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Kinetics of α-(2,6-Dimethylphenl)vinyllithium: How to Control Errors Caused by Inefficient Mixing with Pairs of Rapidly Competing Ketones

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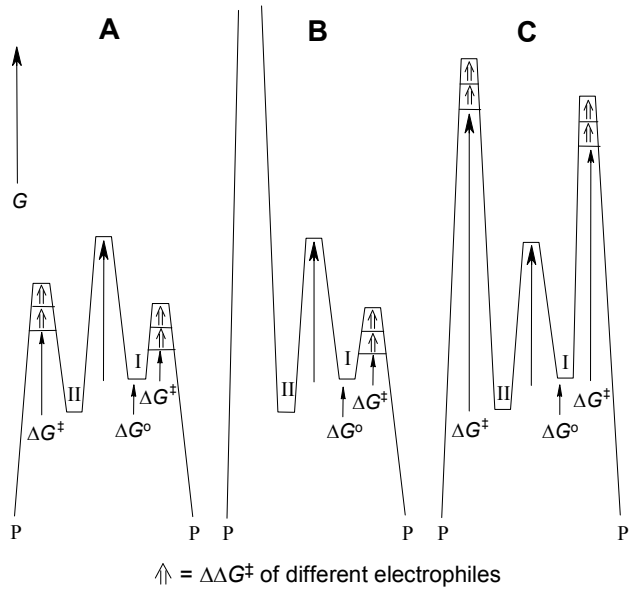
Key words. Aggregate reactivity; alkenyllithium selectivity; broken kinetic order; carbonyl competition constants; trimethylsilylation.

Abstract. Kinetic studies are a suitable tool to disclose the role of tiny reagent fractions. The title compound **2** reacted in a kinetic reaction order of 0.5 (square root of its concentration) with an excess of the electrophiles $ClSiMe_3$, 1-bromobutane (*n*-BuBr), or 1-iodobutane (*n*-BuI) at 32 °C in Et_2O or in hydrocarbon solvents. This revealed that the tiny (NMR-invisible) amount of a deaggregated equilibrium component (presumably monomeric **2**) was the reactive species, whereas the disolvated dimer **2** was only indirectly involved as a supply depot. Selectivity data (relative rate constants κ_{obs}) were collected from competition experiments with the faster reactions of **2** in THF and the addition reactions of **2** to carbonyl compounds. This provided the rate sequences of $Et_2C{=}O$ > dicyclopropyl ketone > *t*-Bu–C(=O)–Ph > diisopropyl ketone >> *t*-$Bu_2C{=}O$ > $ClSiMe_3$ > *n*-BuI > *n*-BuBr ≈ (bromomethyl)cyclopropane (but *t*-$Bu_2C{=}O$ < $ClSiMe_3$ in THF only) and also of cyclopropanecarbaldehyde > acetone ≥ *t*-Bu–CH=O. It is suggested that a deceivingly depressed selectivity ($1 < \kappa_{obs} < k_A/k_B$), caused through inefficient microscopic mixing of a reagent X with two competing substrates A and B, may become evident through its toward zero deviation from the correlation line of the usual inversely ($1/T$) linear temperature dependence of $\ln\kappa_{obs}$.

1. INTRODUCTION

Kinetic studies of organolithium compounds deserve renewed attention in view of some recently published applications of the rapid injection NMR (RINMR)[1] method: Meticulous investigations[2–4] at the lowest possible temperatures disclosed instructive (sometimes spectacular) reactivity differences of the various organolithium species (such as tetrameric, dimeric, monomeric), related mixed aggregates,[5] and solvent-separated ion pairs (SSIP) which may be present in a common solution. If these species compete for an electrophile, the fastest of them (I in Scheme 1) might be observed by RINMR to be the first one to disappear through product (P) formation, followed by the slower (less reactive) species (II) which may form the same or a related product P. The chance to detect such a fascinating sequence hinges on a sufficient height of the II,I interconversion barrier as the highest free-enthalpy (*G*) level in profile A of Scheme 1: II and I will then react independently of each other across the lower barriers ($\Delta G^{\ddagger}$) of their product-forming steps toward the left and right, respectively, of profile A. The appertaining rates depend on the concentrations of II or I and on individual rate constants *k* (whose $-\log k$ are proportional to $\Delta G^{\ddagger}$), and they are also plainly proportional to the electrophile concentration (a "first-order" rate dependence).

Scheme 1. Qualitative Free-enthalpies (*G*) as Functions of the Reaction Coordinates (horizontal): Descent to (often the same) Product P is thought to occur across Barriers $\Delta G^{\ddagger}$ from Species II toward the left Side and from Species I toward the right Side in Profiles A and C.



A sequential disappearence of I and II would be compatible also with profile B where either II (as shown) or I may be thermodynamically favored by a free-enthalpy difference ΔG^0. The disappearence rate of II, however, will no longer depend directly on the concentration of an electrophile that reacts with I; instead, the consumption rate of II should equal the interconversion rate between II and I (after an initiation period as long as I is significantly populated). For example, such a deaggregation (II $\rightarrow$ I) was identified to be a rate-limiting step in the deprotonation of alkynes[2] and in reactions of some other substrates[2,3] with organolithiums. Clearly, kinetic reaction orders (concentration dependencies of the rate) can be important for the interpretation of RINMR results. Less sophisticated, conventional techniques of rate measurements can be appropriate if the product-forming component I is NMR-invisible and if the rates are slow enough, as indicated by the higher barriers in profile C: Due to the much faster I/II interconversion ("Curtin-Hammett" condition[1,6]), kinetic quantification of reactivities may now require the additional consideration of an equilibrium constant K (or the corresponding free-enthalpy difference ΔG^0 that is proportional to $-\ln K$ or $-\log K$). Although knowledge of K may be unavailable if, for instance, a very low population of I cannot be detected, even such a situation can provide significant relative reactivities: The molar ratios of products formed with pairs of electrophiles reacting in the same solution can furnish competition (relative rate) constants κ and barrier differences $\Delta\Delta G^{\ddagger}$ (which are proportional to $-\ln\kappa$ or $-\log\kappa$) of the product-forming steps. Since these $\Delta\Delta G^{\ddagger}$ values depend neither on the II/I interconversion rate nor on ΔG^0 in profile C, κ data alone cannot provide direct mechanistic evidence; but in combination with at least one kinetically significant experiment that includes the I/II equilibrium, κ can acquire such a significance and may also extend it. The present work searched for two or three such kinetically conclusive experiments with the title compound and for amplifications of their results by κ data from competitive pairs of intercepting electrophiles.

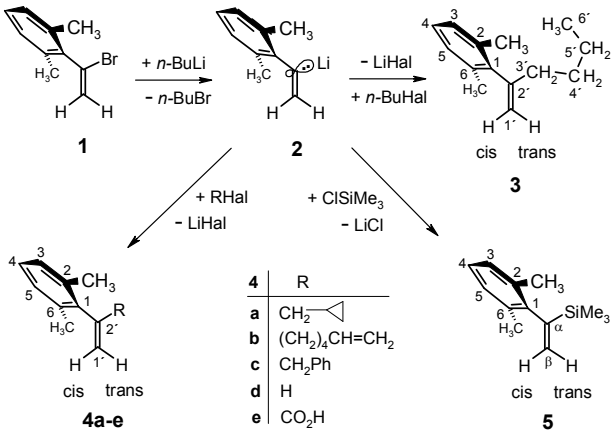
2. RESULTS AND DISCUSSION

2.1. Derivatizations of 2 by Slow Interceptors

The title compound **2** (Scheme 2) is known[7] to exist exclusively as the trisolvated monomer **2**&3THF in tetrahydrofuran (THF) as the solvent and (almost) only as the disolvated dimers $(\mathbf{2}\&Et_2O)_2$ in Et_2O or $(\mathbf{2}\&t\text{-BuOMe})_2$ in *tert*-butyl methyl ether (*t*-BuOMe). In the absence of such electron-pair donor ligands, the aggregation state of **2** is higher than dimeric in hydrocarbon solvents. The crystalline samples of dimeric **2**&*t*-BuOMe[8] used in this work were prepared from

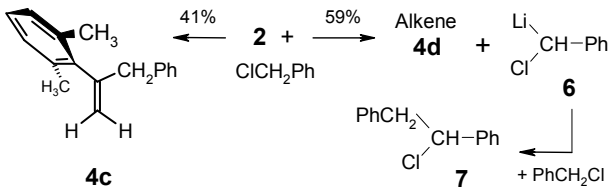
the bromoalkene[8] **1** with *n*-butyllithium (*n*-BuLi). This Br/Li interchange reaction should not be carried out in THF as the solvent, because the emerging monomer **2**&3THF would very rapidly be butylated by its coproduct 1-bromobutane (*n*-BuBr) to give **3**. The rate studies in Section 2.2 will reveal why *n*-BuBr and *n*-BuI form **3** much more slowly in Et_2O. These two *n*-BuHal electrophiles had been observed[9] to undergo butylation reactions in *N*,*N*-dimethyl formamide by single-electron-transfer (SET) in parallel with the S_N2 pathway. Therefore, frequent observations of deeply red colors in THF solutions of **2** raised our suspicion that **2** might also be able to participate in SET reactions. However, treatment of **2** with the SET indicator (bromomethyl)cyclopropane furnished the expected product **4a** (Scheme 2) in THF or Et_2O as the solvents without any trace of the isomeric SET product 2-arylhexa-1,5-diene. Likewise, the alternative SET indicator 6-bromo-1-hexene afforded the expected 2-aryl-1,7-octadiene (**4b**) in THF without any hint to formation of the isomeric α-(cyclopentylmethyl) derivative of **2**. Thus, neither of these two indicator reagents afforded positive evidence of an SET event.

Scheme 2. Synthesis of and Products from α-(2,6-Dimethylphenyl)vinyllithium (**2**).



Benzyl chloride reacted with **2** in Et_2O somewhat faster (within 150 min at rt) than the above butyl halides, albeit with a meagre yield of the expected benzyl derivative (**4c**) of **2**. In THF as the solvent (Scheme 3), **4c** was formed in parallel with proton transfer from benzyl chloride to **2** that gave 1-chloro-1,2-diphenylethane (**7**; product ratio **4c**/**7** = 41:59 after < 10 min at rt): The presumed short-lived Li,Cl carbenoid **6** was apparently trapped by benzyl chloride, yielding **7** and slightly more than the expected equivalent amount of the alkene **4d**. The 2′-$SiMe_3$ derivative **5** (Scheme 2) was obtained from purified[8] **2**&*t*-BuOMe with $ClSiMe_3$. This trimethylsilylation reaction proceeded rapidly at 32 °C in either Et_2O or cyclopentane (Section 2.2); it occurred at least 50-times as fast as butylation of **2** by *n*-BuBr in THF at –78 °C (Section 2.4).

Scheme 3. Competition of Benzylation and Protonation of **2** by Benzyl chloride in THF.



2.2. Some Electrophiles Require the Deaggregation of Dimeric 2 (Profile C)

Recent RINMR studies[3] revealed that methylation of monomeric organolithiums by CH_3I can be excedingly rapid even at –132 °C in THF/Me_2O, where the active species was reported to be the SSIP that played the role of I in profile B. In search of preparatively useful, quantified knowledge of the slower rate of the above butylation of **2** by *n*-BuBr in solvents other than THF, we chose Et_2O which tolerates (almost) only dimeric **2** and disfavors formation of a highly reactive SSIP species[7] of **2** in the absence of THF. Our rate measurements[10] in Et_2O at 32 °C revealed that the rate constants k_ψ (entries 1–4 in Table 1) increased in proportion with the concentration of RHal = *n*-BuBr. This kinetic participation of the electrophile *n*-BuBr excluded deaggregation of dimeric **2** (II in profile B) from being a rate-limiting step. Table 1 shows the use of the convenient method of employing a sufficiently large (at least 7-fold) excess of the electrophiles RHal, whose effective concentrations were taken as usual to be the average of the initial and (calculated) final values of [RHal]. This setup served to determine the rate dependency on the concentration [D] of dimeric **2** ("D") as follows. If D reacted directly with RHal, the rate would be proportional to [D] (a pseudo-first-order rate dependence) and the process would run with a constant half-reaction time $t_{1/2}$. This possibility was disproved by means of the logarithmic plot (decay of $\ln[D(t)]$ versus time t) in Figure S1,[10] where the downward curvature dismissed the expected linear time dependence. Thus, D cannot be directly involved in the product-forming steps of I or II as depicted in profile A. Consistently, a simple plot of the doubled substrate concentration $2[D(t)]$ versus t in Figure S2 showed[10] that $t_{1/2}$ decreased in the sequence of 109, 77, and 72 min. This implied a kinetic order of $<<1$ for $D(t)$; but a pseudo-zeroth-order reaction would have run with a constant rate (constant slope) toward the end in this setup, in contradiction to Figure S2. Clearly, the reaction order of $D(t)$ must be between zero and one, which indicates some kind of dissociation; but since formation of free ions in our non-THF solvent would not be credible, the explanation should be found in profile C with

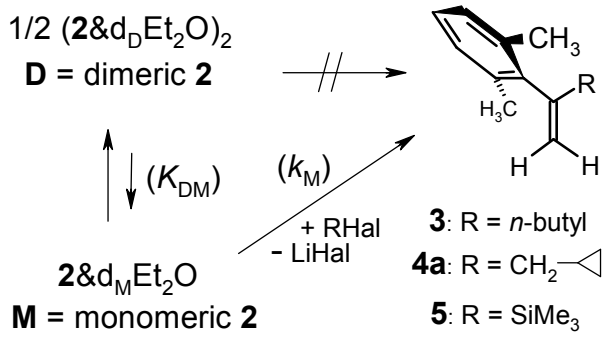
a highly mobile[7] dimer/monomer (II/I) equilibrium: As shown above, the "inactive" D cannot be the directly product-forming component I, so that D must be the precursor II of I, and the reactive intermediate I might be the NMR-invisible monomeric species (M) of **2**. Scheme 4 depicts the proposed kinetic relationships.

