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Carbenoid Chain Reactions: Substitutions by Organolithium Compounds at Unactivated 1-Chloro-1-alkenes†

Rudolf Knorr,* Claudio Pires, Claudia Behringer, Thomas Menke, Johannes Freudenreich, Eva C. Rossmann, and Petra Böhrer

Contribution from the Department of Chemistry and Biochemistry, Ludwig-Maximilians-Universität, Butenandtstr. 5-13, 81377 München, Germany

Received July 11, 2006; E-mail: rhk@cup.uni-muenchen.de

Abstract: The deceptively simple "cross-coupling" reactions $Alk_2C{=}CA{-}Cl + RLi \rightarrow Alk_2C{=}CA{-}R + LiCl$ (A = H, D, or Cl) occur via an alkylidenecarbenoid chain mechanism in three steps without a transition metal catalyst. In the initiating step 1, the sterically shielded 2-(chloromethylidene)-1,1,3,3-tetramethylindans **2a**−**c** ($Alk_2C{=}CA{-}Cl$) generate a Cl,Li-alkylidenecarbenoid ($Alk_2C{=}CLi{-}Cl$, **6**) through the transfer of atom A to RLi (methyllithium, *n*-butyllithium, or aryllithium). The chain cycle consists of the following two steps: (i) A fast vinylic substitution reaction of these RLi at carbenoid **6** (step 2) with formation of the chain carrier $Alk_2C{=}CLi{-}R$ (**8**), and (ii) a rate-limiting transfer of atom A (step 3) from reagent **2** to the chain carrier **8** with formation of the product $Alk_2C{=}CA{-}R$ (**4**) and with regeneration of carbenoid **6**. This chain propagation step 3 was sufficiently slow to allow steady-state concentrations of $Alk_2C{=}CLi{-}Aryl$ to be observed (by NMR) with RLi = C_6H_5Li (in Et_2O) and with 4-$(Me_3Si)C_6H_4Li$ (in *t*-BuOMe), whereas these chain processes were much faster in THF solution. $PhC{\equiv}CLi$ cannot perform step 1, but its carbenoid chain processes with reagents **2a** and **2c** may be started with MeLi, whereafter $LiC{\equiv}CPh$ reacts faster than MeLi in the product-determining step 2 to generate the chain carrier $Alk_2C{=}CLi{-}C{\equiv}CPh$ (**8g**), which completes its chain cycle through the slower step 3. The sterically congested products were formed with surprising ease even with RLi as bulky as 2,6-dimethylphenyllithium and 2,4,6-tri-*tert*-butylphenyllithium.

Introduction

The 2-(chloromethylidene)-1,1,3,3-tetramethylindans (**2**) are sterically shielded examples of unactivated, terminal 1-chloro-1-alkenes. Because they do not carry electron-withdrawing substituents at the C^2 side of the C^2C^α double bond, they should be very reluctant[1,2] to incorporate nucleophiles at C^α with formation of the intermediate **1** of the addition-rotation-elimination mechanism (ARE)[3] of nucleophilic vinylic substitution, because C^2 of **1** would then have to accommodate negative charge between *tert*-alkyl groups, with poor chances of stabilization by solvation in this sterically congested environment. Yet surprisingly, we obtained the substitution products **4d**−**p** with gratifying ease when reacting **2a**−**c** in suitable ethereal solvents with organolithium reagents (RLi), whereas unsatisfactory results were found with some of the approved methods of such cross-coupling using transition metal catalysts, as specified in section 4. A vinylic S_N1 mechanism via an unstabilized carbenium intermediate **3** to give **4** appears improbable for the reagents **2**. Because some RLi compounds are potent reductants, an electron-transfer process (ET) might precede the radical cage recombination **5** → **7** → **4** or initiate the $S_{RN}1$ radical chain mechanism **5** → **7** → **9** → **4**, where intermediate **9** combines features of a stabilized carbanion (if A = chlorine or R = aryl) and a well-built radical. All four of these mechanistic possibilities predict a 1:1 stoichiometry of RLi and **2**, in keeping with most of the cases investigated below. But perusal of the literature[4a] suggested that an alkylidenecarbenoid[5,6] **6** should be generated from **2** with RLi and might then be attacked by a second molar equivalent of RLi with formation of the alkenyllithium product **8** rather than **4**. However, both the verification of the 1:2 stoichiometry to be expected in this case and the interception of **8** by carboxylation with CO_2 to give **10** were successful for a minority of the following experiments only (Scheme 1). The present work collects evidence for the reconciliation of such contradictory observations.

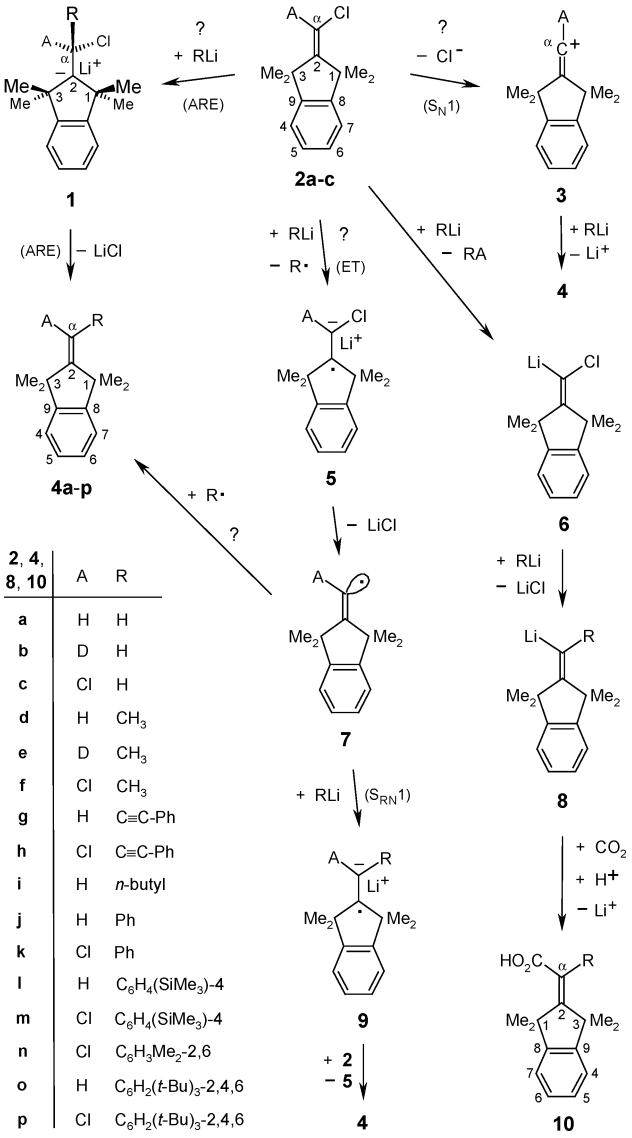
Results and Discussions

1. Syntheses of the Reagents 2. The monochloride **2a** had been observed previously[7] as an inseparable byproduct and was now prepared in two different ways from 1,1,3,3-tetramethyl-

† Sterically Congested Molecules, 18; for Part 17, see: Böhrer, G.; Knorr, R.; Böhrer, P.; Schubert, B. *Liebigs Ann./Recueil* **1997**, 193-202.

(1) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73−80.
(2) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 5961−5962.
(3) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474−479, and cited literature.
(4) (a) Knorr, R. *Chem. Rev.* **2004**, *104*, 3795−3849. (b) Knorr, R. *Chem. Rev.* **2004**, *104*, 3817−3818. (c) Knorr, R. *Chem. Rev.* **2004**, *104*, 3831. (d) Knorr, R. *Chem. Rev.* **2004**, *104*, 3832. (e) Knorr, R. *Chem. Rev.* **2004**, *104*, 3833. (f) Knorr, R. *Chem. Rev.* **2004**, *104*, 3842. (g) Knorr, R. *Chem. Rev.* **2004**, *104*, 3843. (h) Knorr, R. *Chem. Rev.* **2004**, *104*, 3841. (i) pp 3823−3825. (j) Knorr, R. *Chem. Rev.* **2004**, *104*, 3805. (k) Knorr, R. *Chem. Rev.* **2004**, *104*, 3822. (l) Knorr, R. *Chem. Rev.* **2004**, *104*, 3829.
(5) Carbenoids carry both a metal cation and a nucleofugal group at the same carbon atom: Köbrich, G. *Angew. Chem.* **1972**, *84*, 557−570, first footnote therein; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 473−485.
(6) Nomenclature: Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348−354.
(7) Compound **18b** in ref 9.

