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INSTABILITY OF α-PHENYL-β,β-DIMETHYL-VINYLLITHIUM; KINETICS OF AN APPARENT VINYLANION-TO-ALLYLANION REARRANGEMENT

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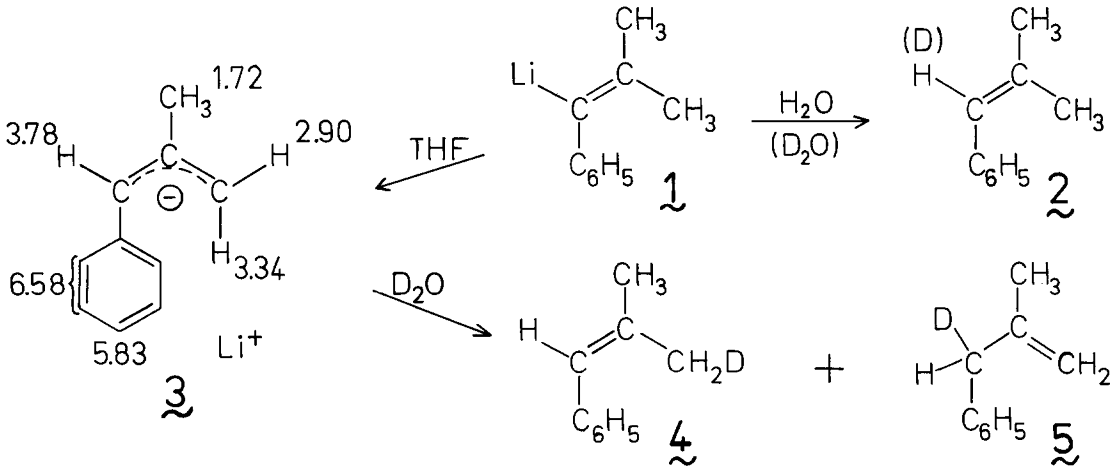
We noticed a peculiar instability of 1-lithio-2-methyl-1-phenyl-propene 1 in tetrahydrofuran (THF) solution during futile attempts to detect carbanion inversion by CH_3-topomerization. Above 0°C, 1 was found to "rearrange" to the isomeric allyllithium derivative 3. This vinyl-to-allyl conversion was traced back to an intermolecular transmetallation mechanism involving small (< 10%) amounts of β,β-dimethylstyrene 2, the hydrolysis product of 1. We further report here on the kinetic behaviour of 1 with a strongly negative entropy of activation and a 0.5 order of reaction.



Preparation and Analysis of Starting Material

1-Bromo-2-methyl-1-phenyl-propene[1,2] was stirred in pentane with excess n-butyllithium at room temperature. After 24 h, the pale yellow, pyrophoric powder containing 1 was filtered under purified nitrogen gas and rinsed with dry pentane; yield up to 86% by weight. ^{1}H nmr at -37° in [D_8]THF: δ = 1.46 ppm (s, CH_3), 1.73 (s, CH_3), 6.34 (para), 6.39 (ortho), 6.82 (meta). Carboxylation of a solution of 1 in diethyl ether gave 3-methyl-2-phenyl-2-butenoic acid[3] (m.p. 151-152.5°). For sample analysis, the solid containing 1 was dissolved in THF at -50°, quenched with D_2O, and distributed between water and ether to yield 29% of LiBr ($AgNO_3$ titration), 6% of 2, and 65% of [1-D_1]2 (nmr integration of mc 6.23 ppm versus CH_3 at 1.80 and 1.85).

Structure of the Product

Solutions of 1 in $[D_8]$THF are quickly and quantitatively converted at ambient temperature to the stable allyl compound 3. The ^1H nmr shifts shown in formula 3 are similar to those of the potassium salt in ammonia.[4] The assignments gain support from signal coalescence at +47° of the geminal protons ($\Delta G^{\ddagger} \sim 16$ kcal/mol). After quenching with D_2O, a 2.4/1 mixture (by nmr) of 4 and 5 is obtained with 15% of non-deuterated 2 as the only impurity. The (Z)-configuration of 4 follows from the reported[1] assignment.