Table 1. The Electrophiles RHal react in Solutions of Dimeric **2**&***t*-BuOMe** ("D") at +32 °C with Pseudo-0.5th-order Rate Constants[a] k_ψ and the Corresponding First Half-Reaction Times $^\psi t_{1/2} = 0.586(2[D(t=0)])^{0.5}/k_\psi$. The Appertaining Rate Expression $d[Product]/dt = k_\psi(2[D(t)])^{0.5} = k_{3/2}[RHal](2[D(t)])^{0.5}$ derives from Scheme 4.

entry	solvent	2[D(*t*=0)] mol/L	RHal	[RHal] mol/L	$10^6 k_\psi$ a	$^\psi t_{1/2}$ min	$10^6 k_{3/2}$ a
1	Et_2O	0.143	*n*-BuBr	1.53	34.0	109	22.2
2	Et_2O	0.200	*n*-BuBr	1.90	40.0	109	21.1
3	Et_2O	0.131	*n*-BuBr	2.69	51.7	68	19.2
4	Et_2O	0.259	*n*-BuBr	2.97	61.3	81	20.6
5	benzene	0.160	*n*-BuBr	1.63	2.33	1515	1.43
6	benzene	0.250	*n*-BuBr	2.54	4.17	1170	1.64
7	$[D_8]$toluene	0.154	*n*-BuI	1.46	3.50	1094	2.40
8	$[D_8]$toluene	0.190	*n*-BuI	1.90	4.73	900	2.49
9	Et_2O	0.104	*n*-BuI	0.84	55.7	57	66.3
10	Et_2O	0.165	*n*-BuI	1.98	125.0	32	63.3
11	Et_2O	0.196	$ClSiMe_3$	1.34	1206	3.6	896
12	C_5H_{10} [b]	0.083	$ClSiMe_3$	1.06	267	11	252

[a] k_ψ in units of $mol^{0.5}\ L^{-0.5}\ s^{-1}$ and $k_{3/2}$ in $mol^{-0.5}\ L^{0.5}\ s^{-1}$. [b] Saturated solution in cyclopentane with ca. 1 equiv of *t*-BuOMe.

Scheme 4. The Mechanistic Proposal of Unreactive **D** and Reactive (yet NMR-Invisible) **M** in Et_2O.



The numerically unknown equilibrium constant K_{MD} of aggregation in eq 1 connects the concentration [M] of the monomer with the molar concentration [D] of the disolvated[7] dimer D. The microsolvation number d_D = 1 Et_2O ligand per Li in the preponderant D is known,[7] whereas d_M of M is unknown (but probably[11] between 2 and 3 Et_2O ligands). We define the reaction rate of this system (Scheme 4) in eq 2 to be the time dependence of the increasing product concentration, which is twice as high as that of the decaying dimer concentration [D(t)]. The choice of 2[D(t)] in eq 2 means that we count the amounts and percentages of all compounds in units of the monomer formula of **2** as also measured through NMR integrations. The monomer concentration [M(t)] decreases with a rate constant k_M (eq 2) of the product-forming step; but [M(t)] is replenished through the mobile equilibrium formulated in eqs 1 and 3, whose combination with eq 2 yields eq 4 with a 0.5th-order (square root) rate dependence on the measured 2[D(t)] values. The integrated form in eq 5 predicts a linear dependence of $(2[D(t)])^{0.5}$ on time t, which was experimentally verified in Figure 1 that furnished the pseudo-0.5th-order rate constant k_ψ (in units of $mol^{0.5}\ L^{-0.5}\ s^{-1}$) in entry 1 of Table 1. According to eq 6, the corresponding (pseudo-0.5th-order) first half-reaction time was $^{\psi}t_{1/2}$ = 109 min. The 1.5th-order rate constants $k_{3/2} = k_\psi/[RHal]$ (eqs 4 and 7) in entries 1–4 were reasonably consistent with each other, affording the averaged value of 21 $mol^{-0.5}\ L^{0.5}\ s^{-1}$ for RHal = *n*-BuBr in Et_2O. In benzene as the solvent, the $k_{3/2}$ values of **2**&*t*-BuOMe were smaller by a factor of only 14 (entries 5 and 6).

$$K_{MD} = [M]^{-2}\,[D]\,[\text{free } Et_2O]^{2d_M - 2d_D} \qquad (1)$$

$$\text{rate} = d[\text{product}]/dt = -2d[D(t)]/dt = k_M\,[RHal]\,[M(t)] \qquad (2)$$

$$[\mathrm{M}(t)] = (2K_{\mathrm{MD}})^{-0.5}(2[\mathrm{D}(t)])^{0.5}[\text{free } \mathrm{Et_2O}]^{d_\mathrm{M}-d_\mathrm{D}} \quad (3)$$

$$\text{rate} = -\mathrm{d}(2[\mathrm{D}(t)])/\mathrm{d}t = k_{3/2}\,[\mathrm{RHal}](2[\mathrm{D}(t)])^{0.5} = k_\psi\,(2[\mathrm{D}(t)])^{0.5} \quad (4)$$

$$\text{Integrated:} \quad (2[\mathrm{D}(t)])^{0.5} = -0.5\,k_\psi\,t + (2[\mathrm{D}(t=0)])^{0.5} \quad (5)$$

$$^{\psi}t_{1/2} = 2(1-2^{-0.5})\,k_\psi^{-1}\,(2[\mathrm{D}(t=0)])^{0.5} = 0.586\,k_\psi^{-1}\,(2[\mathrm{D}(t=0)])^{0.5} \quad (6)$$

$$k_{3/2} = k_\mathrm{M}\,(2K_{\mathrm{MD}})^{-0.5}\,[\text{free } \mathrm{Et_2O}]^{d_\mathrm{M}-d_\mathrm{D}} \quad (7)$$

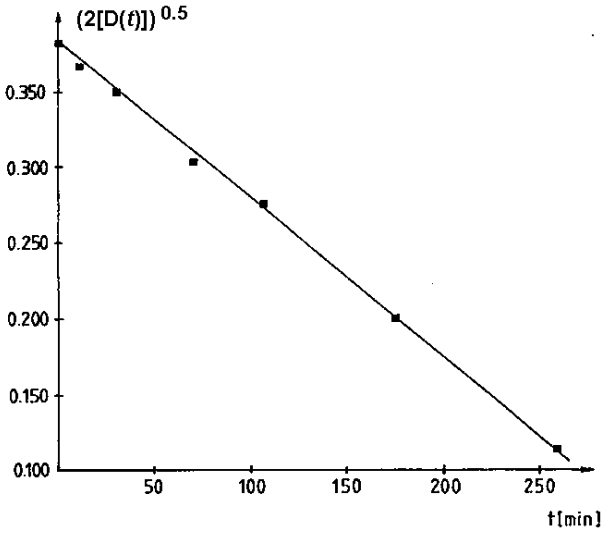


Figure 1. Time dependence of the square root (pseudo-0.5th order) of the doubled concentration $2[\mathrm{D}(t)]$ of dimeric **2** reacting with an excess of *n*-BuBr in Et_2O at 32 °C.

1-Iodobutane (RHal = *n*-BuI) was 1.6-fold more reactive than *n*-BuBr in the aromatic hydrocarbon solvents (entries 7 and 8 versus 5 and 6 in Table 1) and only 3.1-fold in Et_2O (entries 9 and 10 versus 1–4); these rate ratios are compatible with a very roughly estimated 3:1 rate ratio for *n*-BuI/*n*-BuBr reacting with ethyl cyanoacetate in benzene.[12] Under the pseudo-0.5th-order conditions as above, **2** appeared to be consumed by (bromomethyl)cyclopropane (to give **4a** in Scheme 4) in [D_8]toluene at a comparable rate as by *n*-BuHal in entries 5–8; similarly, a competition experiment (documented in Section 2.4) confirmed that (bromomethyl)cyclopropane in Et_2O reacted more slowly than *n*-BuBr at rt by a factor of only 1.5.

The kinetic system depicted in Scheme 4 applied also to the reaction of $ClSiMe_3$ with dimeric **2** in Et_2O to give product **5** (Scheme 2). This followed from the linear dependence of $(2[D(t)])^{0.5}$ on time *t* in the pseudo-0.5th-order plot shown in Figure 2; it gained support from the non-linear, downward-curved time dependence of $\ln(2[D(t)])$ in Figure S3 of the Supporting Information, which excluded a pseudo-first-order behavior of D. As before (eqs 1–7) with RHal = *n*-BuHal, we ascribe this 0.5th order to the role of the monomeric fraction ("M") of **2** as the NMR-invisible, product-forming intermediate. With $|k_{3/2}| = 896$ ($^{\Psi}t_{1/2}$ = 3.6 min from eq 6) in entry 11 of Table 1, $ClSiMe_3$ reacted 896/21 = 43-fold faster than *n*-BuBr (entries 1–4) at 32 °C, but the D,M interconversion of **2** occurred still much faster, namely, with $t_{1/2} < 7$ s already below −81 °C,[13] at which temperatures trimethylsilylation would of course be much slower than at 32 °C. Under the same conditions but in cyclopentane as the solvent (entry 12), **2**&*t*-BuOMe was consumed by $ClSiMe_3$ with $|k_{3/2}| = 252$ ($^{\Psi}t_{1/2}$ = 11 min), again much more slowly than the corresponding D,M interconversion.[14] Thus, trimethylsilylation of **2**&*t*-BuOMe occurred in either Et_2O or cyclopentane under the Curtin-Hammett[1,6] conditions of a free-enthalpy profile of type C. It may be noticed that the $k_{3/2}$ values in Table 1 do not very much depend on the polar character of these non-THF solvents. With the more stringent requirement of unchanged magnitudes of the parameters in eq 7 (namely, K_{MD}, [free donor], and the microsolvation numbers d_M and d_D), the $k_{3/2}$ quotient (the above selectivity of 43:1) for the pair of $ClSiMe_3$ and *n*-BuBr will be equal to the appertaining k_M quotient (selectivity) of the product-forming intermediate (barrier difference $\Delta\Delta G^{\ddagger}$ of I in profile C). For comparison, an independent competition experiment (documented in Section 2.4) revealed that the bona-fide monomer **2**&3THF in THF at −78 °C reacted with $ClSiMe_3$ faster than with *n*-BuBr by a factor of $\kappa = 50$. In spite of the different solvent and temperature, the similarity of these two selectivities might be taken to support our interpretation of the reactive intermediate ("M") as being an Et_2O-solvated monomer of **2** rather than a reactive substrate complex of the type postulated by Brown[15] and advocated by Klumpp.[16] With any such NMR-invisible intermediate, a kinetic system of the type depicted in Scheme 4 would presumably be unsuitable for investigations by the powerful RINMR method.