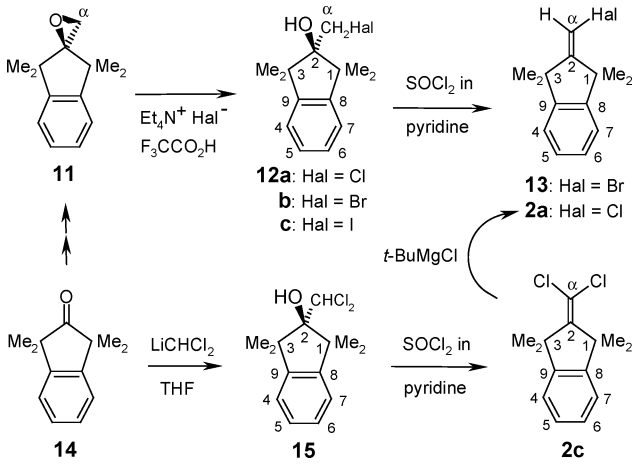
Scheme 1



2, 4, 8, 10	A	R
a	H	H
b	D	H
c	Cl	H
d	H	CH_3
e	D	CH_3
f	Cl	CH_3
g	H	C≡C-Ph
h	Cl	C≡C-Ph
i	H	*n*-butyl
j	H	Ph
k	Cl	Ph
l	H	$C_6H_4(SiMe_3)$-4
m	Cl	$C_6H_4(SiMe_3)$-4
n	Cl	$C_6H_3Me_2$-2,6
o	H	$C_6H_2(t\text{-Bu})_3$-2,4,6
p	Cl	$C_6H_2(t\text{-Bu})_3$-2,4,6

2-indanone[8] (**14**). In analogy to the preparation[9] of the known monobromide **13**, a five-step synthesis was conceived via "nucleophilic chlorination" of the oxirane[9] **11** with dry tetraethylammonium chloride and trifluoroacetic acid in boiling chloroform. The ring-opened product **12a** was dehydrated[9] to give **2a**, but a corresponding iodoalkene could not be obtained from **12c**.[10] A shorter synthesis of **2a** used *tert*-butylmagnesium chloride for the reduction of **2c** (Scheme 2), but a quantitative yield required prolonged refluxing in THF with 4 equiv of this stable Grignard reagent over a period of time that varied in an unpredictable manner. In a less suitable alternative, **2a** was the only reduction product after irradiation of **2c** in the presence of tributylstannane, but it could not be separated from accompanying tributyltin products. The deuterated oxirane [α,α-D_2]-**11** was obtained from **14** with [D_3]-methyllithium in three steps via the olefin [α,α-D_2]-**4a** as published[9] for the unlabeled substance; the subsequent ring opening to [α,α-D_2]-**12a** and dehydration to give **2b** were performed as above for **2a**.

Scheme 2

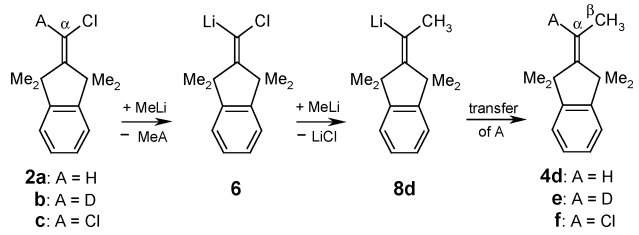


Dichloromethyllithium ($LiCHCl_2$) is a rather unstable carbenoid. For the preparation of alcohol **15**, $LiCHCl_2$ is most conveniently[11] generated by the deprotonation of methylenechloride with lithium diisopropylamide (LDA) in THF in the presence of the sterically congested ketone **14**. The exothermic reaction sequence must be controlled to keep the internal temperature below −20 °C, because the lithium alcoholate of **15** would cyclize at temperatures above −10 °C to produce an α-chlorooxirane.[12,13] Cyclization during workup was avoided by low-temperature protonation, which afforded clean **15** in high yield. The subsequent dehydration of **15** furnished the pure dichloride[14] **2c** without side-products.

2. Methyllithium (RLi = MeLi) and Lithium Phenylacetylide: The Mechanism. Small-scale[15] exploratory experiments with MeLi (0.6−0.8 M) and reagents **2a**−**c** (ca. 0.3 M) *in diethyl ether* (Et_2O) were performed in NMR tubes (5 mm) at +23 °C, revealing by ^{1}H NMR spectroscopy the approximate first half-reaction times ($t_{1/2}$) of 3 h for **2a**, 4 days for **2b**, and 2 h for **2c**.[16] The conspicuous deceleration of **2b**, obviously a primary kinetic isotope effect[17] with respect to **2a**, indicates a rate-limiting loss of A = deuterium from **2b** (Scheme 3), which implies the intermediacy of the Cl,Li-alkylidenecarbenoid **6** and excludes all other mechanisms[18] that would not allow for such an A−C$^\alpha$ bond scission (Scheme 1) or would accomplish it in a step that does not cross the activation barrier. Although most types of such unsaturated[4a] carbenoids are unstable above −60 °C, they can be intercepted[4b−f] by RLi in a fast[19] vinylic substitution reaction: In the example of Scheme 3, the alkenyl-

(8) Knorr, R.; Mehlstäubl, J.; Böhrer, P. *Chem. Ber.* **1989**, *122*, 1791−1793 and refs therein.
(9) Knorr, R.; Freudenreich, J.; von Roman, T.; Mehlstäubl, J.; Böhrer, P. *Tetrahedron* **1993**, *49*, 8837−8854.
(10) Details are given in the Supporting Information.
(11) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010−3011.
(12) Köbrich, G.; Grosser, J.; Werner, W. *Chem. Ber.* **1973**, *106*, 2610−2619.
(13) Hofmann, P.; Perez-Moya, L. A.; Kain, I. *Synthesis* **1986**, 43−44.
(14) Mloston, G.; Romanski, J.; Swiatek, A.; Heimgartner, H. *Helv. Chim. Acta* **1999**, *82*, 946−956. These authors prepared **2c** in a different way and reported its unassigned ^{13}C NMR spectrum incompletely (C$^\alpha$ missing).
(15) Most of the yields (up to 85% of **4**) were determined in small-scale runs (0.1−1 mmol) under nonoptimized conditions.
(16) All $t_{1/2}$ values in this work are meant to convey semiquantitative rate information only and to point at primary kinetic isotope effects in reactions of **2b**. They cannot be used directly to quantitate k_H/k_D ratios because $t_{1/2}$ increases with decreasing initial concentrations [RLi], which varied by factors up to three here.
(17) In a related example, the authors conjectured that a tunnel effect contributed to $k_H/k_D = 15$ as measured for the dedeuteration of (*E*)-Ph-CH=CD-Cl in Et_2O at 0 °C: Schlosser, M.; Ladenberger, V. *Chem. Ber.* **1967**, *100*, 3877−3892.
(18) For example, $k_H/k_D = 1.22$ was measured for the S_N1 solvolysis of D_3C−(*t*-Bu)C=C=CD-Br by: Schiavelli, M. D.; Ellis, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 7916−7917.
(19) Release of an alkylidenecarbene[6] $R_2C{=}C{:}$ from a carbenoid $R_2C{=}CLiCl$ is usually[4a] much slower than the substitution reaction and hence unlikely.