For a chemical proof of the structure we carboxylated a THF solution of 3 and isolated a pure mixture (1.2/1 by nmr, yield 95%) of 3-methyl-4-phenyl-3-butenoic and 3-methyl-2-phenyl-3-butenoic acids. Their ethyl esters, obtained in the same ratio, were labile towards rearrangement and therefore hydrogenated to give the corresponding butanoic esters which were separable by preparative vpc. These structures were proved by independent syntheses.

Kinetics

Concentrations were monitored as a function of time by nmr integration relative to residual protons of $[D_8]$THF or to a calibrated internal capillary filled with $Cl-CH_2-CN$ (s, δ = 4.33 ppm). Increasing intensities of the three allylic signals of product 3 (see formula) and decreasing intensity of the upfield methyl signal of educt 1 led to identical rates, initial and final concentrations being equal within experimental error. Concentrations of olefin 2 were independent of time (olefinic and methyl signals).

Having shown that only the species RLi ($1 \rightarrow 3$) is time-dependent, we used the Noyes equation[5] to determine the order of reaction from each conversion

Table I. Formal concentrations (molar) and rate constants k in $[D_8]$THF for conversion of 1 (RLi) to the allyl-derivative 3 in presence of 2 (RH).

Run no.	RLi M	RH M	LiBr M	Temp. °C	$10^4\ k_{1/2}$ $M^{1/2}\ s^{-1}$	$10^3\ k_{3/2}$ $M^{-1/2}\ s^{-1}$	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ eu
1a	0.14	0.07	0.46	26.5	0.81	0.82 ±0.12		
b	0.14	0.10	0.46	26.5	1.02	0.72 ±0.07		
2a	0.27	0.04	0.93	26.5	1.12	1.98 ±0.2		
b	0.27	0.08	0.93	26.5	2.28	2.02 ±0.2		
c	0.27	0.11	0.93	26.5	3.75	2.41 ±0.3		
3a	0.38	0.03	0.63	8.0	0.405	0.96 ±0.15	7.6 ±0.5	-45.3 ±2
b	0.38	0.03	0.63	27.0	0.97	2.28 ±0.35		
c	0.38	0.03	0.63	37.3	1.65	3.90 ±0.7		
d	0.38	0.03	0.63	51.0	2.78	6.56 ±1.4		
4a	0.16	0.03	0.35	27.0	0.51	1.21 ±0.16	8.8 ±0.5	-42.7 ±2
b	0.16	0.03	0.35	37.3	0.81	1.91 ±0.2		
c	0.16	0.03	0.35	51.0	1.62	3.83 ±0.35		

$$-d[RLi]/dt = k_{1/2}\sqrt{[RLi]} \quad (1); \qquad \sqrt{[RLi]} = -0.5k_{1/2}t + \text{const} \quad (2)$$

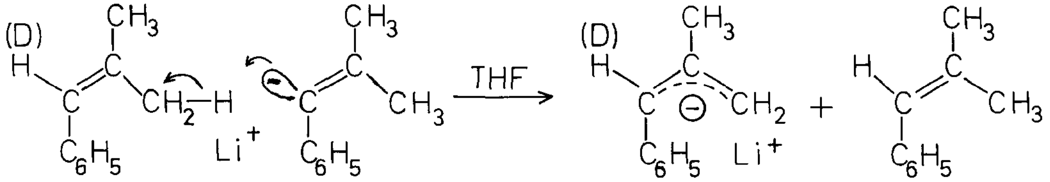
curve and found n(RLi) = 0.5 (±0.2). Hence, the reaction is of pseudo-0.5 order as noted in eq. (1) which integrates to eq. (2). Accordingly, plots of square roots of formal concentrations [RLi] versus time were linear over two half-lives or more, whereas first- and zeroeth-order plots were not. Nevertheless, all slopes and $k_{1/2}$ increased with the sample weights, indicating the presence of a catalyst. The catalytic role of the parent olefin RH (2) was cleanly proved by injecting additional amounts of 2 into solutions of 1 made up from the same sample (runs 1a,b and 2a-c in Table I). This was necessary because the rate constants depend also on LiBr (Table I), the amount of which differs widely in different batches. In this way, a first order of reaction was found for 2: *m*(RH) = 1.1 (±0.2). *The total order is thus 3/2.*

