3.69; N, 4.67. Found: C, 59.96; H, 3.52; N, 4.59.

2,4,5-Triphenyl-2-benzoyl-2*H*-1,3-oxaselenole. Sodium hydride (2.05 g, 57% dispersion in oil, 0.049 mol) was washed with hexane several times under nitrogen and finally with dry dimethoxyethane. It was combined with dry dimethoxyethane (30 mL) in a flask cooled in an ice–salt bath. A chilled solution of desyl selenocyanate (15 g, 0.05 mol) in dry dimethoxyethane (80 mL) was added in one portion to the stirred suspension of sodium hydride, resulting in the vigorous evolution of hydrogen. The reaction mixture exhibited a series of color changes from yellow to red and finally to red-orange. Inorganic salts were removed by filtration; ether was added to the filtrate, and this solution was washed with water. The orange organic layer was separated and dried over $MgSO_4$. Ether was removed under reduced pressure to give a red-orange oil, which was recrystallized from methanol to give the bright yellow oxaselenole (9.1 g, 0.02 mol, 39%), mp 96–103 °C. Further recrystallizations from methanol gave a sample: mp 111–114 °C; IR ($CHCl_3$) 1690 (s), 1230 (s) cm^{-1}; UV (CH_3CN) 230 (ϵ 21 400), 300 (5600), 336 (3980) nm; fluorescence emission (CH_3CN, excitation at 235 nm) 242, 355, 479, 715 nm; ^{1}H NMR ($CDCl_3$) δ 7.0–7.8 (m); ^{13}C NMR ($CDCl_3$) δ 194.7 (CO), 143.3 (C-5), 139.9, 133.5, 133.3, 132.9, 130.7, 130.2, 129.4, 129.0, 128.9, 128.6, 128.3, 128.1, 128.0, 127.6, 125.8, 109.8 (C-4), 99.1 (C-2); ^{77}Se NMR ($CDCl_3$) δ 622 (relative to dimethyl selenide); MS (70 eV), *m/e* (relative abundance) 468 (17, M$^+$), 363 (41.5, M$^+$ – PhCO), 178 (32.8, PhC≡CPh) 105 (100, PhCO), 77 (50, Ph). Anal. Calcd for $C_{28}H_{20}O_2Se$: C, 71.95; H, 4.31. Found: C, 72.03; H, 4.22.

2,4,5-Triphenyl-2*H*-1,3-oxaselenole. The procedure for the synthesis of the preceding oxaselenole was followed except that an excess of sodium hydride (2.3 g, 57% in oil, 0.053 mol) in dimethoxyethane (40 mL) was used. Desyl selenocyanate (10 g, 0.033 mol) in dimethoxyethane (80 mL) was added as before to give after workup and recrystallization from methanol the yellow-orange product (8.0 g, 0.022 mol, 66%), mp 70–73 °C. Further recrystallizations give orange crystals: mp 72–73 °C; IR ($CHCl_3$) 1220 (s) cm^{-1}; UV (CH_3CN) 226 (ϵ 24 270), 304 (6500), 358 (3400) nm; fluorescence emission (CH_3CN, excitation at 262 nm) 267, 298, 531, 584 nm; ^{1}H NMR ($CDCl_3$) δ 7.05–7.85 (m); ^{13}C NMR ($CDCl_3$) δ 143.7 (C-5), 140.8, 134.2, 129.4, 128.7, 128.62, 128.59, 128.2, 128.0, 125.8, 109.3 (C-4), 82.2 (C-2); ^{77}Se NMR ($CDCl_3$) δ 543.8 (relative to dimethyl selenide) ($^2J_{SeH}$ = 15 Hz); MS (70 eV), *m/e* (relative intensity) 364 (19.9, M$^+$), 258 (18.6, M$^+$ – PhCHO), 178 (96.9, PhC≡CPh), 105 (100 , PhCO), 77 (37, Ph). Anal. Calcd for $C_{21}H_{16}OSe$: C, 69.42; H, 4.44. Found: C, 69.51; H, 4.54.

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Registry No. 1, 89936-26-5; 2, 89936-27-6; PhCH(SeCN)COPh, 89936-28-7; PhCHClCOPh, 447-31-4; KSeCN, 3425-46-5; NaH, 7646-69-7.

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^{1}H NMR Spectrum of Hexa-*n*-propylbenzene

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The markedly asymmetric pattern of ^{1}H NMR resonances in hexa-*n*-propylbenzene (1) has been attributed to hindered rotation of the *n*-propyl groups which destroys the equivalence of the α-methylene protons.[1] Our recent findings[2] that ethyl group rotation in hexaethylbenzene and its transition-metal complexes requires activation barriers of less than 12 kcal mol^{-1} seemed inconsistent with this interpretation. We have therefore reinvestigated this problem.