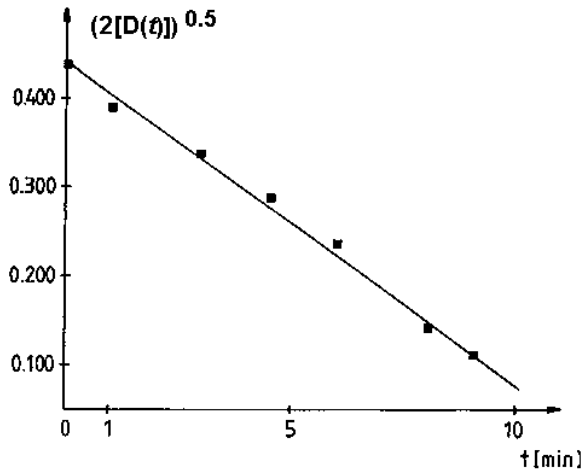
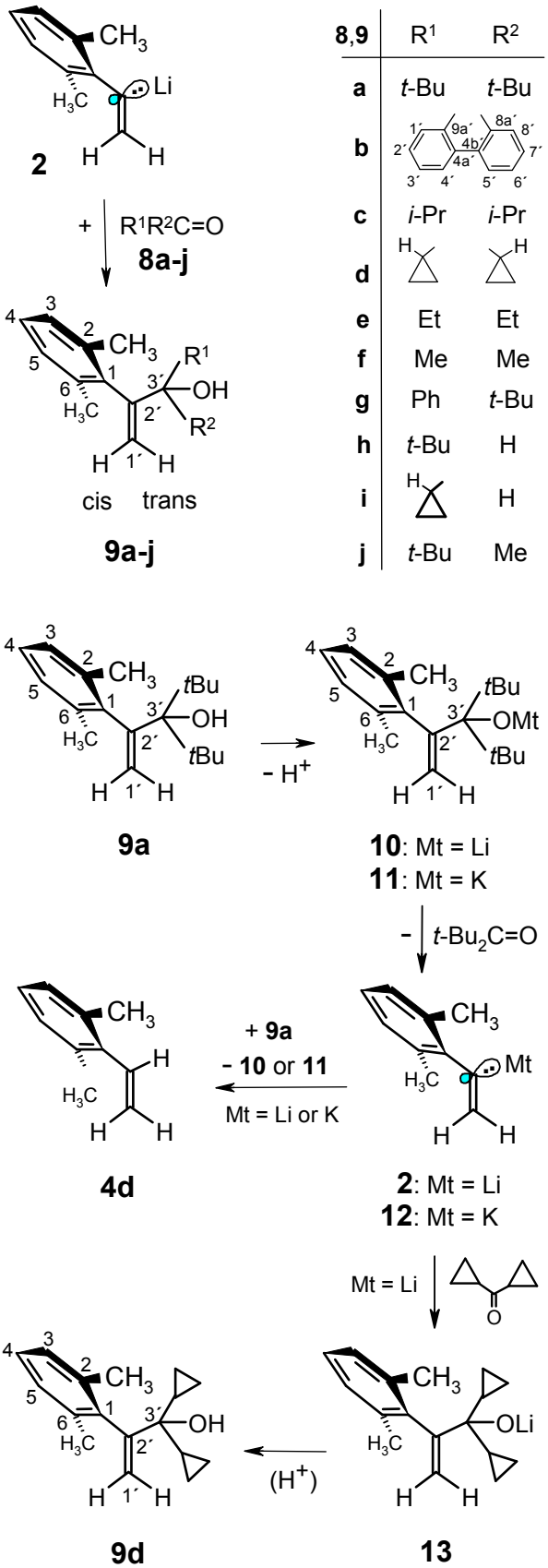


Figure 2. Time dependence of the square root of the doubled concentration 2[D(*t*)] of dimeric **2** reacting with an excess of $ClSiMe_3$ in Et_2O at 32 °C.

2.3. Fast Derivatization of 2 by Aldehydes and Ketones

Based on the conveniently slow butylation (Section 2.2) of **2** with its co-product *n*-BuBr in Et_2O, a simplified General Procedure could be used for derivatizations of **2** with rapidly reacting interceptors: The Br/Li interchange reaction of **1** (Scheme 2) was carried out in *t*-BuOMe or Et_2O with not more than a small excess of *n*-BuLi, whereupon the crude product was not purified but treated directly with a ketone or aldehyde. In order to explore the limit of steric hindrance, we added the sterically shielded di-*tert*-butyl ketone[17] (*t*-Bu_2C=O, **8a**) to **2** in *t*-BuOMe and obtained the precipitating lithium alkoxide **10** (Scheme 5) of the expected adduct **9a**. This smooth addition reaction was very slowly reversible at rt in THF as the solvent: In the presence of dicyclopropyl ketone (**8d**), only 58% of **10** decayed within 15 hours, generating the fragment **2** that was trapped by **8d** to produce the Li alkoxide **13** of **9d**. Consistently, the alcohol **9a** was unstable in the presence of either one of its alkoxides **10** or **11** at rt in THF: After the cleavage of *t*-Bu_2C=O from **10** or **11**, the fragment **2** or **12**, respectively, became quickly protonated by **9a** with formation of the parent alkene **4d** and a new-born equivalent of **10** or **11**. As a sluggish chain carrier, the Li alkoxide **10** needed ten days to consume **9a** with creation of **4d** and remnant **10** in a 95:5 ratio. However, the corresponding but much faster decay of the potassium alkoxide **11** required less than 150 min for the complete consumption of **9a** via **11** and its fragment **12** with generation of *t*-Bu_2C=O and alkene **4d**.[18]

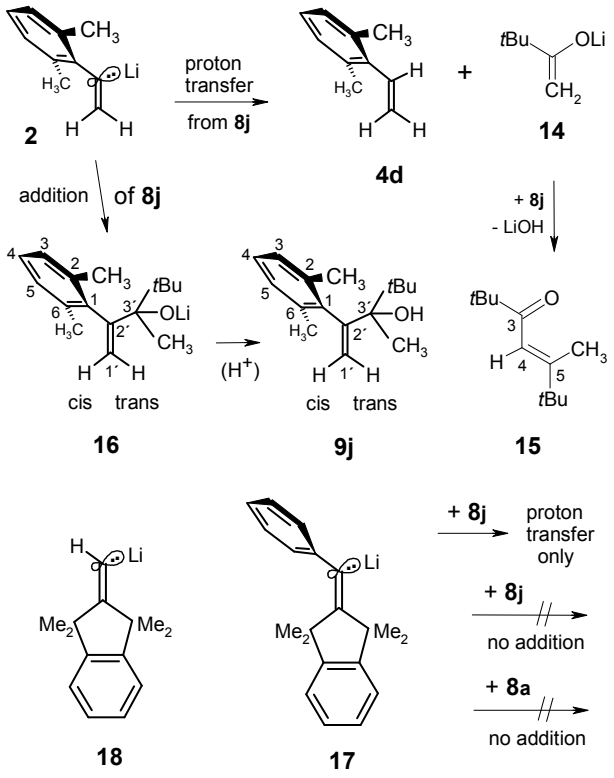
Scheme 5. Carbonyl Addition to **2**, and Cleavage of the Alkoxides **10** and **11** of **9a**.



Fluorenone (**8b**) added rapidly (roughly like **8d**) to **2** in Et_2O and was suspected to react via an SET process since it formed a black suspension before quenching. Nevertheless, it afforded the expected adduct **9b** that showed up at rt in the highest possible symmetry (C_S) of an achiral fluoren-9-ol derivative without signs of hindered internal rotation. On the other hand, rotation of the 2′-aryl group in the chiral adduct **9g** of pivalophenone (**8g**) was "frozen" at rt on the ^1H and ^{13}C NMR time scales, while a less impeded rotation of the 3′-phenyl group in **9g** was indicated through a weak line broadening of its C-*ortho* and C-*meta* NMR signals; however, not even the potassium alkoxide of **9g** succumbed to the *t*-Bu_2C=O expulsion that could have relieved its internal overcrowding. No signs of retarded rotation were observed for the adducts **9c**–**9f** of diisopropyl ketone (**8c**), dicyclopropyl ketone (**8d**), pentan-3-one (**8e**), and acetone (**8f**), while **9c** and **9e** exhibited the expected NMR nonequivalences of both the diastereotopic isopropyl methyl groups in **9c** and the ethyl CH_2 protons in **9e**. However, 2′-aryl rotation was again frozen in the chiral adducts **9h**, **9i**, and **9j** of pivalaldehyde (**8h**), cyclopropanecarbaldehyde (**8i**), and pinacolone (**8j**). Remarkably, proton transfer from the CH-acidic ketones **8c**, **8e** and **8f** to **2** was unimportant in *t*-BuOMe as the solvent, since the alkene **4d** was only a minor portion of the crude product mixture. However, the sterically more difficult addition of pinacolone (**8j**) to **2** generated the expected Li alkoxide **16** (Scheme 6) along with significant portions of the enone **15** that resulted through condensation of **8j** with its Li enolate **14**. Thus, the amount of enone **15** specified a minimum contribution of proton transfer from **8j** to **2**, whereas the amount of alkene **4d** feigned a higher portion of that proton transfer since other proton sources (rather than pinacolone) might also have converted **2** into **4d**. The in-situ NMR spectra before workup indicated no significant amounts of side-products or alkene polymerisation; in view of the volatility of alkene **4d**, they provided the most reliable minimum and maximum contributions of proton transfer from **8j**, namely, 39–63% to monomeric **2** in THF and 12–20% to dimeric **2** in Et_2O as the solvent, in partial disagreement with earlier[19] conclusions about the site selectivity of pinacolone with examples of monomeric and aggregated alkyllithium compounds. As an example of extreme predilection, the sterically congested, monomeric alkenyllithium **17** did not (or not irreversibly) add to pinacolone (**8j**) and *t*-Bu_2C=O[20,21] (**8a**) but succumbed to proton transfer from **8j** in either THF or *t*-BuOMe, whereas the predominantly dimeric 2-(lithiomethylene)-1,1,3,3-tetramethylindane (**18**) added readily[22] to *t*-Bu_2C=O in THF at –34 °C with a very coarse estimate of $t_{1/2}$ = ca. 30 min. Similarly, the addition of **8a** to dimeric α-(2,6-diisopropylphenyl)vinyllithium[11] in *t*-BuOMe was finished within a few minutes at –30 °C.[10]

These examples defined some limits of ketone addition to sterically congested alkenyllithiums and indicated that rate measurements of the present, less shielded (hence faster) "headliner" **2** would probably require more advanced equipment or considerably lower temperatures (at the expense of a decreased solubility of **2**).

Scheme 6. Addition versus Proton Transfer of Pinacolone (**8j**) to **2** and to **17**; addition of *t*-Bu_2C=O (**8a**) Occurred[22] with **18** but Failed with **17**.



2.4. Controlling the Problem of Microscopic Mixing that Threatens Rapid Competition Reactions

Aryl ketones can add to tetrameric CH_3Li in Et_2O[23] or to hexameric *n*-BuLi in benzene[24] with reaction rates on the millisecond time scale at 25 °C. In analogy with the considerations detailed in Section 2.2, the broken reaction orders[23,24] (0.25 and 0.17 in RLi, respectively) suggested that monomeric, NMR-invisible equilibrium components were the active reagents; this means that ketone addition to **2** may be subject to the same kinetic system as deduced in Section 2.2 (Scheme 4) for butylation and trimethylsilylation of **2**. More recent studies by the RINMR technique agreed with that notion: Monomeric aryllithiums can add to aryl ketones very rapidly even at –140 °C in THF/Me_2O,[25] whereas the appertaining aggregated species were observed to

react much more slowly (by sometimes several orders of magnitude), which implies that the aggregation equilibrium was not mobile at these very low temperatures ("non-Curtin-Hammett" condition, profile A). Being confined to our time scale of minutes and hours (Section 2.2), we resorted to measurements of relative rate constants through competition experiments. This method determines the quotient $\kappa_{A/B} = k_A/k_B$ of the rate constants of a mixture of two substrates A and B which compete for a reagent X that enters with the same exponent (kinetic order) of its concentration [X] into formation of the products AX and BX. In a convenient variant of this setup, $\kappa_{A/B}$ (or κ_{obs}) can be calculated from eq 8 as long as the concentrations obey the relationship $[X] << [A] + [B]$.[26] Such an excess (at least 8-fold) of the substrates is usually employed with the intention that both substrates should be present with practically unchanged concentrations during the whole reaction period. By this means, we estimated the competition constant κ_{obs} of *n*-BuBr and the sterically shielded *t*-Bu_2C=O (**8a**) competing for **2** in the following manner (entries 1 and 2 of Table 2). A deficient amount of purified **2**&*t*-BuOMe in Et_2O was added dropwise to a rapidly stirred Et_2O solution of **8a** and *n*-BuBr (molar ratio 1:20), which furnished a 98:2 mixture of the corresponding products **9a** and **3**, respectively; a second version of this competition experiment using **8a**/*n*-BuBr = 1:39 yielded **9a**/**3** = 96:4. Taking the average of the two κ_{obs} values that resulted from eq (8), *t*-Bu_2C=O (**8a**) had reacted ca. 960-times faster than *n*-BuBr at 22 °C. Comparison with $^{\Psi}t_{1/2}$ = typically 90 min for *n*-BuBr at 32 °C (Table 1, entries 1–4) indicated a time scale of about 90/960 ≈ 0.1 min for the addition of *t*-Bu_2C=O to **2** in Et_2O at ambient temperatures. This example of a competition experiment extended the kinetically 1.5th-order butylation reaction of **2** and showed how rapidly *t*-Bu_2C=O reacted with **2** in Et_2O. Incidentally, this comfortably slow butylation of dimeric **2** in Et_2O was hardly faster than alkylation by (bromomethyl)cyclopropane in entry 10.

