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# REACTIVITY SCALE OF VINYLLITHIUM COMPOUNDS IN TRANSMETALLATION WITH ß,ß-DIMETHYL-STYRENE

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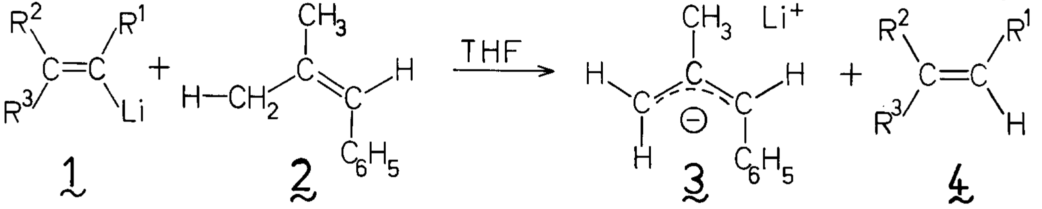
We have discovered a large ($>10^4$) reactivity change of vinyllithium derivatives **1** in the transmetallation reaction with 2-methyl-1-phenyl-propene **2** to give the allyl anion **3** together with **4**, the parent hydrocarbon of **1**. Studying the kinetics in tetrahydrofuran (THF) solution by $^1$H nmr, we found the sequence of reactivities to resemble that for (Z/E)-isomerization[1] of **1**.

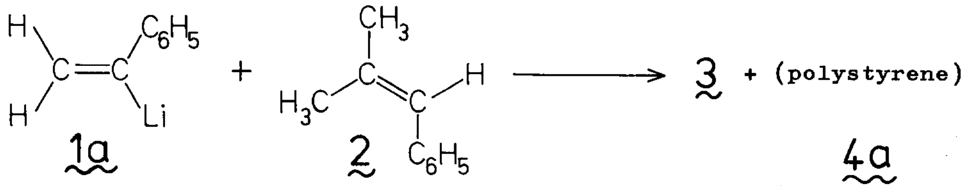


For an evaluation of the general rate equation (1), one has to know the order of reaction, n, as well as the aggregation number, x, for the organolithium compound $R_xLi_x$ which deprotonates **2**. Approximate reactivities $k_\psi$ may be determined under pseudo-first order conditions, eq. (2); if $R_xLi_x$ is present in excess and its concentration not far from unity, the numerical error is not large.

$$-d[R_xLi_x]/dt = k\,[R_xLi_x]^n\,[\mathbf{2}] \tag{1}$$

$$-d[\mathbf{2}]/dt = -xd[R_xLi_x]/dt = k_\psi\,[\mathbf{2}] \tag{2}$$

## α-Aryl-vinyllithium Compounds with Reaction Order 3/2



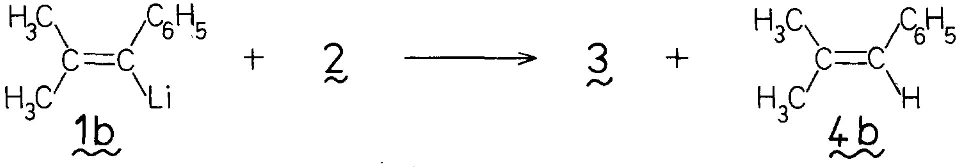
Deprotonation of **2** by an excess of α-phenyl-vinyllithium[1] **1a** proceeds with quantitative formation of **3**. Concentrations were monitored as a function of time as described previously.[2] The concentration of **3** increased at a rate equal to that measured for the decrease of the formal concentration, f, of RLi (**1a**) and that of the olefin (**2**) concentration, c. After consumption of **2**, f remained constant until the reaction was started again by injection of more olefin **2**. Thus stoichiometric conversion of **1a** is observed even though the expected styrene **4a** polymerizes immediately.