Scheme 3

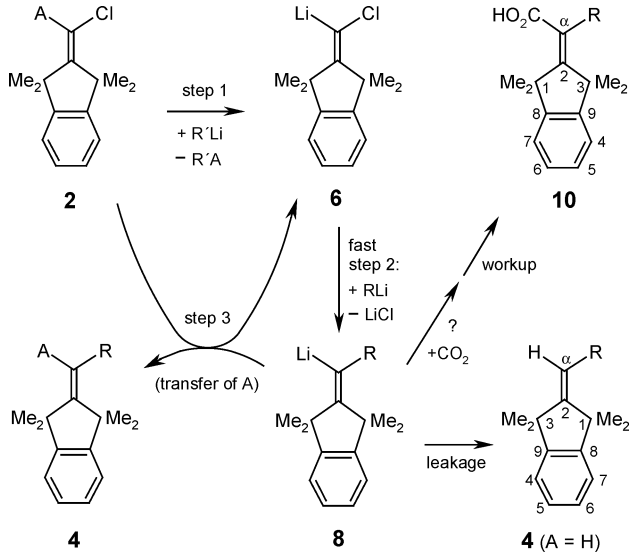


lithium compound **8d** will then arise through incorporation of a second equivalent of MeLi. However, only one equivalent of MeLi rather than two (by ^{1}H NMR integration at $\delta \approx -2$) was consumed by both reagents **2a** and **2c**, and the attempted trapping of **8d** by carboxylation (solid CO_2) afforded no trace of the expected carboxylic acid **10d** (which can be isolated if **8d** is generated[20] by an Sn/Li interchange reaction). Instead, the only products obtained were **4d** from **2a**,[21] **4d** plus **4e** (6:4) from **2b**, and **4f** from **2c**. An independent synthesis of **4d** was carried out by preparation of a crystalline specimen of **8a**[22] and its methylation with iodomethane.

In tetrahydrofuran (THF) solution, MeLi (3 equiv) reacted much more readily at +23 °C, with the roughly estimated first $t_{1/2}$ values < 2 min for **2a**, 15 min for **2b**, and < 1 min for **2c**. This evidence[16] for a primary kinetic H/D isotope effect[23] (**2a** versus **2b**) points to the alkylidenecarbenoid mechanism **2a** → **6** → **8d** of Scheme 3; but again only one equivalent of MeLi was consumed by both **2a** and **2c** according to the ^{1}H NMR integrations, and none of the attempted final carboxylations delivered the acid **10d** to be expected from **8d**. Only **4d** was obtained from **2a**, and only **4f** from **2c**, while **2b** furnished a pure 15:85 mixture of **4d** and **4e**, showing that atoms of types A (albeit lost during the formation of carbenoid **6**) were transferred chiefly (**4e**) or totally (**4d**, **4f**) to **8d**. Reagents **2a**−**c** are obvious sources of A for a transfer to **8d**, as formulated in more general terms in Scheme 4.

This kind of trapping of an alkenyllithium intermediate such as **8** by the starting material has been noted occasionally[24−26] in the field of alkylidenecarbenoids and explains why the carboxylations did not provide an acid **10**. Such a transfer of A can also explain the 1:1 stoichiometry, because carbenoid **6** is regenerated in step 3 of Scheme 4 and will be recycled by the fast attack of RLi (= MeLi here) in step 2 to give **8**, which then awaits the A transfer in step 3, and so forth, creating a carbenoid chain reaction with **8** (and **6**) as the chain carrier(s). This implies that the reagents **2a**−**c** react faster with the emanating alkenyllithium compound **8** in step 3 than with R′Li (= MeLi here) in step 1, so that only a small fraction of another equivalent of MeLi will be "wasted" in step 1. It follows that the primary kinetic isotope effects of **2a**/**2b** must arise pre-

Scheme 4

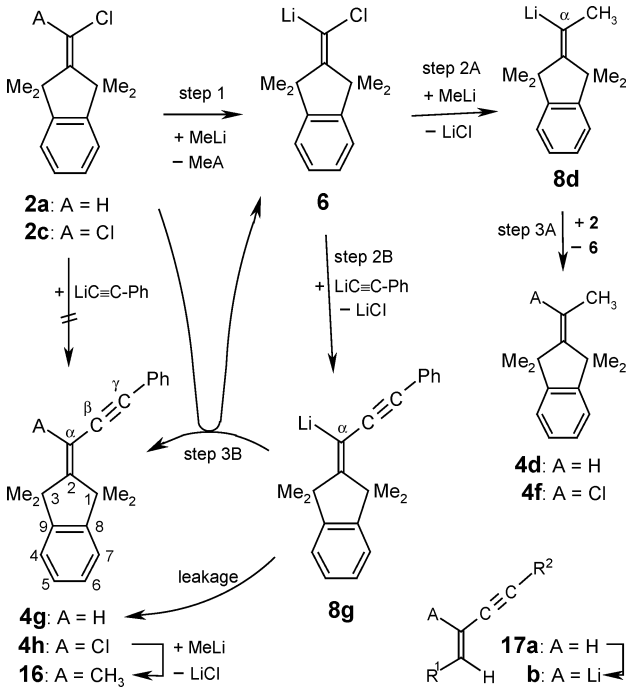


dominantly in step 3, so that step 3 is rate-limiting in the chain cycle and hence slower than the isotope-independent step 2.[27] A ranking of the step rates (velocities of the flux of material) may thus be expressed in a shorthand notation as $2 > 3 \gg 1$ under the reaction conditions.[27] Methyllithium, a tetrameric aggregate, has in fact proved quite often to be the kinetically least active base,[28,29] despite its high thermodynamic basicity. The kinetically more active base **8d** is more inclined to seize a proton from other sources in the environment; such a "leakage" reaction (Scheme 4) will interrupt a running chain, of course, and the aforesaid chain reaction of **2b** was indeed terminated very soon because the decelerated transfer of A = deuterium to give **4e** entailed the leakage portions 15% (in THF) or 60% of **4d** (in Et_2O), demanding a corresponding input of additional R′Li = MeLi for restarting the chains. Thus, an efficient alkylidenecarbenoid chain process requires both step 1 and the leakage reaction to be significantly slower than steps 2 and 3, so that the intermediate **8** and the reagent **2** react almost exclusively with each other.

The transfer of chlorine from dichloride **2c** (Scheme 3) to **8d** seemed to be usually fast enough to sustain a carbenoid chain reaction, unless a lower concentration of **2c** (as during the dropwise addition and especially at the end) retarded the formation of **4f** in step 3, in which case **4d** began to appear as a side-product through leakage as depicted in Scheme 4. This established a participation of the carbenoid route; but how can one be sure of a predominance of the chain mechanism in the absence of the isotope criterion? A convincing demonstration can be built upon realizing that the organolithium reagents play the role of bases R′Li (with **2a**) or of chlorine acceptors R′Li (with **2c**) in step 1, whereas they are employed as nucleophiles RLi in step 2. In the presence of a different RLi reagent, less basic but significantly more nucleophilic, the carbenoid **6** would be consumed preferentially by RLi in step 2, and the role of

(20) Knorr, R. and co-workers, unpublished.
(21) The presence of ethoxyethane (4 equiv) did not impair the substitution reaction with **2a** and furnished no product of a cycloaddition reaction to **6**, although the generation of $Me_2C{=}CLiBr$ with MeLi in Et_2O in the presence of enol ethers had afforded (2-propylidene)cyclopropanes[55] in high yields.
(22) Knorr, R.; Freudenreich, J.; Polborn, K.; Nöth, H.; Linti, G. *Tetrahedron* **1994**, *50*, 5845−5860.
(23) A rough estimate, $k_H/k_D \approx 11$ (± 4), for the primary kinetic isotope effect in THF was determined[10] through competition of **2a** with **2b** for a substoichiometric amount of MeLi.
(24) Curtin, D. Y.; Richardson, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 4719−4728, on p 4721.
(25) Günther, H.; Bothner-By, A. A. *Chem. Ber.* **1963**, *96*, 3112−3119, on p 3115.
(26) Cunico, R. F.; Han, Y.-K. *J. Organomet. Chem.* **1978**, *162*, 1−16, on p 3.
(27) With the assumption that the substitution step 2 with LiCl elimination is practically irreversible. To be successful, step 2 must occur more rapidly than the decomposition of the alkylidenecarbenoid which is usually[4a] fast at room temperature.
(28) Schlosser, M. *Struktur und Reaktivität polarer Organometalle*; Springer-Verlag: NewYork, 1973; p 126.
(29) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. A. G., Abel, E. W., Eds.; Pergamon: Oxford 1982; Vol. 1, p 50.

Scheme 5



R′Li would be confined to step 1. In the sequel, we have tested this concept with **2a**, whose carbenoid chain mechanism was established above, and applied it then to **2c** for an elucidation of its behavior.