Parameters of Activation and Solvent Dependence

The temperature dependence was studied for two different batches (runs 3 and 4). The resultant values in Table I for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are almost equal. 1 is stable for days in diethyl ether at 25°. In a mixture of THF and benzene (molarities ca. 2/1) the rate constant decreases roughly twentyfold.

Discussion

The first-order dependence on olefin 2 (RH) is incompatible with an intramolecular mechanism. Deprotonation of 2 by some reactive intermediate 6 proceeds with regeneration of 2. The order of reaction for RLi, which was found less than unity, means that the transition state is preceded by dissociation.



2 6 3 2

A common-ion rate depression[6] would be expected for dissociation of 1 into the free carbanion and free lithium ion. Inspection of Table I shows, however, *that LiBr does not retard the rates; such dissociation is therefore* kinetically not important. Since organolithium compounds tend to aggregate even in THF,[7] we conclude that de-aggregation of the ground state R_xLi_x into two sub-units is a kinetically important step. The simplest possibility is that of a dimeric ground state R_2Li_2 which dissociates into two monomers RLi to give rise to a $[R_2Li_2]^{0.5}$ rate law. (The instability of 1 obviously defeats molecular mass determinations.) Under this presupposition, the actual rate law would be that of eq. (3); the rate constants $k_{3/2}$ were computed by eq. (4) from $k_{1/2}$. Table I lists the results together with the formal starting concentrations [RLi].

$$-d[R_2Li_2]/dt = k_{3/2}\ [RH]\ [R_2Li_2]^{-0.5} \qquad (3)$$

$$k_{3/2} = k_{1/2}\ [RH]^{-1}\ 2^{-0.5} \qquad (4)$$

The nature of the monomeric intermediate 6 may be assessed from the solvent dependence and activation parameters. With respect to these criteria and the 0.5 order of reaction, the kinetic behaviour of 1 in deprotonation of 2 parallels that for the (Z/E)-isomerization of α-aryl-vinyllithium.[8] The similarity extends to acceleration by LiBr and by traces of tris-(dimethylamino)-phosphinoxide (HMPA, 0.1 equivalents, $k_{3/2}$ ca. 0.0006 at -18°). Therefore, intermediate 6 is formulated as a (monomeric) ion pair; part of the strongly negative entropy of activation is certainly due to increasing solvent immobilization on the way to a more polar transition state.[8]

A logical confirmation of the intermolecular transmetallation mechanism would be the reaction of $[1\text{-}D_1]_2$ with unlabelled 1 (or 6); experimentally, deuterium was indeed incorporated into 3. However, $[1\text{-}D_1]_2$ was also found to equilibrate with unlabelled 3 at a comparable rate, as shown by the high isotope content of the aforementioned carboxylation products.

The vinyl-to-allyl conversion (1→3) appears to have no precedent. It may be formally related to conversion of o-methyl-phenyllithium to benzyllithium which does not take place in hexane.[9] 1-Phenyl-1-butenyllithium was described[10] to be stable in THF. We could not detect rearrangements of (Z)-1-lithiopropene and 2-lithio-propene in THF containing propene. Olefin 2 is perhaps exceptionally reactive since (E)-1-phenyl-propene was deprotonated much more slowly by 1.

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