$$\kappa_{A/B} = k_A/k_B = ([B]/[A])([AX]/[BX]) \qquad (8)$$

Table 2. Competition Constants $1 \le \kappa_{obs} \le \kappa_{A/B} = k_A/k_B$ (Error Limits up to ca. 15%) of Binary Mixtures of Electrophiles A and B Reacting with α-(2,6-Dimethylphenyl)vinyllithium (**2**&***t*-BuOMe**).[a]

entry	competitors	**A/B**, mmol	product ratio	°C, solvent	κ_{obs}
1	*t*Bu_2C=O / *n*-BuBr	**8a**/BuBr, 0.54/10.8	**9a**/**3** = 98/2	+22, Et_2O	980
2	*t*Bu_2C=O / *n*-BuBr	**8a**/BuBr, 0.26/10.2	**9a**/**3** = 96/4	+22, Et_2O	942
3	*t*Bu_2C=O / $ClSiMe_3$	**8a**/$ClSiMe_3$, 0.41/0.82	**9a**/**5** = 97/3	–78, C_5H_{10} [b]	65

4	tBu$_2$C=O / ClSiMe$_3$	**8a**/ClSiMe$_3$, 0.46/1.37	**9a/5** = 95/5	+22, C_5H_{10} [b]	57
5	tBu$_2$C=O / ClSiMe$_3$	**8a**/ClSiMe$_3$, 0.49/2.96	**9a/5** = 77/23	+22, Et$_2$O	20
6	ClSiMe$_3$ / tBu$_2$C=O	ClSiMe$_3$/**8a**, 0.83/0.42	**5/9a** = 96/4	–78, THF	12.1
7	ClSiMe$_3$ / tBu$_2$C=O	ClSiMe$_3$/**8a**, 1.00/1.00	**5/9a** = 93/7	+22, THF	13.3
8	ClSiMe$_3$ / n-BuBr	ClSiMe$_3$/BuBr, 0.57/2.84	**5/3** = 91/9	–78, THF	50
9	ClSiMe$_3$ / n-BuBr	ClSiMe$_3$/BuBr, 0.28/2.84	**5/3** = 50/50	+22, THF	10.1
10	n-BuBr / cprCH$_2$Br	1.23/1.23	**3/4a** = 60/40	+22, Et$_2$O	1.5
11	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.40/8.00	**9d/9c** = 78/22	–78, THF	71
12	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.42/1.42	**9d/9c** = 98.6/1.4	–78, THF	70
13	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.28/4.26	**9d/9c** = 76/24	–45, THF	48
14	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.28/5.50	**9d/9c** = 70/30	–30, THF	46
15	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.50/0.50	**9d/9c** = 94/6	0, THF	16 [c]
16	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.58/2.89	**9d/9c** = 77/23	0, THF	17 [c]
17	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.56/2.24	**9d/9c** = 75/25	+22, THF	12.0 [c]
18	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.57/3.98	**9d/9c** = 65/35	+22, THF	13.0 [c]
19	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.50/4.00	**9d/9c** = 53/47	–78, Et$_2$O	9.0
20	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.00/5.00	**9d/9c** = 53/47	–30, Et$_2$O	5.6
21	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.00/3.00	**9d/9c** = 51/49	+22, Et$_2$O	3.1 [c]
22	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.42/1.42	**9d/9c** = 91/9	–78, t-BuOMe	10.1
23	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 0.57/3.98	**9d/9c** = 59/41	–78, t-BuOMe	10.0
24	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.42/1.42	**9d/9c** = 68/32	+22, t-BuOMe	2.1 [c]
25	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.07/2.14	**9d/9c** = 49.5/50.5	+22, t-BuOMe	2.0 [c]
26	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.42/1.42	**9d/9c** = 88/12	–78, toluene	7.3
27	cpr$_2$C=O / iPr$_2$C=O	**8d/8c**, 1.42/1.42	**9d/9c** = 69/31	+22, toluene	2.2
28	cpr$_2$C=O / iPr$_2$C=O [d]	**8d/8c**, 1.49/2.23	**9d/9c** = 49.8/50.2	+22, toluene	1.5 [d]
29	cpr$_2$C=O / iPr$_2$C=O [e]	**8d/8c**, 1.08/1.08	**9d/9c** = 62/38	+22, pentane	1.6 [e]
30	cpr$_2$C=O / Ph–C(O)–tBu	**8d/8g**, 1.42/1.42	**9d/9g** = 94/6	–78, THF	16
31	cpr$_2$C=O / Ph–C(O)–tBu	**8d/8g**, 0.57/2.84	**9d/9g** = 78/22	–78, THF	18
32	cpr$_2$C=O / Ph–C(O)–tBu	**8d/8g**, 1.42/1.42	**9d/9g** = 79/21	+22, THF	3.8
33	Et$_2$C=O / cpr$_2$C=O	**8e/8d**, 2.87/2.87	**9e/9d** = 67/33	–78, t-BuOMe	2.0
34	Et$_2$C=O / cpr$_2$C=O	**8e/8d**, 0.77/3.08	**9e/9d** = 33/67	–78, t-BuOMe	2.0
35	Et$_2$C=O / cpr$_2$C=O	**8e/8d**, 1.42/1.42	**9e/9d** = 66/34	–78, t-BuOMe	1.9

36	Et_2C=O / cpr_2C=O	**8e/8d**, 0.94/0.94	**9e/9d** = 62/38	+22, *t*-BuOMe	1.6
37	Et_2C=O / cpr_2C=O	**8e/8d**, 1.42/1.42	**9e/9d** = 78/22	–78, THF	3.5
38	Et_2C=O / cpr_2C=O	**8e/8d**, 1.42/1.42	**9e/9d** = 61/39	+22, THF	1.6
39	cpr–CH=O / *t*Bu–CH=O	**8i/8h**, 0.89/4.44	**9i/9h** = 46/54	–78, THF	4.2
40	cpr–CH=O / acetone	**8i/8f**, 1.15/1.15	**9i/9f** = 72/28	–78, THF	2.6
41	acetone / *t*Bu–CH=O	**8f/8h**, 1.09/1.09	**9f/9h** = 55/45	–78, THF	1.2
42	acetone / *t*Bu–CH=O	**8f/8h**, 2.0/2.0	**9f/9h** = 57/43	+22, THF	1.3
43	acetone / *t*Bu–CH=O	**8f/8h**, 2.0/2.0	**9f/9h** = 53/47	+22, *t*-BuOMe	1.1

[a] Bu = *n*-butyl, cpr = cyclopropyl, Et = ethyl, *i*Pr = isopropyl, Ph = phenyl, *t*Bu = *tert*-butyl. [b] C_5H_{10} = crystals of **2**&*t*-BuOMe dissolving in cyclopentane. [c] Presumably a disturbed value due to a mixing problem. [d] Donor-free **2** prepared through an I/Li interchange reaction[7] in toluene. [e] Donor-free **2** prepared through a Hg/Li interchange reaction[7] in pentane.

Competition between *t*-Bu_2C=O (**8a**) and $ClSiMe_3$ for **2** disclosed a remarkable behavior: In cyclopentane at both –78 and 22 °C (entries 3 and 4), dimeric **2**&*t*-BuOMe (or its active species) preferred *t*-Bu_2C=O by a factor of 61(±4). This preference was in the same direction albeit lower for dimeric **2** in Et_2O (entry 5). In THF, however, monomeric **2**&3THF preferred $ClSiMe_3$ (entries 6 and 7) by a factor of 12.7(6) in THF at either –78 or 22 °C, perhaps due to a considerably increased trimethylsilylation preference. This discrepancy mirrored .a similarly changing selectivity that was reported[27] for $ClSiMe_3$ and benzophenone competiting for phenyllithium at 0 °C in Et_2O (preference, 2/77) versus THF (68/0). We estimated the presumed acceleration of $ClSiMe_3$ in THF in the following way. The 1.5th-order kinetics in Section 2.2 had established that the NMR-invisible intermediate (monomeric **2**) was much more reactive than dimeric **2** in Et_2O. Therefore, the completely monomeric status of **2** in THF can explain our preperative experience (Section 2.1) that **2** reacted with its coproduct *n*-BuBr in THF "immediately" at either rt or –78 °C. Such a strong acceleration must be ascribed also to $ClSiMe_3$ which remained favored over *n*-BuBr in THF by factors of κ_{obs} = 10.1 and 50 (entries 9 and 8), which are compatible with the 896/21 = 43:1 preference in Et_2O at 32 °C (Table 1, entries 11 versus 1–4). This suggested that the $ClSiMe_3$/*n*-BuBr selectivities were similar for monomeric **2**&3THF in THF and the active species of dimeric **2**&Et_2O (formed through replacement of the ligand *t*-BuOMe by Et_2O) in Et_2O. Consequently, $ClSiMe_3$ and *n*-BuBr were similarly accelerated by the solvent change from Et_2O to THF, whereas the electrophile *t*-

$Bu_2C=O$ was less strongly accelerated since it lagged behind $ClSiMe_3$ in THF as shown by the above selectivity reversal between Et_2O and THF. Although we cannot quantify any of these accelerations, we can estimate in the following way that *t*-$Bu_2C=O$ was less strongly accelerated than *n*-BuBr by a factor of ca. 10^3 in THF. The above selectivity of 12.7(6) for $ClSiMe_3$/*t*-$Bu_2C=O$ in THF (entries 6 and 7) resembled the 10.1 selectivity of $ClSiMe_3$/*n*-BuBr (entry 9); therefore, *t*-$Bu_2C=O$ and *n*-BuBr appeared to be comparably reactive against **2** in THF. In Et_2O, however, *t*-$Bu_2C=O$ had been 960-fold (entries 1 and 2) more reactive than *n*-BuBr, so that *n*-BuBr had caught up with *t*-$Bu_2C=O$ by a ca. 10^3-fold stronger acceleration in THF. In short, the reactivity ratios were *t*-$Bu_2C=O$/$ClSiMe_3$/*n*-BuBr = 860:43:1 in Et_2O (entry 5 versus Table 1) but 0.8:(10.1 to 50):1 in THF (entries 6 and 7 versus 9). Of course, *t*-$Bu_2C=O$ reacted fast (0.1 min) in Et_2O and faster in THF; but its reactivity should be much lower than that expected for the less shielded ketone examples cited[23–25] above. We checked this for our substrates with an equimolar mixture of *t*-$Bu_2C=O$ and diisopropyl ketone (**8c**) competing for **2** in *t*-BuOMe at rt, which afforded only the adduct **9c** of **8c**. A similar result had been obtained[22] with **18** which added to *t*-$Bu_2C=O$ in *t*-BuOMe only in the absence of **8c** or **8d**. In contrast to *t*-$Bu_2C=O$, however, the faster ketones and aldehydes may meet a serious problem that is decribed in the sequel.