Phenylethynyllithium is dimeric[30,31] in THF and is a much weaker base ($pK_a \approx 31$)[32,33] than methyllithium. Accordingly, a THF solution containing 1.8 equivalents of PhC≡CLi did not react with **2a** overnight at ambient temperature; but two small portions of MeLi (2 × 0.09 equiv, in Et_2O) were consumed rapidly, whereafter the product **4g** (Scheme 5) was observed by ^{1}H NMR to increase steadily over the next 140 min at a strongly *diminished* velocity. This established that PhC≡CLi generated **4g** by chain propagation (step 3B, alternating with step 2B) without participation of MeLi, that is, with step 1 shut down. Due to interruptions by the leakage reaction, the chain had to be restarted with a third portion of MeLi (0.09 equiv) and reached completion in 6 h. Carboxylation afforded PhC≡C−CO_2H (0.8 equiv, from residual PhC≡CLi) as the only acid (no **10g**), while almost pure **4g** was isolated without a detectable amount of **4d** (Scheme 5), showing that MeLi (if added in small doses) could not compete successfully for **6** (step 2A) with the more concentrated PhC≡CLi (step 2B). However, **4d** became a byproduct in the presence of more MeLi (0.30 equiv), especially so in Et_2O solution where the very slow reaction of PhC≡CLi, as initiated and sustained by MeLi (0.7 equiv, 0.11 M initially), occurred with a first $t_{1/2}$ of roughly 50 h at room temperature.[16]

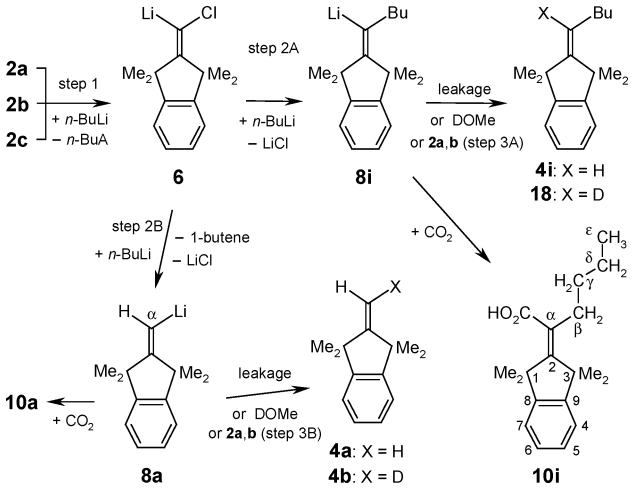
Viewed superficially, it may perhaps come as a surprise that product formation with PhC≡CLi was able to suppress the much faster chain process with MeLi completely. But this amazing deceleration is easily rationalized by taking into consideration that the choice for PhC≡CLi and against MeLi is made by carbenoid **6** in the fast product-determining steps 2B versus 2A, while the rate-limiting step 3B with the stabilizing α-alkynyl substituent in **8g** can be slower than step 3A with a destabilizing α-methyl in **8d**. Such a *deceleration* provides independent evidence for the carbenoid mechanism with MeLi, because a noncarbenoid process would not have decreased its rate of production of **4d** so much from MeLi in the presence of PhC≡CLi.[34] Conversely, a significantly increased observed rate would be compatible with a mainly noncarbenoid route from **2a** to **4d** if combined with a tiny contribution of the carbenoid chain A, because a catalytic amount of carbenoid **6** might then divert the majority of **2a** to the faster reaction with PhC≡CLi via steps 2B and 3B, leaving less material for the formerly main (noncarbenoid) route.

The dichloride **2c** did not react with PhC≡CLi (0.32 M, 1.52 equiv) in THF during 3 days at ambient temperature (nor in *t*-BuOMe at +34 °C). An added portion (0.25 equiv) of MeLi was consumed slowly in the course of 40 min, surprisingly generating **16** as the main product, observed in situ (^{1}H NMR) and isolated after carboxylation (≈ 15 h later), together with a small amount of the "normal" product **4h** (expected from chlorine transfer), much of the starting material **2c**, and PhC≡C−CO_2H (1.40 equiv) but not more than a trace of the product **4f** of MeLi incorporation. This *decelerating* diversion to chain B established chain A for **2c** and verified that **2c** was consumed in step 1 much more slowly than in step 3B (since **8g** did not accumulate). The conclusion that most of **4h** must have been converted rapidly to **16** was confirmed through a control experiment which furnished **16** from **4h** with MeLi in THF. (Pure **4h** can be prepared with 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$Li in place of MeLi, as will be shown in section 4.) Owing to this extra drain on MeLi, the carbenoid chain had to be sustained by a higher dose (1.1 equiv) of MeLi for a complete conversion of **2c**, with the drawback of an interference by the competing MeLi chain (steps 2A and 3A in Scheme 5): Carboxylation after one night yielded **16** (46%), **4f** (23%), and PhC≡C−CO_2H as the only products, which indicated that PhC≡CLi (1.0 equiv) and **4f** had coexisted in THF over an extended period of time instead of forming **16** (as proved true in a control experiment). The leakage reaction should be relatively slow in the special case of **8g**, because **4g** could not be detected in these runs with **2c** and because closely related alkenyllithium compounds **17b** appear to be comparatively weak bases in view of their ready formation through deprotonation[35,36] of **17a**. Considering the above product ratio of **16**/**4f** = 46:23, the ranking of step rates for MeLi reacting with **2c** was 2B > 2A ≫ 3A > 3B ≫ 1 under the reaction conditions.[27] The employment of *t*-BuC≡CLi provided completely analogous results.[10]

3. *n*-Butyllithium (RLi = *n*-BuLi): Counter-Example, and also Confirmation. The following investigations were confined to THF solutions, which are known[37−40] to contain mainly

(30) Hässig, R.; Seebach, D. *Helv. Chim. Acta* **1983**, *66*, 2269−2273.
(31) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972−1988.
(32) Antipin, I. S.; Gareyev, R. F.; Vedernikov, A. N.; Konovalov, A. I. *J. Phys. Org. Chem.* **1994**, *7*, 181−191; *Chem. Abstr.* **1994**, *121*, 255158s.
(33) $pK_a \leq 21.2$ in water: Kresge, A. J.; Pruszynski, P.; Stang, P. J.; Williamson, B. L. *J. Org. Chem.* **1991**, *56*, 4808−4811.
(34) Several of the decelerations observed in this system are too large to be ascribed to hypothetic mixed aggregates of PhC≡CLi with RLi causing a retardation of noncarbenoid substitution processes. Such aggregates are weakly bound and usually hard to detect as the components of very mobile equilibria in solution. An elucidation of their role would require extended series of precise rate measurements which are beyond the scope of this work.
(35) Zweifel, G.; Rajagopalan, S. *J. Am. Chem. Soc.* **1985**, *107*, 700−701.
(36) Brandsma, L.; Hommes, H.; Verkruijsse, V. D.; Kos, A. J.; Neugebauer, W.; Baumgärtner, W.; Schleyer, P. v. R. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 286−295.
(37) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308−337.

Scheme 6



tetrameric and dimeric *n*-BuLi aggregates. Within 25 min at room temperature after the addition (at −78 °C) of *n*-BuLi (2.1 equiv), the monochloride **2a** had vanished from the red THF solution whose ^{1}H NMR spectrum revealed that almost two equivalents of *n*-BuLi ($\delta_H \approx -0.75$) had been consumed. Carboxylation after another 30 min afforded a 3:7 mixture of **10a**[22] and **10i** (Scheme 6) as the only organic acids, establishing the alkenyllithium compounds **8a**[22] and **8i** as final products before workup. **8a** was formed here through hydride transfer[4d] (step 2B) from *n*-BuLi to **6** with expulsion of LiCl (not through a Cl/Li interchange reaction), as was proven below with the deuterio reagent **2b**. Together with the 1:2 (**2a**/*n*-BuLi) stoichiometry, this evidence for intermediates **8a** and **8i** tells that the material had passed through steps 1 and 2 in Scheme 6 but could not be carried through step 3 because **2a** had been deprotonated (step 1) more rapidly by *n*-BuLi (which is considerably more active[28,29] than MeLi). Hence, the carbenoid chain was not achieved for want of **2a**. The known nonacidic byproducts **4a**[41a] and **4i**[41b] (ca. 1:4) can be ascribed to the leakage reactions of **8a** and **8i**, respectively, with proton transfer from the solvent or impurities. They were also main products of a run with **2a** and *n*-BuLi (10 equiv) at −78 °C, which had been terminated by the addition of $DOCH_3$ (20 equiv) after 7 h when reagent **2a** was almost totally consumed. The crude material after workup was a mixture of **4a**, **4b**, **4i**, and **18** in the molar ratio 23:12:43:22, suggesting that only 34% of both **8a** and **8i** could be trapped by deuteration because 66% had already fallen victim to adventitious protonation (leakage).