A first order of reaction with respect to **2** was estimated from the slopes of the conversion curves at equal RLi concentration, $f_o$, but varying amounts of **2**. Accordingly, pseudo-first order plots, eq. (2), were linear for **2** if $f_o$ was large, yielding the approximate rate constants $k_\psi$ in Table I. Since $k_\psi$ varied roughly as $\sqrt{f_o}$, we considered the reaction to be of 0.5 order with respect to **1a**. As explained previously,[1,2] it may then be inferred that dissociation of $R_xLi_x$ into two sub-units is kinetically important. Taking the simplest possibility of a dimeric ground state, the rate law of eq. (3) applies. This may be rewritten as eq. (4) with $c = [\mathbf{2}]$ and $f = 2[R_2Li_2]$ (as measured by nmr intensities). It turns out that integration is possible in closed form to give y in eq. (5) which is valid for $f_o > c_o$ (starting concentrations). Plots of y versus time showed good linearity over up to 2.5 half-lives, confirming a total order 3/2 for the reaction.

$$-d[R_2Li_2]/dt = k_{3/2}\,[\mathbf{2}]\,\sqrt{[R_2Li_2]} \qquad (3)$$

$$-df/dt = \sqrt{2}\,k_{3/2}\,(f - f_o + c_o)\sqrt{f} \qquad (4)$$

$$\frac{1}{\sqrt{f_o-c_o}}\log\frac{\sqrt{f}-\sqrt{f_o-c_o}}{\sqrt{f}+\sqrt{f_o-c_o}} = y = -2.303\sqrt{2}\,k_{3/2}t + \text{const} \qquad (5)$$



The rate constants $k_{3/2}$ (Table I) are smaller than those for α-phenyl-β,β-dimethyl-vinyllithium **1b**. The orders of reaction in this case have been shown[2] to be 0.5 for **1b** and unity for **2**. Since **1b** metallates **2** with regeneration of **2** (**4b**), pseudo-first order constants (with respect to **2**) cannot be measured, but were computed from $k_\psi = \sqrt{2}\,k_{3/2}\sqrt{f_o}$ for comparison with other derivatives (entry 5 in Table I). The known temperature dependence[2] was used to extrapolate the rate constant to -44° (entry 6), relating it to the next example.

### Fast Deprotonation by 2-(1-Lithio-benzylidene)-1,1,3,3-tetramethyl-indan

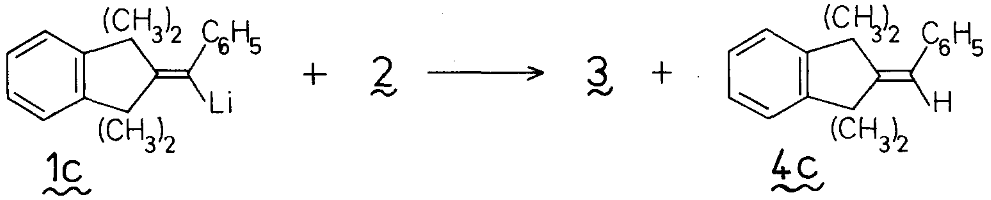


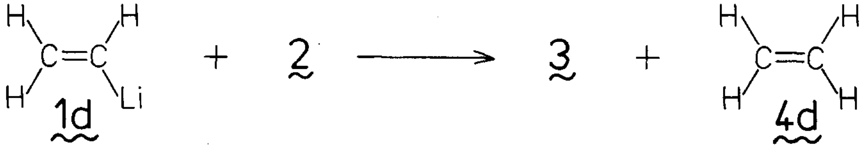
Table I. Formal starting concentrations ($f_o$) and rate constants k for reactions of vinyllithium derivatives RLi with olefin 2 ($c_o$) in [$D_8$]THF.

| Entry | RLi | $f_o$ M | $c_o$ M | Temp. °C | $10^4\ k_\psi$ $s^{-1}$ | | $10^4\ k_{3/2}$ $M^{-1/2}\ s^{-1}$ | | relative rates $k'_\psi$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1a | 0.77 | 0.27 | +25 | 1.54 | | 1.24 | ±0.12 | |
| 2 | 1a | 0.50 | 0.16 | +25 | 1.13 | | 1.15 | ±0.17 | |
| 3 | 1a | 0.60 | 0.20 | +25 | 1.50 | | 1.31 | ±0.13 | ≡1 |
| 4 | 1a | 0.40 | 0.35 | +25 | - | | 0.95 | ±0.2 | |
| 5 | 1b | 0.27 | 0.08 | +26.5 | 14.7 [a] | | 20 | ±2 | 10 |
| 6 | 1b | 0.27 | 0.08 | -44 | ca. 0.07 [b] | | ca. 0.1[b] | | 10 |
| 7. | 1c | 0.28 | 0.14 | -44 | 0.78 | ±0.15 | - | | 110 |
| 8 | 1d | 2.6 | 0.38 | +26 | 0.0084 | ±0.002 | - | | 0.006 |
| 9 | $nC_4H_9Li$ | 1.2 | 0.45 | +29 | 2.6 | ±0.4 | - | | 1.7 |