The above-mentioned proviso of practically constant competitor concentrations may become violated if A and B react with X already during the initial period of microscopic mixing, so that an instilled droplet or an injected portion containing the reagent X may consume the whole locally available quantities of both A and B in the boundary zone before mixing is finished.[28,29] If so, the products AX and BX would be generated in a molar ratio that equals the initial A/B ratio, in which case eq 8 will lead to the erroneous apparent competition constant $\kappa_{obs} = 1$ instead of $\kappa_{A/B} = k_A/k_B$. Therefore, experimental results with $\kappa_{obs} \approx 1$ are not always trustworthy, even though they may be correct, of course. Generally, the magnitudes of κ_{obs} are confined by the relationship $k_A/k_B = \kappa_{A/B} \geq \kappa_{obs} \geq 1$, since they may be depressed from the wanted ("true") $\kappa_{A/B}$ value when the concentration of at least the faster competitor A becomes significantly depleted through its more rapid comsumption in the boundary zone, while B lags behind and hence becomes less handicapped. The initial depression of κ_{obs} may be partially counteracted if only a fraction of X in the boundary zone suffices to consume A and B, whereupon the rest of X proceeds with generating undisturbed $\kappa_{obs} = \kappa_{A/B}$ data in the free solution. With sufficiently high values of κ_{obs} (or $1/\kappa_{obs}$) >> 1, it follows that B cannot have reacted extensively in the boundary zone, because otherwise κ_{obs} would approach the value of 1

(provided that the reaction of B is irreversible, which means that BX is not transformed into AX via temporarily regenerated X). On this basis, we interpreted the data in Table 2 by the following rules. (i) Supposing a substantial magnitude (>> 1) of the κ_{obs} factor, the much *slower* (by at least κ_{obs}) member of a competing pair cannot have reacted extensively within the boundary zone of microscopic mixing. (ii) Under the same conditions as above and again with a substantial magnitude (>> 1) of the κ_{obs} factor, the much *faster* (by at least κ_{obs}) member of a competing pair cannot have reacted extensively already in the boundary zone if it is found to be the much slower member of another competing pair. (iii) Temperatures should be chosen as low as possible with the intention to decrease fast reaction rates down to below the rate of microsopic mixing; in this work, runs at –78 °C were considered to be more reliable (though not infallible) than those at rt. (iv) More strictly, the strongly temperature-dependent κ_{obs} values (entries 11–18) for dicyclopropyl ketone (**8d**) in competition with diisopropyl ketone (**8c**) in THF provided an opportunity to qualitatively separate the κ_{obs} perturbations (as caused by inefficient mixing) from the intrinsic temperature dependence of $\kappa_{A/B}$ in the following manner. The expected relationship of $\ln\kappa_{A/B} = -\Delta\Delta G^{\ddagger}/(RT) = \Delta\Delta S^{\ddagger}/R - \Delta\Delta H^{\ddagger}/(RT)$, a consequence of the Eyring equation, can furnish a simple tool for identifying disturbed $\ln\kappa_{obs}$ candidates in a set of values from different Kelvin temperatures T: As illustrated by Figure 3, the necessarily straight correlation line of $\ln\kappa_{obs}$ versus $1/T$ should be drawn through the most probably "true" data points (usually those at the lowest T). This line should pass through close to the origin (where $\ln\kappa_{obs} = 0$ and $1/T = 0$) if $\Delta S^{\ddagger}_A - \Delta S^{\ddagger}_B = \Delta\Delta S^{\ddagger} \approx 0$, which may be (almost) correct for two structurally similar competitors. More generally, a guess of $\Delta\Delta S^{\ddagger} = y \pm 2$ cal mol^{-1} K^{-1} would confine a guessed correlation line to intersect the $\ln\kappa$ axis in the region of ca. $\pm 1 + \ln(y/R)$, where $R = 1.98$ cal mol^{-1} K^{-1}. Such a (guessed) correlation line is intended to provide reasonably (if qualitatively) extrapolated $\ln\kappa_{A/B}$ data for comparison with the experimental $\ln\kappa_{obs}$ values at the same temperature: Since $\kappa_{A/B} \geq \kappa_{obs} \geq 1$ (or $1/\kappa_{A/B} \leq 1/\kappa_{obs} \leq 1$), disturbed $\ln\kappa_{obs}$ candidates will deviate from the corresponding extrapolated $\ln\kappa_{A/B}$ data toward closer to the horizontal axis (where ln 1 = 0). Even though the amount and quality of our present data set did not suffice to determine the activation enthalpy difference $\Delta\Delta H^{\ddagger}$, the most strongly deviating $\ln\kappa_{obs}$ values (probably those at the highest temperatures) can be recognized from Figure 3 and were labeled with the footnote "c" in Table 2. This qualitative differentiation disclosed that the **8d**/**8c** pair in Et_2O (entries 19–21) had a mixing problem at 22 °C but (probably) not at –30 and

–78 °C. Figure 3 revealed also the κ_{obs} data at 22 and 0 °C in THF (entries 15–18) to be disturbed, whereas those at –30, –45, and –78 °C (entries 11–14) should not (or not strongly) be disturbed. This would agree with entry 37 where the fast dicyclopropyl ketone (**8d**) was the slower member of a pair with κ_{obs} = 3.5 at –78 °C and hence (according to the above rule iv) was hardly qualified to react extensively in the boundary zone.

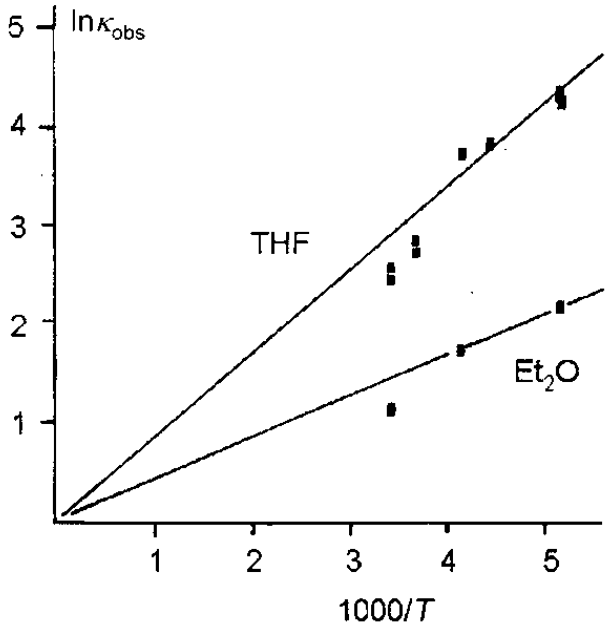


Figure 3. Inverse (1000/T) Kelvin-temperature dependence of the apparent logarithmic competition constants $\ln\kappa_{obs}$ as observed with dicyclopropyl ketone and diisopropyl ketone competing for **2** in THF (entries 11–18 of Table 2) and in Et_2O (entries 19–21). Note that the straight lines are not regression lines: They were drawn from the low-temperature data points toward close to the origin under the assumption of $R\ln\kappa_{A/B} = \Delta S^{\ddagger}_A - \Delta S^{\ddagger}_B = \Delta\Delta S^{\ddagger} \approx 0$ if $1000/T \rightarrow 0$.

Comparisons of the various κ_{obs} data for **8d**/**8c** at –78 °C showed that the selectivity (κ_{obs} = 71 in entries 11 and 12) of monomeric **2** in THF differed from that of the reactive intermediate in Et_2O, *t*-BuOMe, and toluene with κ_{obs} = ca. 9(1) in entries 19, 22, 23, and 26. The lower selectivity in the three non-THF solvents might be described as a lower sensitivity of the reactive species against the steric shielding of diisopropyl ketone (**8c**) as compared with dicyclopropyl ketone (**8d**). This trend continued in the absence of donor ligands (other than the ketone substrates **8d** and **8c**) with astonishingly weak preferences at rt in toluene (entry 28) and pentane (entry 29), which solvents would admit only much lower reaction rates and hence would not be

expected to create a mixing problem with **2**. Perhaps surprisingly, pivalophenone (**8g** in entries 30 and 31) is more reactive than diisopropyl ketone (**8c**): In competition with dicyclopropyl ketone (**8d**) in THF, the relative reactivity of **8g** was 1/17(1) at –78 °C, to be compared with 1/71 for **8c** relative to **8d** (entries 11 and 12), which indicated a reactivity sequence of **8c** < **8g** < **8d**; the change of the **8d**/**8g** selectivity from κ_{obs} = 17(1) at –78 °C to 3.8 at 22 °C (entry 32) may be due to the intrinsic temperature dependence of the related $\kappa_{A/B}$ values. The weak preference of **2** for pentan-3-one (**8e**) over **8d** (entries 33–36 and 38) was also independent of temperature and solvent, so that a mixing problem appeared unlikely in view of the tiny monomer fraction and hence lower rates in *t*-BuOMe. The value of κ_{obs} = 3.5 (entry 37) of this pair at –78 °C in THF would also be compatible with an intrinsic temperature dependence. With cyclopropanecarbaldehyde (**8i**) as the faster member of a pair, the magnitudes of κ_{obs} = 4.2 (entry 39) and 2.6 (entry 40) indicated that the slower competitors pivalaldehyde (**8h**) and perhaps also acetone (**8f**), respectively, did not react very extensively within the boundary zone of microscopic mixing. Consistently, their mutual competition constants κ_{obs} = 1.2(1) for **8f**/**8h** in entries 41–43 should also be not very much disturbed, which conclusion appeared again compatible with the missing influence of temperature and solvent.

3. CONCLUSION

(a) The reactions of **2** with *n*-BuHal or $ClSiMe_3$ ran on a comfortable time scale in Et_2O at 32 °C because the strongly predominating dimer of **2** is inactive and must rapidly (and reversibly) deaggregate before reacting with the electrophiles (Scheme 4): In consideration of its tiny concentration, an NMR-invisible, probably monomeric equilibrium component of **2** must have reacted with high rate constants k_M (whose magnitudes remained unknown) in eq 2 to account for the observed rates.

(b) The $k_{3/2}$ values (total kinetic order 1.5) in Table 1 showed that trimethylsilylation of **2** proceeded 43-times faster than butylation by *n*-BuBr in Et_2O at 32 °C and that both electrophiles reacted under conditions of profile C in Scheme 1, namely, with a substantially faster monomer/dimer equilibration in the background. The broken (0.5th) kinetic order of the concentration of **2** was found under the following conditions which differed from essential traits[16] of the alternative model[15] of a rate-determing, broken-order substrate-organolithium "complex" intermediate. (i) We verified the broken kinetic order through demonstration of the compatibility of our experimental data with the full rate equation rather than through interpretation of the

initial[16] rates. (ii) Our broken-order reagent **2** was employed as a minority (< 13%) rather than as an excessive[16] component. (iii) Our electrophiles ($ClSiMe_3$ and *n*-BuHal) would hardly be expected to form the strong complexes with our α-arylalkenyllithium **2** that are required[15] by the alternative model. These differences dismiss the alternative model[15] for **2** and confirm the deaggregation model as our explanation of the kinetically 0.5th order of **2**.

(c) Very efficient mixing (vigorous stirring) of a reagent X with the dissolved competing substrates (A and B) is a most important condition for conclusive competition experiments of this type, because an apparent (deceiving) competition constant value of $\kappa_{obs} \approx 1$ would arise if both competitors reacted already in the boundary zone of microscopic mixing. Thus, the magnitudes of κ_{obs} may always be suspected to be lower than the desired quorients k_A/k_B of the rate constants.[29] Therefore, single errors may change the presently found relative-rate sequences of $Et_2C{=}O$ > $cpr_2C{=}O$ > *t*-Bu–C(=O)–Ph > *i*-$Pr_2C{=}O$ > *t*-$Bu_2C{=}O$ > (or < in THF) $ClSiMe_3$ > *n*-BuBr and of cprCH=O > acetone ≥ *t*-BuCH=O in a given solvent.

(d) The "slow" ketone *t*-$Bu_2C{=}O$ added to **2** on a roughly estimated time scale of 0.1 min in Et_2O at rt; this reaction occurred 960-fold faster than that of *n*-BuBr. The relative reactivities of *t*-$Bu_2C{=}O$/$ClSiMe_3$/*n*-BuBr toward **2** were 860/43/1 at rt in Et_2O but 0.8/(10 to 50)/1 in THF. The strongly accelerated reactions of $ClSiMe_3$ and *n*-BuBr in THF as the solvent are performed by the entirely monomeric, trisolvated state of **2** and may be ascribed to its ability to generate the previously[30] proposed, solvent-separated ion pair (SSIP) species of **2** that may serve here as a product-forming intermediate if supplied with the required abundance[31] of THF as the solvent. The addition reaction of *t*-$Bu_2C{=}O$ to **2** was 10^3-fold less strongly accelerated by the same solvent change from Et_2O to THF, irrespective of the actual (still unknown) extent of these accelerations.