The preceding conclusions were confirmed by treatment of reagent **2b** (0.105 M) with *n*-BuLi (2.4 equiv) at room temperature. As expected from steps 1 and 2A,B in Scheme 6, the isotopic label (A = D) was completely absent from all products found after carboxylation, whereas the Cl/Li interchange reaction of **2b** with *n*-BuLi would have produced [α-D]-**8a** and its derivatives. The acids **10a** and **10i** (28:72) were accompanied by pentanoic acid (from residual *n*-BuLi), while the nonacidic fraction contained the leakage product **4i**[41b] but no reagents **2a** and **2b**. The missing steps 3A,B could be achieved simply by using **2b** in excess: In a run with a 27:73 mixture (0.118 M) of reagents **2a** and **2b** competing for a substoichiometric amount of *n*-BuLi at room temperature, the in situ ^{1}H and ^{13}C NMR spectra revealed the presence of **4i** plus **18** (0.21 equiv, 62:38) together with some **4a** (step 3B) and 0.79 equiv of **2a** + **2b** (0.093 M). The formation of **18** confirmed step 3A, whereas some portion of **4i** may have resulted from leakage. The main component was residual reagent **2b**, whereas its unlabeled congener **2a** was hardly detectable. This large (albeit not quantifiable) kinetic H/D isotope effect established the rate-limiting generation of alkylidenecarbenoid **6** in steps 1 and 3A,B. The efficient formation of substitution products despite the deficiency of *n*-BuLi proved that step 2 occurred significantly faster than step 1, in contrast to the reversed rate relation reported[42] for Ph(Me)C═CHCl with *n*-BuLi.

The dichloride **2c** disappeared from its green THF solution containing *n*-BuLi (3.1 equiv, added at −78 °C) within 10 min at room temperature, as shown by in situ ^{1}H NMR which revealed the consumption of 2.4 equivalents of *n*-BuLi with formation of **8a**[22] (═CHLi at $\delta_H \approx 6.6$). This suggested that steps steps 3A,B in Scheme 6 had not been achieved. Indeed, carboxylation after 40 min furnished the acids **10a** and **10i** (29:71) in the same ratio as with **2a** and **2b** (and as also with **2c** in the solvent *t*-BuOMe), supporting the validity of Scheme 6 with carbenoid **6** as the common intermediate formed through either α-deprotonation of **2a** or dedeuteration of **2b** or the Cl/Li interchange reaction of **2c**. But it must be remarked that to expect such equal product ratios one would have to presuppose that the **8a**/**8i** ratio should be changed by the leakage reactions to a comparable degree in all of these cases. A similar run with **2c** and *n*-BuLi (2.0 equiv) performed at −78 °C in THF/cyclohexene (2:3) was carboxylated after 2 h, providing **4a** and **4i** (≈ 1:3) and the acids **10a** and **10i** (32:68) but no pentanoic acid (no *n*-BuLi left) and no cycloaddition[4a] product of **6** to the olefinic cosolvent. The different behavior of *tert*-butyllithium will be reported separately.

4. Aryllithium [RLi = PhLi, 4-(Me_3Si)C_6H_4Li, 2,6-$Alk_2C_6H_3$Li, and 2,4,6-(*t*-Bu)$_3C_6H_2$Li]: Not Insurmountably Impeded in Step 2. As an equilibrium mixture of the monomer and the dimeric aggregate in THF solution,[31,43−45] *phenyllithium* exhibited a reactivity pattern[28,29] intermediate between those of MeLi and *n*-BuLi. Will PhLi opt for or against the chain process in the presence of dichloride **2c**? The elucidation was easy *in Et_2O solution* at room temperature because the chain carrier **8k**, generated with PhLi (1.3 equiv) in step 2A of Scheme 7, was observed by ^{1}H NMR in situ (*p*-H as a triplet at $\delta \approx 6.35$ and *o*-H as a doublet at $\delta \approx 6.58$ for α-phenyl of **8k**),[46] whereupon the product **4k** of chlorine transfer in step 3A was isolated (yield at least 50%).[15] The small steady-state concentration (∼0.04 M, ∼0.15 equiv) of **8k** remained approximately constant during the time period from 40 min, when **2c** was

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(39) Heinzer, J.; Oth, J. F. M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1848−1862.
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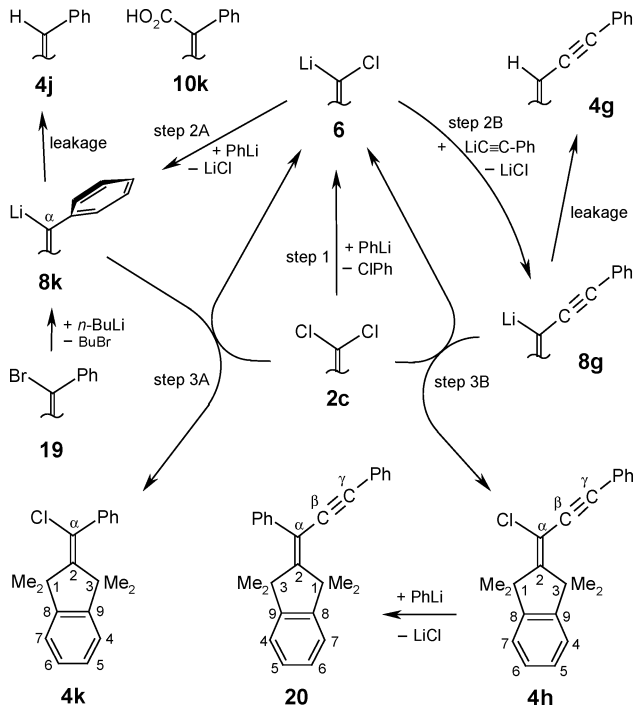
(41) (a) Compound **6** in ref 9. (b) Compound **43** in ref 9.
(42) Köbrich, G.; Ansari, F. *Chem. Ber.* **1967**, *100*, 2011−2020, on p 2014.
(43) Bauer, W.; Winchester, W.; Schleyer, P. v. R. *Organometallics* **1987**, *6*, 2371−2379.
(44) (a) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444−3445. (b) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1991**, *113*, 1414−1416.
(45) Gerold, A.; Jastrzebski, J. T. B. H.; Kronenburg, C. M. P.; Krause, N.; van Koten, G. *Angew. Chem.* **1997**, *109*, 778−780; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 755−757.
(46) Knorr, R.; Hoang, T. P.; Nöth, H.; Linti, G. *Organometallics* **1992**, *11*, 2669−2673.