a) see ref. 2; 0.93 M LiBr b) extrapolated

The title compound 1c is very reactive[1] and metallates 2 readily at -44° to yield 3 and 2-benzylidene-1,1,3,3-tetramethyl-indan 4c quantitatively. A pseudo-first order plot with respect to 2 showed acceptable linearity over more than two half-lives. No attempts were made to determine the orders of reaction more precisely because the numerical value of the rate constant would not have changed very much. Table I (entry 7) shows that 1c is more reactive than 1b (entry 6) at the same temperature.

### Slow Deprotonation by Vinyllithium [3]



A very slow reaction (entry 8 in Table I; half-life ca. 43 h) occurs with vinyllithium 1d after introduction of olefin 2. Formation of 3 and ethylene 4d is equal within experimental error to the consumption of 1d and 2. As above, the order of reaction was not investigated.

### Butyllithium

The deprotonation of 2 by n-butyllithium can be conveniently followed at +29° in the usual way. The pseudo-first order constant (entry 9 in Table I) is comparable to that of 1a. A little more than one equivalent of butyllithium was consumed per mol of 2, but no attempts were made to correct for the very slow decomposition by [$D_8$]THF and for ethylene addition.[4]

## Discussion

Vinyllithium (1d) and butyllithium are reported to be tetrameric in THF[5] and to deprotonate triphenylmethane[5] with a rate ratio of ca. 1/5. The ratio for addition to 1,1-diphenyl-ethylene[5] was 1/2640. In metallation of olefin 2, we find relative rates of ca. 1/300. Such sequences may be somewhat dependent on concentrations if compounds with different orders of reaction are to be compared.[5] The reactivity scale ($k'_{\psi}$ relative to 1a) of vinyllithium derivatives for deprotonation of 2 in THF is shown in the last column of Table I. It may depend on an interplay of several contributions: (i) Change of aggregation in the ground state, (ii) substituent-dependent basicity, and (iii) steric hindrance against approach of olefin 2 in the transition state.

An α-phenyl group is not expected to increase the basicity of 1a over that of 1d or to decrease steric hindrance. Therefore, the considerably enhanced reactivity of 1a as compared to the tetrameric vinyllithium 1d indicates 1a to be less aggregated (perhaps dimeric,[1] factor i). Further substitution of the vinylic ß-hydrogen atoms by two methyl groups in 1b will increase the basicity (or nucleophilicity; factor ii) and results in a tenfold rate enhancement. Another elevenfold acceleration is caused by two bulky tert.-alkyl substituents in 1c (perhaps monomeric[1]) and may reflect competition of factors (i) and (iii).

The deprotonation reactions described here exhibit kinetic features[2] very similar to those of (E/Z)-isomerization (topomerization)[1] of 1a. The occurence of some common intermediates in both cases is compatible with the observed 0.5 orders of reaction and the activation parameters.[1,2] Considering substituents, we note that tetrameric vinyllithium and its alkyl-substituted derivatives do not show any tendency for (E/Z)-topomerization.[6] As above, an α-phenyl group is essential for obtaining measurable rates,[1] presumably because of de-aggregation (factor i) and charge stabilization (factor ii). Since factor (iii) is irrelevant for carbanion inversion, it is reasonable that steric compression in 1c accelerates the topomerization 24200fold[1] (compared to 1a) but impedes the approach of 2 (110fold acceleration only, Table I). However, the relative importance of steric acceleration must be evaluated from further studies on model compounds.

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## REFERENCES AND NOTES

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