(e) By a simple albeit lenghthy test with data from (preferably at least four) different temperatures down to below –70 °C, the probable candidate for a mixing problem might be recognized through its one-sided deviation from a linear correlation with the inverse (1/*T*) Kelvin temperatures: The disturbed κ_{obs} value would be positioned substantially closer to the horizontal (1/*T*) axis than expected from extrapolation by the chosen correlation line. This line should be drawn from close to the most "reliable" (least disturbed) data points at low temperatures and should aim to intersect the vertical (lnκ) axis at a reasonably guessed (or measured) value of $\Delta S_A^{\ddagger} - \Delta S_B^{\ddagger} = \Delta\Delta S^{\ddagger}$.

4. EXPERIMENTAL SECTION

General Remarks. The preparation of **2**&*t*-BuOMe was carried out as published[8] along the lines[7,20] of handling such alkenyllithiums in NMR tubes. All ^{1}H and ^{13}C chemical shifts were referenced to internal TMS and are presented with the abbreviations d = doublet, m = multiplet, q = quartet, qi = quintet, quat = quaternary, s = singlet, sext = sextet, sept = septet, t = triplet. Most of the competition experiments were performed through slow introduction (< 1 drop per s) of solutions of **2**&*t*-BuOMe in THF, Et_2O, *t*-BuOMe, or toluene under argon gas cover into a *vigorously* stirred solution of an excess of the binary electrophile mixture in the same solvent. These runs were terminated with methanol after 5–120 min at the reaction temperature before workup. A reversed mode of addition seemed appropriate for runs in cyclopentane (and sometimes in *t*-BuOMe) because of the lower solubility of **2**&*t*-BuOMe: Crystalline **2**&*t*-BuOMe was prepared and washed[8] in an NMR tube, separated from the pentane wash, then cooled to the reaction temperature, and covered in one shot with the (eventually cooled) binary mixture of the competitors. Forthwith, the tightly closed NMR tube was gently shaken (no stirring) at the reaction temperature for a slow introduction of **2** in rather small concentrations till undissolved **2**&*t*-BuOMe had completely disappeared (usually within a few minutes). These runs[32] were quenched with methanol or solid CO_2 (the latter as a control of the total consumption of **2** that would generate the acid **4e**).

2´-(2,6-Dimethylphenyl)hex-1´-ene (3). Purified[8] **2**&*t*-BuOMe, obtained from bromoalkene[8] **1** (200 mg, 0.95 mmol), was dissolved in anhydrous THF (2.0 mL) under argon gas cover and cooled to –78 °C. After the dropwise addition of 1-bromobutane (0.112 mL, 1.04 mmol) and warm-up to rt for 30 min, the mixture was diluted with Et_2O (10 mL) and distilled water (30 mL). The aqueous layer was shaken with Et_2O (3 × 10 mL) and then discarded. The combined four Et_2O phases were washed with distilled water (10 mL), dried over $CaCl_2$, filtered, and concentrated to afford a liquid (113 mg, ca. 0.60 mmol) that contained mainly **3** and was distilled at 120–130 °C (bath temp.)/14 Torr.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, ^{3}J = 7.4 Hz, 3H), 1.36 (sext, ^{3}J = 7.3 Hz, 2H), 1.49 (tt, compatible with ^{3}J = 8.1 and 7.3 Hz, 2H), 2.19 (tm, ^{3}J = 8.1 Hz, ^{4}J = 1.3 Hz, 2H), 2.23 (s, 6H), 4.80 (dt, ^{2}J = 1.9 Hz, ^{4}J = 1.1 Hz, 1H), 5.25 (dt, $^{2}J = {}^{4}J$ = 1.9 Hz), 7.02 and 7.05 (A_2B system, ^{3}J = 7.2 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 14.1 (q), 19.9 (q), 22.8 (t), 29.6 (t), 36.7 (t), 112.7 (t), 126.3 (d), 127.3 (d), 134.9 (quat), 143.4 (quat), 149.0 (quat) ppm, assigned as above; IR (film) ν 3070

(w), 3017 (w), 2958, 2929, 2873, 1718 (w), 1637 (w), 1467, 899, 768 (s) cm^{-1}. Anal. calcd for $C_{14}H_{20}$ (188.31): C, 89.30; H, 10.70. Found: C, 89.53; H, 10.75.

2′-(2,6-Dimethylphenyl)-3′-cyclopropyl-1′-propene (4a). (Bromomethyl)cyclopropane (0.11 mL, 1.14 mmol) was injected into a solution of purified **2**&*t*-BuOMe (prepared from 0.76 mmol of the bromoalkene[8] **1**) in anhydrous THF (1.2 mL) under argon gas cover at ambient temperature. After the slightly exothermic reaction, the mixture was set aside and then diluted with Et_2O (5 mL) and distilled water (5 mL). The aqueous layer was shaken with Et_2O (2 × 5 mL) and then discarded. The combined Et_2O phases were washed with distilled water until neutral, dried over $MgSO_4$, filtered, and concentrated at rt in vacuo, yielding a yellow liquid (100 mg) that contained mainly **4a** but no trace of the isomeric 2′-(2,6-dimethylphenyl)-1′,5′-hexadiene. The crude products from several runs were combined and purified through column chromatography (2 ×) on silica gel (2.5 g and 1.7 g) with low-boiling petroleum ether (16 mL and 5 mL portions), affording almost pure **4a** as a colorless, rather volatile liquid with bp 78–80 °C (bath temp.)/0.016 mbar.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.075 (AA′ part of an AA′MM′X system, 2H), 0.51 (MM′ part, 2H), 0.87 (X part, 1H), 2.08 (dt, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 2H), 2.24 (s, 6H), 4.84 (dt, ^2J = 2.1 Hz, ^4J = 1.2 Hz, 1H), 5.46 (dt, ^2J = 2.1 Hz, ^4J = 1.7 Hz, 1H), 7.01 and 7.05 (A_2B system, ^3J = 7.2 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 4.8 (t), 9.0 (d), 19.8 (q), 41.9 (t), 113.3 (t), 126.3 (d), 127.2 (d), 135.0 (quat), 143.0 (quat), 148.6 (quat) ppm, assigned as above; IR (film) ν 3075, 3002, 2955, 2923, 1638, 1462, 1017, 904, 768 (s) cm^{-1}.

2′-(2,6-Dimethylphenyl)octa-1′,7′-diene (4b). The purified crystals of **2**&*t*-BuOMe, obtained from bromoalkene[8] **1** (127 mg, 0.60 mmol), were dissolved in anhydrous THF (0.6 mL) under argon gas cover. The dark-red solution became warm and colorless on the dropwise addition of 6-bromo-1-hexene (0.081 mL, 0.60 mmol) at rt. The mixture was diluted with Et_2O (5 mL) and distilled water (5 mL), and the aqueous layer was shaken with Et_2O (2 × 5 mL). The combined Et_2O phases were washed with distilled water until neutral, dried over $MgSO_4$, filtered, concentrated, and dried in vacuo over solid KOH for 3 days, yielding spectroscopically pure, liquid **4b** (24 mg, 18%) without any trace of the isomeric 3′-cyclopentyl-2′-(2,6-dimethylphenyl)-1′-propene.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 and 1.54 (2 m, 2+2H), 2.07 (qm, ^3J = 7.0 Hz, 2H), 2.19 (tm, ^3J = 7.6 Hz, 2H), 2.23 (s, 6H), 4.81 (dt, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 1H), 4.93 (ddt, ^3J = 10.2 Hz, ^2J = 2.1 Hz, ^4J = 1.2 Hz, 1H), 4.99 (ddt, ^3J = 17.1 Hz, ^2J = 2.1 Hz, ^4J = 1.5 Hz, 1H), 5.25 (q, ^4J = ^2J = 1.8 Hz, 1H), 5.81 (ddt, ^3J = 17.1 Hz, ^3J = 10.2 Hz, ^3J = 6.7 Hz, 1H), 7.01 and 7.05 (A_2B system, ^3J = 7.2 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.9 (q), 26.8 (t), 28.9 (t), 33.7 (t), 36.7 (t), 112.8 (t), 114.4 (t), 126.3 (d), 127.3 (d), 134.9 (quat), 138.9 (d), 143.3 (quat), 148.8 (quat) ppm, assigned as above.

2′-(2,6-Dimethylphenyl)-3′-phenyl-1′-propene (4c). Purified **2**&*t*-BuOMe, prepared from bromoalkene[8] **1** (150 mg, 0.71 mmol), was dissolved in anhydrous THF (0.3 mL) under argon gas cover and cooled to –78°C. The deep-red solution was treated with benzyl chloride (0.082 mL, 0.71 mmol), warmed up and shown by ^{1}H NMR to contain the olefin **4d** and remnant benzyl chloride but no **2** within the first 10 min at rt. Aqueous workup (2 × Et_2O) afforded a mixture (114 mg) of **4c** (25%), a trace of benzyl chloride, olefin **4d** (40%), and 1-chloro-1,2-diphenylethane (**7**, 35%), the latter two in nearly the expected equivalent amounts. **4d** and all other volatiles were removed in a desiccator over solid KOH under 15 Torr, furnishing the final mixture (75 mg) of **4c** and **7** (49:51).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.18 (s, 6H), 3.46 (s, 2H), 4.84 (dt, ^2J = 1.8 Hz, ^4J = 1.2 Hz, 1H), 4.99 (dt, ^4J = ^2J = 1.8 Hz, 1H), 7.01 and 7.06 (A_2B system, ^3J = 7.5 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 19.7 (q), 43.6 (t), 114.8 (t), 126.6 (d), 127.3 (d), 135.1 (quat), 142.3 (quat), 148.7 (quat) ppm, assigned as above.

^{1}H NMR of **7** ($CDCl_3$, 400 MHz) δ 3.33 (dd, ^2J = 14 Hz, ^3J = 6.9 Hz, 1H), 3.37 (dd, ^2J = 14 Hz, ^3J = 7.8 Hz, 1H), 5.03 (dd, ^3J = 7.8 and 6.9 Hz, 1H) ppm, assigned in the Supporting Information;

^{13}C NMR of **7** ($CDCl_3$, 100.6 MHz) δ 46.5 (t), 64.1 (d), 126.8 (d), 127.1 (d), 128.25 (d), 128.29 (d), 128.5 (d), 129.4 (d), 137.4 (quat), 141.1 (quat) ppm, assigned as above.

2,6-Dimethyl-α-(trimethylsilyl)styrene (5). Chlorotrimethylsilane (0.211 mL, 1.66 mmol) was added dropwise to a saturated solution of purified **2**&*t*-BuOMe (obtained from 1.66 mmol of bromoalkene[8] **1**) in warm, anhydrous *t*-BuOMe (4.7 mL) under argon gas cover. After dilution with Et_2O (10 mL) and distilled water (30 mL), the aqueous layer was shaken with Et_2O (3 × 10

mL) and then discarded. The combined Et_2O phases were washed with distilled water (10 mL), dried over $MgSO_4$, filtered, and evaporated. The residue (127 mg, 37%) was distilled at 96–114 °C (bath temp.)/13 Torr, affording pure **5** as a colorless oil (39 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.09 (s, 9H), 2.14 (s, 6H), 5.62 (d, ^2J = 3.3 Hz, 1H), 5.81 (d, ^2J = 3.3 Hz, 1H), 7.00 (quasi-s, 3H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ –0.5 (q), 20.9 (q), 125.3 (d), 127.1 (d), 128.2 (t), 134.9 (quat), 144.2 (quat), 154.1 (quat) ppm, assigned as above; IR (film) ν 3038, 2955, 1708 (w), 1462, 1249 (sharp), 934, 854, 840, 766 cm^{-1}. Anal. calcd for $C_{13}H_{20}Si$ (204.39): C, 76.40; H, 9.86. Found: C, 76.41; H, 9.68.