Scheme 7

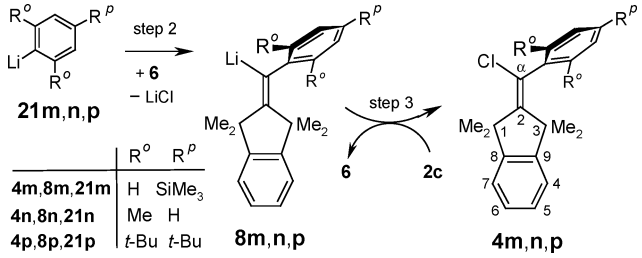


present in a roughly 10-fold amount, till 40 h when the concentration of **2c** had dropped to zero, leaving **8k** and half as much of PhLi. Thus ∼1.2 equiv of PhLi was required for total conversion, indicating that the diminution of **2c** via step 3A of Scheme 7 was sufficiently slow to allow step 1 to consume a considerable portion of **2c**. Indeed, a bona fide sample[46] of **8k** (∼0.08 M, prepared from the known[47] bromoalkene **19**) was still observed in Et_2O solution at room temperature 45 min after an addition of **2c** (∼0.27 M), and it vanished within <95 min, providing **4k** and **4j**[47] in a 2:1 ratio and thus confirming the slowness of step 3A (ascribable to a weakened kinetic basicity of **8k**). It follows that **8k** and **2c** could not have coexisted for up to 40 h but that **8k** was continuously replenished through the faster step 2A, so that the step rates can be ranked[27] as 2A ≫ 3A > 1 (disturbed chain reaction). Analytically pure **4k** was prepared from bona fide[46] **8k** and hexachloroethane.[10]

In THF solution, the reaction of dichloride **2c** with PhLi (0.21 M, 1.4 equiv) was over in <10 min at room temperature, and residual PhLi (1 equiv consumed) was seen in situ by ^{1}H NMR in an amount corresponding to the small quantity of benzoic acid (not contaminated by **10k**) formed through carboxylation 1 h later, along with **4k** (yield 80%) and **4j** (13%). The chain carrier **8k** could not be observed under these conditions; but competition of PhLi with PhC≡CLi (∼1:2) provided evidence for at least partial reaction via carbenoid **6** in Scheme 7: The products deriving from the intermediates **8k** and **8g** were formed in a roughly 1:3 ratio, so that chain B was established, whereas the fast consumption of **2c** did not allow one to demonstrate the deceleration as required (section 2) for a more quantitative assessment of chain A. The slow conversion of **4h** to **20** was verified independently with PhLi in THF.

The consumption of **4-(trimethylsilyl)phenyllithium** (**21m**) in THF by an excess of the dichloride **2c** could be watched by

Scheme 8



^{1}H NMR at room temperature only during the first 2 min and was complete in 5 min. A preparative run (1.3 equiv of **21m**, performed at +2 °C) furnished the purified carbenoid chain product **4m** (Scheme 8) in 56% yield and no leakage product **4l**. Repetitions of this run at +37 °C (17 h) in *tert*-butyl methyl ether (*t*-BuOMe) rather than in THF afforded at most 30−33% of purified **4m**, accompanied by residual **2c** and varying portions of **4l**, because the rate of chlorine transfer in step 3 (Scheme 8) was strongly reduced (a nonchain condition). In fact, the hampered chain carrier **8m** was observed now in situ [δ_H 0.22 (s, Me_3Si), 6.65 (d, $^3J \approx 8$ Hz, *o*-H)] at +35 °C (first $t_{1/2} \approx 1$ h with 1.1 equiv of **21m**)[16] and at room temperature (first $t_{1/2} \approx 2$ h with 2 equiv of **21m**) in the presence of **2c**, and its leakage product **4l** was not formed during the first 4 h.

2,6-Dimethylphenyllithium (**21n**), which is monomeric[48] or dimeric[49] in THF, was studied at room temperature in *t*-BuOMe because of its lower solubility[49] in Et_2O. Reagent **2c** (0.17 M) consumed 1.1 equiv of **21n** (initially 0.32 M) with a first $t_{1/2} \approx$ 30 min[16] and disappeared in ∼6 h, providing mainly the desired chain product **4n**. Thus this conversion proceeded more rapidly than had been noted above for PhLi in Et_2O and for **21m** in *t*-BuOMe. Apparently, the chain carrier **8n** (taken for granted in analogy with PhLi) was consumed only through chlorination by **2c** in the chain propagation step 3 of Scheme 8, as indicated by the observed 1:1 stoichiometry and the absence of a leakage product (H in place of Cl in **4n**). The 52% yield of purified **4n** (attained on a larger scale) was higher than in any of numerous orientating attempts aiming at a cross-coupling catalyzed by Ni or Pd complexes to give **4n**: Reagent **2c** appeared to react more slowly with **21n** in the presence of those transition metal catalysts or of one equivalent of CuCl, whereas 2,6-dimethylphenylmagnesium bromide in Et_2O was practically unreactive toward **2c**.

2,4,6-Tri-tert-butylphenyllithium (**21p**, "supermesityllithium = LiMes*"),[43] which is monomeric[43,50,51] in THF solution, consumed dichloride **2c** (∼0.034 M, [LiMes*] ≈ 0.035 M in THF) with a first $t_{1/2} \approx 6$ min[16] at room temperature; a trace of residual LiMes* was detected through carboxylation after 48 min. A preparative run with [**2c**] = 0.37 M furnished the chloroalkene **4p** (Scheme 8, crude yield 78%) together with an unidentified side-product and ClMes* (yield 8%), which is the byproduct[10] generated along with carbenoid **6** in step 1, so that (78+8)/78 = 1.1 equiv of LiMes* were consumed. The good yield of **4p** indicates that the substitution step 2 was not

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insurmountably impeded by repulsive interactions between *t*-Bu in **21p** and the Me groups in reagent **2c**. Despite the 8% contribution of step 1, the competing chain propagation in step 3 must be reasonably efficient because intermediate **8p** was not accumulated and hence the leakage product **4o**[52] not detected, not even in case of a shortage of reagent **2c**. The carbenoid chain mechanism was proven through the deceleration[34] test: The formation of **4p** was completely suppressed by the significantly slower chain process of PhC≡CLi (0.45 M, 1.5 equiv), which had to be started and later restarted with 0.3 equivalent of LiMes* in two batches. Carboxylation after 6 days furnished the chloroalkyne **4h** (53%, Scheme 5), ClMes* (32%), residual **2c** (28%), and PhC≡CCO_2H.

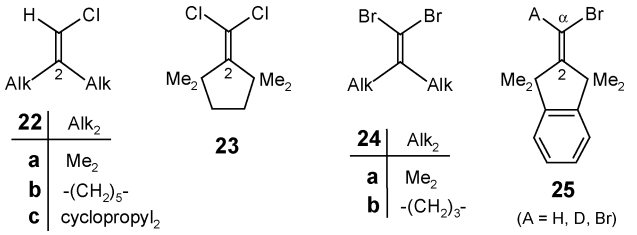
The deprotonation of reagent **2a** (0.10 mmol, 0.19 M in THF) with an excess of LiMes* took place with a first $t_{1/2} \approx 20$ min,[16] furnishing **4o**[52] (merely 0.021 mmol), HMes*, and unknown side-products.[10] The intermediacy of carbenoid **6** was established under the same conditions with reagent **2b** which reacted much more slowly than **2a** (at least 10-fold)[16] to afford plenty of ethylene (from THF with LiMes*) and, through a carboxylative workup 28 h later, HO_2C-Mes* (0.13 mmol) and the totally unlabeled leakage product **4o** (again merely 0.021 mmol) but no rearranged[10] material. Such a loss of deuterium revealed that chain propagation (step 3) was no longer achieved here because the leakage reaction of intermediate **8p** was faster than deuterium transfer from **2b** to **8p**.

Conclusions

The 2-(halogenomethylidene)-1,1,3,3-tetramethylindan reagents (**2a**−**c**) constitute a well-suited model system for collecting evidence of alkylidenecarbenoid chain reactions, particularly because their structural features prevent or disfavor disturbing alternative modes such as β-elimination,[4h] ring expansion,[4i] or substitution reactions via the ARE[3] or S_N1[4j] pathways. A helpful property of this model system is that several of the carbenoid processes occur slowly enough at room temperature to estimate first half-conversion times ($t_{1/2}$). Suitable mechanistic criteria are primary kinetic H/D isotope effects, the **2**/RLi stoichiometry (1:1 or 1:2), the deceleration test with PhC≡CLi as a nucleophile, and the observation of intermediates by NMR in situ. The reaction rates depend strongly on the solvent (THF ≫ Et_2O or *t*-BuOMe) and on the α-substituents R in the chain carriers performing the transfer step 3 which was always rate-limiting in the chain cycles studied here and hence slower than the substitution step 2. An undisturbed carbenoid chain process requires (i) that step 2 occurs significantly faster than both the initiating step 1 (which is very often[4a] not so) and carbenoid decomposition, and (ii) that step 3 be substantially faster than both step 1 and the leakage reaction. Initial cooling (to ≈ −78 °C) may be advisable to minimize leakage and carbenoid decomposition during reactant mixing.

