^{13}C spectra, to the Stiftung Volkswagenwerk, and to the Leibniz-Rechenzentrum der Bayerischen Akademie der Wissenschaften for computer time.

REFERENCES AND NOTES

1. (a) D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958); (b) D. Y. Curtin and W. J. Koehl, Jr., *ibid.*, **84**, 1967 (1962).
2. See also: D. Y. Curtin and E. E. Harris, *ibid.*, **73**, 2716, 4519 (1951); A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).
3. E. J. Panek, B. L. Neff, H. Chu, and M. G. Panek, *J. Am. Chem. Soc.*, **97**, 3996 (1975).
4. S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963); F. A. L. Anet and A. J. R. Bourn, *J. Am. Chem. Soc.*, **89**, 760 (1967).
5. T. L. Brown, *Pure Appl. Chem.*, **23**, 447 (1970).
6. T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).
7. W. Strohmeier, H. Landsfeld, and F. Gernert, *Ber. Bunsenges. Physik. Chem.*, **66**, 823 (1962); T. E. Ellingsen and J. Smid, *J. Phys. Chem.*, **73**, 2712 (1969).
8. D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *ibid.*, **69**, 612 (1965); H. Hostalka and G. V. Schulz, *Z. Phys. Chem.*, **45**, 286 (1965).
9. (a) Note the hazards in deducing aggregation numbers from kinetics.[9b,10] (b) S. Bywater and D. J. Worsfold, *J. Organomet. Chem.*, **10**, 1 (1967); E. A. Kovrizhnykh and A. I. Shatenshtein, *Russ.Chem.Rev.*, **38**, 840 (1969).
10. P. D. Bartlett, C. V. Goebel, and W. P. Weber, *J. Am. Chem. Soc.*, **91**, 7425 (1969).
11. H. L. Lewis and T. L. Brown, *ibid.*, **92**, 4664 (1970).
12. J. A. Dixon, P. A. Gwinner, and D. C. Lini, *ibid.*, **87**, 1379 (1965); Y. Okamoto and H. Yuki, *J. Organomet. Chem.*, **32**, 1 (1971).
13. R. Waack, M. A. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, **88**, 2109 (1966).
14. B. Y. Kimura and T. L. Brown, *J. Organomet. Chem.*, **26**, 57 (1971).
15. L. L. Chan and J. Smid, *J. Am. Chem. Soc.*, **89**, 4547 (1967); W. Martír, A. E. Alegría, and G. R. Stevenson, *ibid.*, **98**, 7955 (1976).
16. J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *ibid.*, **94**, 2306 (1972); D. H. O'Brien, C. R. Russell, and A. J. Hart, *ibid.*, **98**, 7427 (1976); M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Vol. 1, Wiley-Interscience, New York, N. Y., 1972, pp 107 - 109.
17. H. Kessler, *Tetrahedron*, **30**, 1861 (1974).
18. Manuscript in preparation.
19. See: W. H. Glaze and C. H. Freeman, *J. Am. Chem. Soc.*, **91**, 7198 (1969).