3′-*Tert*-butyl-4′,4′-dimethyl-2′-(2,6-dimethylphenyl)pent-1′-en-3′-ol (9a). The bromoalkene[8] **1** (114 mg, 0.54 mmol) was dissolved in anhydrous *t*-BuOMe (0.4 mL), then cooled at –30 °C under argon gas cover, treated with *n*-BuLi (0.59 mmol) in hexane (0.25 mL), and warmed up during the precipitation of **2**&*t*-BuOMe. After 2 min at rt, di-*tert*-butyl ketone (**8a**, 0.14 mL, 0.81 mmol) was added, and the vessel was gently agitated so that the precipitate dissolved completely (within ca. 13 min at rt) before the emerging lithium alkoxide **10** of the product **9a** began to precipitate. This mixture was cooled to –78 °C, whereupon the supernatant was withdrawn and discarded. The remaining **10** was washed with dry pentane for removal of all contaminants, then dissolved in aqueous HCl (2 M) and Et_2O. This wahed and dried Et_2O solution was evaporated in vacuo until all volatiles had disappeared, leaving the colorless alcohol **9a** (63 mg, 42%). Analytically pure **9a** had mp 73–74 °C (from methanol).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (broadened s, 18H), 1.75 (s, 1H, exchangeable with D_2O), 2.48 (s, 6H), 5.37 (d, ^2J = 0.91 Hz, 1H), 5.71 (d, ^2J = 0.91 Hz, 1H), 7.00 and 7.03 (A_2B system, ^3J = ca. 6.8 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 23.8 (q), 30.6 (q), 42.8 (quat), 86.2 (quat), 122.7 (t), 126.7 (d), 128.9 (d), 138.4 (quat), 143.0 (quat), 149.9 (quat) ppm, assigned as above; IR (KBr) ν 3585 (very sharp, O–H), 3019, 2987, 2960, 2926, 1619 (w), 1393, 1067, 997, 931, 775 cm^{-1}. Anal. calcd for $C_{19}H_{30}O$ (274.45): C, 83.15; H, 11.02. Found: C, 82.98; H, 11.03.

Cleavage of di-*tert*-Butyl Ketone (8a) from the Alkoxides 10 and **11**

a) Slow Cleavage of the unsoluble Lithium Alkoxide 10. *a1) Trapping of **2** with dicyclopropyl ketone (**8d**):* A dry NMR tube (5 mm) was charged with the alcohol **9a** in THF, cooled at –78 °C, and treated with CH_3Li (1.5 equiv), which caused vivid bubbling (CH_4) and

precipitation of a few crystals. Dicyclopropyl ketone (**8d**, 2 equiv) was added at rt but did not yet change the precipitate. Aqueous workup after ca. 15 hours at rt afforded residual alcohol **9a** together with the adduct **9d** of **8d** in a 44:56 ratio.

*a2) Trapping of **2** through proton transfer from **9a**:* The crystalline alcohol **9a** (75 mg, 0.27 mmol) was placed in a dry NMR tube (5 mm) and dissolved in anhydrous THF (0.65 mL), then cooled to –60 °C and treated with *n*-BuLi (0.14 mmol) in hexane (0.057 mL). The immediately precipitating Li alkoxide **10** needed ten days at rt for complete redissolution, affording unconsumed Li alkoxide **10** and the olefin **4d** in a 5:95 ratio.

b) **Rapid Cleavage of the soluble Potassium Alkoxide 11.** *Trapping of **2** through proton transfer from **9a**:* A solution of the alcohol **9a** (80 mg, 0.29 mmol) in anhydrous THF (0.4 mL) was treated with solid KH (0.11 mmol in 17 mg of a suspension in mineral oil). The vividly bubbling (H_2 eliminating) mixture deposited no precipitate and was analyzed after 150 min at rt through ^{1}H NMR, showing that the potassium alkoxide had been completely converted into the olefin **4d**.

General Procedure (GP) for the Addition of 2 to Ketones and Aldehydes. α-Bromo-2,6-dimethylstyrene[8] (**1**) was dissolved in anhydrous *t*-BuOMe (1.3–2.1 mL per mmol of **1**) and cooled with stirring under argon gas cover at or below –30 °C, then treated with *n*-BuLi (1.1 equiv) in hexane and warmed up after 15 min. After ca. 30 min at rt, the mixture was recooled at or below –30 °C, treated with the ketone or aldehyde (0.77–1.2 equiv), then kept at rt, and diluted with Et_2O and distilled water. The aqueous layer was shaken with Et_2O (3×) and then discarded. The combined Et_2O extracts were washed with distilled water until neutral, dried, filtered, and concentrated under conditions that removed all volatile contaminants.

9′-[α-(2,6-Dimethylphenyl)vinyl]fluoren-9′-ol (9b). The GP protocol was applied to bromoalkene[8] **1** (150 mg, 0.71 mmol) in *t*-BuOMe (1.0 mL), *n*-BuLi (0.78 mmol), and fluorenone (**8b**, 0.154 mg, 0.85 mmol), forming a black suspension. After work-up, the crude material (242 mg) was filtered through silica gel (5 g) with low-boiling petroleum ether/Et_2O (9:1) and then separated from unconsumed fluorenone through crystallization from cyclohexane: Yield of **9b**, 98 mg (44%), mp 113–114 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.11 (s, 6H), 2.17 (s, 1H, exchangeable with D_2O), 4.92 (d, ^2J = 1.2 Hz, 1H), 5.38 (d, ^2J = 1.2 Hz, 1H), 7.05 and 7.12 (A_2B system, ^3J = 7.5 Hz, 2+1H), 7.20

(td, ^3J = 7.5 Hz, 2H), 7.30 (d, ^3J = 7.5 Hz, 2H), 7.34 (t, ^3J = 7.4 Hz, 2H), 7.61 (d, ^3J = 7.4 Hz, 2H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.3 (q, ^1J = 127 Hz), 85.7 (quat), 118.6 (sharp t, ^1J = 158.1 Hz), 120.0 (dd, ^1J = 159 Hz, ^3J = 7.8 Hz), 125.3 (dd, ^1J = 160.5 Hz, ^3J = 7.9 Hz), 127.0 (sharp d, ^1J = 159.0 Hz), 127.4 (ddq, ^1J = 157 Hz, ^3J = 7 Hz, ^3J = 6 Hz), 127.5 (dd, ^1J = 161 Hz, ^3J = 7 Hz), 129.0 (dd, ^1J = 159.9 Hz, ^3J = 7.1 Hz), 137.6 (pseudo-qi, $^2J \approx {}^3J$ = 6.5 Hz), 139.2 (unresolved), 139.6 (td, ^3J = 7.0 Hz, ^3J = ca. 3 Hz), 148.7 (unresolved), 148.8 (t, ^3J = 7.2 Hz) ppm, assigned as above; IR (KBr) ν 3543 (sharp O–H), 3061, 2928, 1629 (broad), 1450, 1037, 929, 773, 757, 740 cm^{-1}. Anal. calcd for $C_{23}H_{20}O$ (312.41): C, 88.43; H, 6.45. Found: C, 88.63; H, 6.41.

3´-Isopropyl-4´-methyl-2´-(2,6-dimethylphenyl)pent-1´-en-3´-ol (9c). Purified **2**&*t*-BuOMe, prepared from bromoalkene[8] **1** (330 mg, 1.53 mmol), was dissolved in anhydrous *t*-BuOMe (3.0 mL) under argon gas cover, then cooled to –78 °C and treated with diisopropyl ketone (**8c**, 0.268 mL, 1.88 mmol). The mixture was kept at rt for 30 min and then diluted with Et_2O (15 mL) and distilled water (50 mL). The aqueous layer was shaken with Et_2O (3 × 15 mL) and discarded. The combined Et_2O phases were washed with distilled water (15 mL), dried over $CaCl_2$, filtered, and concentrated. The residue (322 mg, **9c** with some olefin **4d**) was distilled at 92–100 °C (bath temp.)/0.015 mbar to give the pure oil **9c** (128 mg, 33%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05 (d, ^3J = 7.0 Hz, 6H), 1.09 (d, ^3J = 7.0 Hz, 6H), 1.24 (s, 1H), 2.13 (sept, ^2J = 7.0 Hz, 2H), 2.31 (s, 6H), 5.09 (d, ^2J = 1.2 Hz, 1H), 5.35 (d, ^2J = 1.2 Hz, 1H), 7.03 and 7.08 (A_2B system, ^3J = 7 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.9 and 18.6 (2 q), 21.6 (q), 32.9 (d), 81.8 (quat), 116.6 (t), 126.8 (d), 127.9 (d), 138.2 (quat), 139.5 (quat), 150.4 (quat) ppm, assigned as above; IR (film) ν 3582 (sharp O–H), 2972, 2930, 2879, 1626 (w), 1469, 1458, 1387, 1158, 997, 912, 770 cm^{-1}. Anal. calcd for $C_{17}H_{26}O$ (246.39): C, 82.87; H, 10.64. Found: C, 82.47; H, 10.54.

1´,1´-Dicyclopropyl-2´-(2,6-dimethylphenyl)prop-2´-en-1´-ol (9d). The GP protocol was applied to bromoalkene[8] **1** (450 mg, 2.13 mmol) in pentane (7.0 mL)/Et_2O (0.22 mL), *n*-BuLi (2.35 mmol), and dicyclopropyl ketone (**8d**, 0.20 mL, 1.79 mmol). The crude product (555 mg, almost only **9d**) was distilled and the almost pure liquid **9d** (269 mg, 62 %) redistilled at 104–120 °C (bath temp.)/0.01 mbar (225 mg).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.31, 0.43, and 0.53 (3 × m, 2+4+2H), 1.00 (s, 1H, exchangeable with D_2O), 1.06 (m, 2H), 2.33 (s, 6H), 4.98 (d, ^2J = 1.56 Hz, 1H), 5.79 (d, ^2J = 1.56

Hz, 1H), 7.03 and 7.07 (A_2B system, ^3J = 7.2 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 0.4 (tm, ^1J = 162 Hz), 2.0 (tm, ^1J = 162 Hz), 19.8 (dm, ^1J = 158 Hz), 21.4 (qm, ^1J = 127 Hz), 73.7 (unresolved), 114.8 (sharp t, ^1J = 157 Hz), 126.7 (sharp d, ^1J = 159 Hz), 127.3 (ddq, ^1J = 158 Hz, 2 × ^3J = 6 Hz), 137.1 (sharp qi, $^2J \approx {}^3J$ = 6 Hz), 139.9 (unresolved), 155.2 (unresolved) ppm, assigned as above; IR (film) ν 3572 (narrow, O–H), 3483 (broadened O–H), 3087, 3011 (s), 2925, 2865, 1628 (w), 1459, 1377, 1188, 1025, 993, 915, 770 cm^{-1}. Anal. calcd for $C_{17}H_{22}O$ (242.36): C, 84.25; H, 9.15. Found: C, 84.61; H, 9.33.

3′-Ethyl-2′-(2,6-dimethylphenyl)pent-1′-en-3′-ol (9e). The GP protocol was followed using bromoalkene[8] **1** (200 mg, 0.95 mmol) in *t*-BuOMe (1.7 mL), *n*-BuLi (1.04 mmol), and dry pentan-3-one (**8e**, 0.120 mL, 1.14 mmol). The crude product (221 mg, almost only **9e**) was distilled at 150–160 °C (bath temp.)/15 Torr, yielding 123 mg (59%) of nearly pure **9e**. The analytical sample was obtained through column chromatography on silica gel.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.98 (t, ^3J = 7.5 Hz, 6H), 1.27 (s, 1H, exchangeable with D_2O), 1.67 and 1.72 (2 × dq, ^2J = 14.4 Hz, ^3J = 7.5 Hz, 2+2H), 2.28 (s, 6H), 5.00 (d, ^2J = 1.2 Hz, 1H), 5.31 (d, ^2J = 1.2 Hz, 1H), 7.03 and 7.07 (A_2B system, ^3J = 7.3 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 8.3 (q), 21.3 (q), 30.9 (t), 78.4 (quat), 115.0 (t), 126.8 (d), 127.6 (d), 137.4 (quat), 139.4 (quat), 151.8 (quat) ppm, assigned as above; IR (film) ν 3530 (sharp O–H), 2970, 2937, 2881, 1459, 1378, 1141, 970, 909, 771 cm^{-1}. Anal. calcd for $C_{15}H_{22}O$ (218.34): C, 82.52; H, 10.16. Found: C, 82.86; H, 10.28.

3′-Methyl-2′-(2,6-dimethylphenyl)but-1′-en-3′-ol (9f). The directions given in the GP protocol were followed using bromoalkene[8] **1** (269 mg, 1.27 mmol) in *t*-BuOMe (1.7 mL), *n*-BuLi (1.40 mmol), and dry acetone (**8f**, 0.105 mL, 1.43 mmol). The crude product (239 mg) contained **9f** and the olefin **4d** (ca. 9:1). The liquid analytical sample was obtained through distillation at 130–140 °C (bath temp.)/13 Torr.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 6H), 1.54 (broad s, 1H), 2.29 (s, 6H), 4.94 (d, ^2J = 1.07 Hz, 1H), 5.54 (d, ^2J = 1.07 Hz, 1H), 7.05 and 7.08 (A_2B system, ^3J = 7.2 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.3 (q), 30.94 (q), 73.9 (quat), 114.1 (t), 126.8 (d), 127.4 (d), 136.5 (quat), 139.9 (quat), 155.5 (quat) ppm, assigned as above; IR (film) ν 3533 (sharp

albeit weak O–H), 3438 (broadened O–H), 2979, 2930, 1633 (w), 1462, 1376, 1363, 1165, 956, 912, 770 cm^{-1}. Anal. calcd for $C_{13}H_{18}O$ (190.28): C, 82.06; H, 9.53. Found: C, 82.34; H, 9.43.