Carbenoid chain processes are not confined to this model system: they appear to occur also with **23**[20] (Scheme 9) but should not be expected for 1-halogeno-1-alkenes carrying hydrogen or π-acceptor substituents at the 2-position. Products of the essential proton-transfer step 3 had been observed in earlier studies of **22a**[4d,26] and **22b**,[4c,25] but further conclusions were not drawn. We conjecture that additional examples might

Scheme 9



have been encountered previously where step 3 involved proton transfer[53] from **22c**[4l,54] or bromine transfer from **24a**[55] and **24b**.[4k,56] The carbenoid substitution mechanism of the bromoalkenes **25** will be elucidated with subsequently[57] reported evidence.

Experimental Section[10]

2-(Chloromethylidene)-1,1,3,3-tetramethylindan (2a). (a) From 2c: The dichloride **2c** (2.50 g, 9.80 mmol) in anhydrous THF (20 mL) was added to a THF solution of *tert*-butylmagnesium chloride (1.36 M, 29.0 mL, 39.4 mmol) under argon cover gas and was heated to reflux for 120 h. The cooled mixture was cautiously hydrolyzed with 10 mL of 2 M HCl and diluted with another 200 mL, then extracted with Et_2O (3×). The combined extracts were washed until neutral, dried over $MgSO_4$, and concentrated to afford 2.16 g (100%) of oily monochloride **2a**, contaminated with only a trace of **4a**. One crystallization from cooled methanol furnished a colorless powder (1.48 g, 68%) with mp 39−42 °C (see below).

(b) From 12a: The alcohol **12a**[10] (471 mg, 1.97 mmol) was mixed with dry pyridine (1.4 mL) under argon cover gas and cooled in ice. Thionyl chloride (0.28 mL, 3.8 mmol) was added dropwise with stirring. After further stirring at room temperature for 2 h, the mixture was diluted with 2 M HCl (30 mL) and extracted with Et_2O (3×). The combined extracts were washed with 2 M HCl (2 × 5 mL), washed until neutral, and dried over Na_2SO_4. The residue after concentration (280 mg) was distilled at 140−155 °C (bath temp.)/14 Torr to give 141 mg (32%) of the slightly contaminated product **2a**. Crystallization from cooled methanol provided an analytically pure powder with mp 44−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.387 (s, 2 3-CH_3), 1.600 (s, 2 1-CH_3), 6.093 (s, α-H), 7.14, 7.18, 7.24, and 7.25 (4 m, C_6H_4); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.49 (qq, ^1J = 127.5 Hz, ^3J = 4.5 Hz, 2 1-CH_3), 32.34 (qq, ^1J = 127.5 Hz, ^3J = 4.5 Hz, 2 3-CH_3), 47.89 (m, C^1), 48.39 (broader m, C^3), 112.49 (d, ^1J = 191.5 Hz, C^α), 122.33 (dm, ^1J = 157 Hz, C^7), 122.43 (dm, ^1J = 157 Hz, C^4), 127.26 (ddd, ^1J = 159 Hz, ^3J = 7.4 Hz, C^5), 127.45 (ddd ^1J = 159 Hz, ^3J = 7.4 Hz, C^6), 148.09 (m, C^9), 149.70 (m, C^8), 160.23 (m, $^3J \approx 3.7$ Hz, C^2), assigned by comparison with the corresponding bromo compound;[58] IR (KBr) 2962, 2925, 2863, 1634 (w), 1484, 1457, 846, and 759 cm^{-1}. Anal. Calcd for $C_{14}H_{17}Cl$ (220.7): C, 76.18; H, 7.76; Cl, 16.06. Found: C, 76.45; H, 7.81; Cl, 15.90. Residual =CH NMR absorptions (^{1}H s δ 6.09, ^{13}C δ 112.5) could not be detected for the α-D derivative **2b**.

2-(Dichloromethylidene)-1,1,3,3-tetramethylindan (2c). 2-(Dichloromethyl)-1,1,3,3-tetramethyl-2-indanol[10] (**15**, 16.84 g, 61.64 mmol) was

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(53) With certain *saturated* carbenoids, a carbenoid chain based on proton transfer was apparently progressing in THF solution but obviously not in Et_2O, as judged from the stoichiometries (1:1 and 2:1, respectively) reported by: Molines, H.; Normant, J.-M.; Wakselman, C. *Tetrahedron Lett.* **1974**, 951−954, Tableau I therein.

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dissolved in distd. pyridine (81.4 mL) and cooled in ice. Thionyl chloride (11.30 mL, 154.0 mmol) was added dropwise over 40 min with stirring under argon gas. The mixture was left at room-temperature overnight and was then poured into 300 mL of 2 M HCl, which was extracted with Et_2O (3 × 300 mL). The combined extracts were shaken with 2 M HCl (2 × 200 mL), washed until neutral, and dried over Na_2SO_4. Concentration and drying in vacuo afforded 15.30 g (97%) of pure dichloride **2c**: pale-yellow plates with mp 119−121 °C from ethanol (ref 14: 119−121 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (s, 4 1-/3-CH_3), 7.14 (m, 4-/7-H), 7.25 (m, 5-/6-H), as in ref 14; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 27.4 (qq, ^1J = 127.8 Hz, ^3J = 4.5 Hz, 4 1-/3-CH_3), 50.2 (m, $C^{1,3}$), 115.8 (sharp s, C^{α}), 122.4 (dm, ^1J = 158 Hz, $C^{4,7}$), 127.5 (ddd, ^1J = 159.9 Hz, ^3J = 7.5 Hz, $C^{5,6}$), 148.7 (m, $C^{8,9}$), 155.1 (m, C^2), in disagreement with ref 14; IR (KBr) 2990, 2963 (s), 2928, 2867, 1583, 1485, 1454, 1363, 900 (s), 856 (s), and 755 (s) cm^{-1} (compare ref 14). Anal. Calcd for $C_{14}H_{16}Cl_2$ (255.2): C, 65.89; H, 6.32; Cl, 27.79. Found: C, 66.02; H, 6.35; Cl, 27.65.

2-Ethylidene-1,1,3,3-tetramethylindan (4d). MeLi (8.60 mmol) in Et_2O (6.90 mL) was added with stirring under argon cover gas to the solution of monochloride **2a** (633 mg, 2.87 mmol) in Et_2O (10.0 mL). After one night at room temperature, the mixture was poured onto solid CO_2, warmed, and diluted with Et_2O and 2 M NaOH. The acidified NaOH layer furnished no organic acid. The Et_2O phase was washed until neutral, dried with $MgSO_4$, and concentrated to yield **4d** (490 mg, 85%) along with a trace of residual reagent **2a**. The material was distilled at 120−170 °C (bath temperature)/12 Torr and then crystallized from cooled methanol to give a colorless powder: mp 34−35 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 2 3-CH_3), 1.50 (s, 2 1-CH_3), 1.87 (d, ^3J = 7.3 Hz, α-CH_3), 5.48 (q, ^3J = 7.3 Hz, α-H), 7.15, 7.18, and 7.21 (1 + 1 + 2 arom. H, C_6H_4); ^{13}C NMR;[10] IR (KBr) 2960, 2862, 1483, 1457, and 755 cm^{-1}. Anal. Calcd for $C_{15}H_{20}$ (200.3): C, 89.94; H, 10.06. Found: C, 89.59; H, 9.91.

2-(1-Chloroethylidene)-1,1,3,3-tetramethylindan (4f). Dichloride **2c** (1.53 g, 6.00 mmol) in anhydrous THF (10.0 mL) was added dropwise within 3 min at room temperature under argon cover gas to a stirred solution of MeLi (6.60 mmol) in Et_2O (6.00 mL) and THF (14.8 mL). The exothermic reaction was terminated after another 10 min by carboxylation on solid CO_2. The warmed-up material was dissolved in Et_2O and 2 M NaOH. The separated and acidified NaOH layer afforded no organic acid. The Et_2O phase was washed until neutral, dried with $MgSO_4$, and concentrated to furnish a mixture (1.29 g) of **4f** (yield 82%) and **4d** (9%). Pure **4f** crystallized as a beige powder from methanol (2×): mp 108−109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51 (s, 2 3-CH_3), 1.61 (s, 2 1-CH_3), 2.35 (s, α-CH_3), 7.12 (m, 4-H), 7.14 (m, 7-H), 7.23 (m, 5-H), and 7.24 (m, 6-H), assigned by the NOESY correlations α-CH_3 ↔ 3-CH_3 ↔ 4-H ↔ 5-H and 1-CH_3 ↔ 7-H ↔ 6-H; ^{13}C NMR;[10] IR (KBr) 2959, 2928, 1644 (w), 1487, 1455, and 761 cm^{-1}. Anal. Calcd for $C_{15}H_{19}Cl$ (234.8): C, 76.74; H, 8.16; Cl, 15.10. Found: C, 77.17; H, 8.11; Cl, 14.27.

2-(3-Phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (4 g)[10]; 2-(1-Chloro-3-phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (4h)[10]; 2-Pentylidene-1,1,3,3-tetramethylindan (4i). Spectra in ref 41b**; 2-(α-Chlorobenzylidene)-1,1,3,3-tetramethylindan (4k)[10]; 2-(4-Trimethylsilylbenzylidene)-1,1,3,3-tetramethylindan (4l).**[10]

2-(α-Chloro-4-trimethylsilylbenzylidene)-1,1,3,3-tetramethylindan (4m). An oven-dried Schlenk flask (250 mL) was charged with 1-bromo-4-(trimethylsilyl)benzene[10] (6.430 g, 28.06 mmol) in anhydrous THF (60 mL) and cooled to −78 °C under argon cover gas. *t*-BuLi (56.1 mmol) in pentane (33.00 mL) was added dropwise with stirring, forming 4-trimethylsilylphenyllithium (**21m**): ^{1}H NMR δ +0.16 (s, $SiMe_3$), 7.10 (d, $^3J \approx 7$ Hz, 2 *m*-H), 7.92 (d, $^3J \approx 7$ Hz, 2 *o*-H); in *t*-BuOMe +0.16, 7.24, and 8.08 with ^3J = 7 Hz. The deep-red solution was stirred without cooling for 10 min and then stirred in an ice bath during the slow addition of dichloride **2c** (5.400 g, 21.16 mmol) in small portions. After further stirring for 30 min, the cold solution was poured into distd. water (100 mL) and diluted with Et_2O. The separated aqueous layer was extracted with Et_2O (3 × 80 mL). The combined Et_2O phases were washed until neutral, dried over $MgSO_4$, and concentrated to yield 8.81 g of solid material, consisting of mainly **4m** with only a trace of the leakage product **4l** but no **2c**. Slow recrystallization from ethanol (∼50 mL) afforded almost pure **4m** as colorless needles in two fractions (4.404 g, 56%): mp 134−135 °C (ethanol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, $SiMe_3$), 1.18 (s, 2 3-CH_3), 1.76 (s, 2 1-CH_3), 7.04 (dm, 4-H), 7.19−7.27 (m, 5-/6-/7-H), 7.32 (dm, ^3J = 8 Hz, 2 *o*-H), and 7.52 (dm, ^3J = 8 Hz, 2 *m*-H); ^{13}C NMR;[10] IR (KBr) 2955, 1649 (w), 1588, 1486, 1363, 1250 (s), 1115, 840, 808, and 758 cm^{-1}. Anal. Calcd for $C_{23}H_{29}ClSi$ (369.0): C, 74.86; H, 7.92; Cl, 9.61. Found: C, 75.19; H, 7.78; Cl, 9.33. − The mother liquor, concentrated to 5 mL, deposited small needles of 1,4-bis-(trimethylsilyl)benzene (108 mg, 1.7%) that had been imported with the starting material: mp 85−86 °C (ref 59: 88 °C; ref 60: 88−89 °C; ref 61: 94−96 °C); ^{1}H NMR as in ref 62.

2-(α-Chloro-2,6-dimethylbenzylidene)-1,1,3,3-tetramethylindan (4n). *t*-BuLi (4.49 mmol) in pentane (2.64 mL) was added dropwise with stirring at −78 °C under argon cover gas to 2-bromo-1,3-dimethylbenzene (0.30 mL, 2.24 mmol) in *t*-BuOMe (4.0 mL), affording 2,6-dimethylphenyllithium (2.24 mmol): ^{1}H NMR δ 2.50 (s, 2 *o*-CH_3) and 6.77 (narrow m, 3 H). The solution deposited a copious precipitate of LiBr and was stirred at room temperature for 30 min, then treated with reagent **2c** (500 mg, 1.96 mmol), warmed at 32−35 °C for 3 h, and diluted with Et_2O and water. The aqueous layer was extracted with Et_2O (3×), and the combined Et_2O phases were washed until neutral, dried over $MgSO_4$, and concentrated to give 655 mg of crude **4n**, contaminated with *m*-xylene and other side-products but not more than a trace of reagent **2c**. One crystallization from EtOH afforded 334 mg (52%) of pure **4n**: mp 130−131.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 2 1-CH_3), 1.79 (s, 2 3-CH_3), 2.37 (s, 2 *o*-CH_3), 7.03 (m, 4-H or 7-H), 7.06 (d, ^3J = 7.5 Hz, 2 *m*-H), 7.17 (pseudo-t, ^3J = 7.7 Hz, *p*-H), 7.22 (m, 3 H of C_6H_4); ^{13}C NMR;[10] IR (KBr) 2992, 2961, 2927, 2865, 1640 (w), 1591 (w), 1485, 1459, 1360, 838, 784, 777, and 760 cm^{-1}. Anal. Calcd for $C_{22}H_{25}Cl$ (324.9): C, 81.33; H, 7.76; Cl, 10.91. Found: C, 81.03; H, 7.92; Cl, 10.42. In cases of inefficient stirring but otherwise identical conditions, the crude material contained some residual reagent **2c** and a "carbene dimer"[57] as a side-product.

2-(2,4,6-Tri-*tert*-butylbenzylidene)-1,1,3,3-tetramethylindan (4o)[10]; 2-(α-Chloro-2,4,6-tri-*tert*-butylbenzylidene)-1,1,3,3-tetramethylindan (4p)[10]; 2-(1,1,3,3-Tetramethyl-2-indanylidene)propanoic Acid (10d). To be published in ref 57; **2-(1,1,3,3-Tetramethyl-2-indanylidene)hexanoic Acid (10i)[10]; 2-Chloromethyl-1,1,3,3-tetramethyl-2-indanol (12a)[10]; 2-(Dichloromethyl)-1,1,3,3-tetramethyl-2-indanol (15)[10]; 2-(1-Methyl-3-phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (16)[10]; 2-(1,3-Diphenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindan (20).**[10]

Preparation of Bromo-2,4,6-tri-*tert*-butylbenzene (BrMes*). We prepared BrMes* from HMes* by a modification of a published[63] procedure, because it cannot be made in a reasonable yield from H_2NMes* by diazotization[64] (compare also ClMes*)[10] and because the commercially available material is very expensive. We found it expedient to double the recommended[63,65] amount (1.2 equiv) of bromine and to raise the reaction temperature to 100 °C in the following protocol.

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2,4,6-Tri-*tert*-butylbenzene (HMes*, 24.44 g, 99.2 mmol) was dissolved in freshly distilled trimethyl phosphate[65] (300 mL) with stirring and warming up to 54 °C. The stirred solution turned red upon the dropwise addition of elemental bromine (11.68 mL, 228 mmol). After heating at a reflux condenser at 100 °C for 22 h, the cooled solution deposited pale yellow crystals which were isolated by suction, washed thoroughly with distd. water, and dried in a desiccator with KOH under vaccum. This crude product (31.43 g, 97%) was almost uncontaminated and could be used as such in most cases. It was recrystallized from ethanol (550 mL) to yield glistening platelets (19.81 g, 61%) with mp 167−169 °C (refs 63, 64: 172−174 °C[63] after two, 177−178 °C[64] after four recrystallizations). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 4-*t*-Bu), 1.58 (s, 2-/6-*t*-Bu), 7.41 (s, 3-/5-H), compare ref 63; ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.0 (2-/6-C*Me*$_3$), 31.4 (4-C*Me*$_3$), 35.0 (4-*C*Me$_3$), 38.4 (2-/6-*C*Me$_3$), 121.6 (C^1), 123.7 (C^{3,5}), 148.4 (C^4), 148.6 (C^{2,6}).

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Supporting Information Available: Preparatory synthetic studies; further substitution products; ^{1}H and ^{13}C NMR assignments; side-products; estimation of a kinetic H/D isotope effect. This material is available free of charge via the Internet at http://pubs.acs.org.

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