4′,4′-Dimethyl-2′-(2,6-dimethylphenyl)-3′-phenylpent-1′-en-3′-ol (9g). As sugested in the GP protocol, the bromoalkene[8] **1** (200 mg, 0.95 mmol) in *t*-BuOMe (2.0 mL), *n*-BuLi (1.04 mmol), and pivalophenone (**8g**, 0.122 mL, 0.73 mmol) furnished a mixture (252 mg) that contained **9g** together with ca. 14% of ketone **8g**. Column chromatography on silica gel (2 × 5 g) with low-boiling petroleum ether/Et_2O (20:1) yielded **9g** as an almost pure, colorless oil (92 mg, 43%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.17 (s, 9H), 1.37 (s, 3H), 1.73 (s, 1H), 2.40 (s, 3H), 5.19 (d, ^2J = 0.7 Hz, 1H), 6.06 (d, ^2J = 0.7 Hz, 1H), 6.80 (X-part of an ABX system, 1H), 6.99 and 7.00 (AB part, 1+1H), 7.21 (tm, 1H), 7.26 (tm, 2H), 7.57 (dm, ^3J = 7.5 Hz, 2H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.2 (sharp qd, ^1J = 127 Hz, ^3J = 4.9 Hz), 22.2 (broademed qm, ^1J = 127 Hz, ^3J = 4.5 Hz), 28.1 (qsept, ^1J = 126 Hz, ^3J = 4.8 Hz), 40.8 (m), 82.9 (m), 116.3 (t, ^1J = 157 Hz), 126.50 (dt, ^1J = 160 Hz, ^3J = 7.5 Hz), 126.58 (broadened dm, ^1J = 160 Hz), 127.2 (sharp d, ^1J = 160 Hz), 127.7 (ddq, ^1J = 159 Hz), 128.3 (ddq, ^1J = 158 Hz), 128.6 (broad d, ^1J = 159 Hz), 137.1 (pseudo-qi, $^2J \approx {}^3J$ = 6 Hz), 139.1 (broadened qi, $^2J \approx {}^3J$ = ca. 6 Hz), 139.8 (unresolved), 142.7 (t, ^3J = Hz), 152.9 (quat) ppm, assigned as above; IR (film) ν 3560 (sharp O–H), 2993, 2963, 2928, 1625 (w), 1490, 1462, 1446, 1057, 1005, 912, 771, 752, 708 cm^{-1}.

In situ spectra of runs in THF showed the Li and K alkoxides of **9g** with upfield ^{1}H NMR shifts relative to **9**. as assigned in the Supporting Information.

4′,4′-Dimethyl-2′-(2,6-dimethylphenyl)pent-1′-en-3′-ol (9h). Along the lines of the GP protocol, the bromoalkene[8] **1** (254 mg, 1.20 mmol) in *t*-BuOMe (1.6 mL), *n*-BuLi (1.32 mmol), and finally pivalaldehyde (**8h**, 0.131 mL, 1.20 mmol) provided a crude yield (210 mg, 80%) of almost pure **9h**. The analytical sample was obtained through distillation at 140–160 °C (bath temp.)/13 Torr.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (s, 9H), 1.69 (broadened s, 1H), 2.33 and 2.37 (2 s, 3+3H), 4.04 (broadened s, 1H), 5.19 (sharp d, ^2J = 1.61 Hz, $|{}^4J| < 0.5$ Hz, 1H), 5.74 (dd, ^2J = 1.61 Hz, ^4J = 1.20 Hz, 1H), 7.03 and 7.06 (A_2B system, ^3J = 7 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.6 and 21.2 (2 q), 26.1 (q), 35.9 (quat), 81.4 (d), 117.8 (t), 126.6 (d), 127.96 and 128.30 (2 d), 134.9 and 135.5 (2 × quat), 141.9 (quat), 150.7 (quat) ppm, assigned as above; IR (film) ν 3496 (O–H), 2954, 2872, 1628 (w), 1463, 1365, 1047, 1006, 920, 770 cm^{-1}. Anal. calcd for $C_{15}H_{22}O$ (218.34): C, 82.52; H, 10.16. Found: C, 82.72; H, 9.83.

3′-Cyclopropyl-2′-(2,6-dimethylphenyl)prop-1′-en-3′-ol (9i). The GP protocol was applied to bromoalkene[8] **1** (213 mg, 1.01 mmol) in *t*-BuOMe (1.6 mL), *n*-BuLi (1.11 mmol), and finally cyclopropanecarbaldehyde (**8i**, 0.083 mL, 1.11 mmol). The crude material was practically clean **9i** (182 mg, 89%). The colorless, liquid analytical sample was obtained through distillation at 155–180 °C (bath temp.)/13 Torr.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.02, 0.31, 0.45, 0.52, and 1.04 (5 m, 5×1H), 1.74 (broad s, 1H), 2.25 and 2.31 (2 s, 3+3H), 3.48 (broadened d, ^3J = 8.6 Hz, 1H), 5.00 (dd, ^2J = 1.63 Hz, ^4J = 1.07 Hz, 1H), 5.73 (t, $^4J \approx {}^2J$ = 1.63 Hz, 1H), 7.03 and 7.08 (A_2B system, ^3J = 7.5 Hz, 2+1H) ppm, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 3.04 and 3.33 (2 t), 17.2 (d), 20.20 and 20.45 (2 q), 78.7 (d), 113.4 (t), 126.8 (d), 127.31 and 127.44 (2 d), 135.82 and 136.01 (2 × quat), 140.1 (quat), 150.6 (quat) ppm, assigned as above; IR (film) ν 3401 (O–H), 3080, 3007, 2923, 2862, 1639 (w), 1461, 1033 (s), 915, 770 cm^{-1}. Anal. calcd for $C_{14}H_{18}O$ (202.36): C, 83.12; H, 8.97. Found: C, 83.42; H, 9.02.

The Li alkoxide of **9i** precipitated rather slowly from *t*-BuOMe, so that some of its ^{1}H NMR data could be measured in situ: δ 2.20 and 2.32 (2 s), ca. 3.60 (obscured d), 4.92 and 5.98 (2 broadened s, 1+1H), 7.02 (quasi-s, 3H) ppm.

3′,4′,4′-Trimethyl-2′-(2,6-dimethylphenyl)pent-1′-en-3′-ol (9j). Purified[8] **2**&*t*-BuOMe was dissolved in Et_2O or in THF under argon gas cover and treated at –70 °C with pinacolone (**8j**, 1.5 equiv), then analyzed for alkene **4d**, adduct **9j**, enone **15**, and lithium alkoxide **16** by ^{1}H and ^{13}C spectroscopy at rt both in situ and after workup.

^{1}H NMR of adduct **9j** ($CDCl_3$, 400 MHz) δ 1.02 (s, 9H), 1.51 (s, 3H), 1.60 (s, 1H), 2.35 (s, 3H), 2.39 (s, 3H), 5.09 (d, ^2J = 1.2 Hz, 1H), 5.40 (d, ^2J = 1.2 Hz, 1H), 7.04 and 7.08 (A_2B system, ^3J = 7 Hz, 2+1H) ppm, assigned in the Supporting Information; ^{1}H NMR of adduct **9j** (Et_2O, 400 MHz) δ 1.02 (s, 9H), 1.45 (s, 3H), 2.32 (sharp s, 3H), 2.35 (sharp s, 3H), 5.00 (d, ^2J = 1.3

Hz, 1H), 5.40 (d, ^2J = 1.2 Hz, 1H), 6.94 (narrow m, 3H) ppm, assigned in the Supporting Information;

^{13}C NMR of adduct **9j** ($CDCl_3$, 100.6 MHz) δ 21.8 (qd, ^1J = 126.5 Hz, ^3J = 4.5 Hz), 22.6 (qd, ^1J = 126.5 Hz, ^3J = 4.5 Hz), 25.3 (q, ^1J = 126.6 Hz), 26.4 (qm, ^1J = 125.1 Hz, ^3J = 4.8 Hz), 39.0 (m, apparent J = 3.5 Hz, containing q ^3J = 2.5 Hz), 80.4 (m, apparent J = 3.5 Hz), 118.6 (sharp t, ^1J = 156.6 Hz), 126.7 (sharp d, ^1J = 159.0 Hz), 127.6 (ddq, ^1J = 157 Hz, ^3J = 7.5 and 5 Hz), 128.2 (ddq, ^1J = 157 Hz, ^3J = 7.5 and 5 Hz), 136.2 (dq, ^3J = 7 Hz, ^2J = 6 Hz), 139.0 (dq, ^3J = 7 Hz, ^2J = 6 Hz), 140.5 (unresolved), 153.0 (unresolved) ppm, assigned as above;

^{13}C NMR of adduct **9j** (THF, 100.6 MHz) δ 39.5 (quat), 80.4 (quat), 118.2 (t), 126.8 (d), 128.0 (d), 128.4 (d), 136.5 (quat), 139.1 (quat), 142.4 (quat), 155.3 (quat) ppm;

^{1}H NMR of lithium alkoxide **16** (Et_2O, 400 MHz) δ 1.00 (s, 9H), 1.40 (s, 3H), 2.33 (broadened s, 3H), 2.35 (sharp s, 3H), 4.94 (s, 1H), 5.32 (broadened s, 1H), ca. 6.90 (narrow m, 3H) ppm, assigned in the Supporting Information; ^{1}H NMR of lithium alkoxide **16** (THF, 400 MHz) δ 4.97 (s, 1H), 5.40 (s, 1H) ppm, assigned as above;

^{13}C NMR of lithium alkoxide **16** (Et_2O, 100.6 MHz) δ 22.1 (slender q), 23.1 (broad q), 39.6 (quat), 80.6 (quat), 117.5 (broad t), 126.8 (d), 128.0 and 128.8 (2 d), 136.2 and 138.7 (2 × quat), 143.0 (very broad), 156.4 (very broad) ppm; ^{13}C NMR of lithium alkoxide **16** (THF, 100.6 MHz) δ 39.5 (quat), 80.4 (quat), 118.1 (broadened t), 126.8 (d), 128.0 and 128.4 (2 d) ppm.

2,2,5,6,6-Pentamethylhept-4-en-3-one (15). This known[33,34] enone was obtained as the condensation product of the lithium enolate **14** that certifies the proton-transfer from pinacolone (**8j**). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.12 (s, 9H), 1.15 (s, 9H), 2.06 (d, ^4J = 1.18 Hz, 3H), 6.38 (q, ^4J = 1.18 Hz, 1H) ppm; ^{1}H NMR (Et_2O or THF, 400 MHz) δ 6.36 or 6.37 (unresolved q) ppm, respectively, assigned in the Supporting Information;

^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 15.7 (qd, ^1J = 125.5 Hz, ^3J = 8.1 Hz), 26.8 (qm, ^1J = 125.8 Hz, ^3J = 4.7 Hz), 28.7 (qm, ^1J = 125.8 Hz, ^3J = 4.7 Hz), 38.0 (m), 44.1 (m, apparent J = 3.8 Hz), 116.5 (dq, ^1J = 151.8 Hz, ^3J = 4.5 Hz), 164.9 (m), 207.6 (m), ppm, assigned as above.

ASSOCIATED CONTENT

Reactivity of α-(2,6-diisopropylphenyl)vinyllithium; rate measurements (Figures S1–S3, Tables S1–S12); assignments and Figures of the ^{1}H and ^{13}C NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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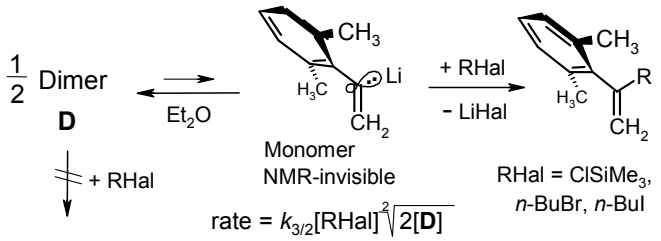
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n-BuBr, n-BuI
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