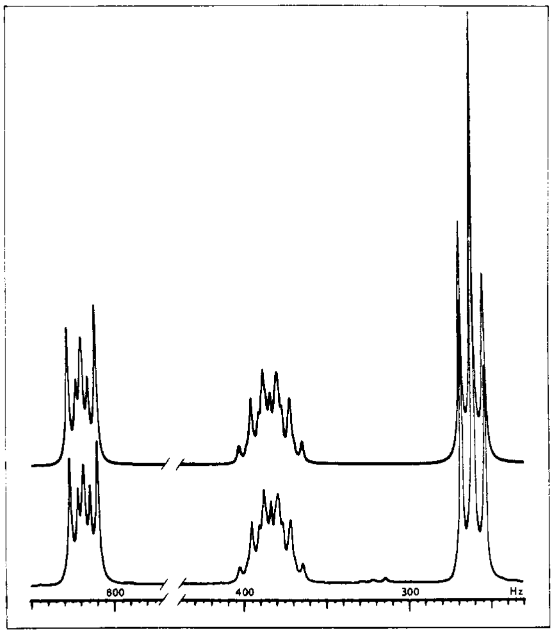

Figure 1. Lower trace: observed 250-MHz ^{1}H NMR spectrum of 1 in $CDCl_3$ at ambient temperature. The scale is divided into 5-Hz increments. Upper trace: simulated spectrum, AA′BB′C_3 spin system.

Table I. ^{1}H NMR Spectral Parameters for 1 and 2 at Room Temperature[a]

	δ_A	δ_B	δ_C	$J_{AA'}$	$J_{BB'}$	$J_{AB'}$	J_{AB}	J_{BC}	J_{AC}
1	2.47	1.53	1.04	−13.57	−13.75	12.18	4.82	7.26	<1
2	2.57	1.63	0.93	−12.8	−12.6	8.99	6.26	7.37	<1

[a] Chemical shifts (δ) in ppm relative to Me_4Si. Coupling constants (*J*) in hertz. Subscripts refer to α-methylene (A, A′), β-methylene (B, B′), and methyl (C) protons.

The analysis of AA′BB′C_3 spin systems for *n*-propyl derivatives[3,4] is directly applicable to 1 and *n*-propylbenzene (2). The spin system of the *n*-propyl groups in 1 and 2 is described by three chemical shifts and six coupling constants (Table I),[5] and the spin-simulated ^{1}H NMR spectrum of 1 matches the experimentally observed spectrum (Figure 1). The spectrum of 1 is therefore fully accounted for by the *magnetic* nonequivalence of the α- and β-methylene protons, and there is no need to invoke hindered rotation.[7]

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(2) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073. Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Iverson, D. J.; Mislow, K. *Organometallics* **1982**, *1*, 448. Blount, J. F.; Hunter, G.; Mislow, K. *J. Chem. Soc., Chem. Commun.* **1984**, 170. Hunter, G.; Mislow, K. *Ibid.* **1984**, 172.

(3) Schrumpf, G. *J. Magn. Reson.* **1972**, *6*, 243.

(4) Aksnes, D. W.; Støgård, J. *Acta Chem. Scand.* **1973**, *27*, 3277.

(5) Data for the analysis of the AA′BB′C_3 spin systems were obtained from degassed $CDCl_3$ (Me_4Si) solutions on a JEOL FX-90Q spectrometer (1 and 2) and on a Bruker WM 250 spectrometer (1). Spin simulations were performed by using the Bruker PANIC simulation program and were iteratively fitted by using several dozen lines. Geminal coupling constants were taken to be negatively signed[6] and were strongly interdependent. The magnitude of the geminal coupling constants was fixed by the observation and assignment of small-intensity lines occurring about the α- and β-methylene signals. J_{AC} as well as any long-range couplings among the six *n*-propyl groups was assumed to be negligible ($J \approx 0$).

(6) Hirst, R. C.; Grant, D. M. *J. Chem. Phys.* **1964**, *40*, 1909 and references therein.

0022-3263/84/1949-2058$01.50/0

Because of the sterically crowded environment about the hexasubstituted benzene ring, 1 is likely to exist predominantly in the all-anti conformation (D_{3d}). On the assumption that the vicinal coupling constants $J_{AB'}$ and J_{AB} of 1 represent the unaveraged $^3J_{anti}$ and $^3J_{gauche}$ couplings in the CH_2CH_2 fragment of a 1-methyl-2-aryl-substituted ethane, the observed values of the vicinal coupling constants of 2 correspond to a slight preponderance of the anti conformer.[8]

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Registry No. 1, 2456-68-0; 2, 103-65-1.

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(7) In compounds of the type XCH_2CH_2Y, the vicinal coupling constants $J_{AB'}$ and J_{AB} remain nonequivalent (anisogamous) even under conditions of rapid internal rotation.[3] Barring accidental equivalence, $J_{AB'} \approx J_{AB}$ only when $p = {}^1/_3$, where p is the mole fraction of anti conformer.[4]

(8) In previous studies, the ^1H NMR spectrum of 2 was analyzed under the simplifying assumption that the seven propyl protons could be treated as an $A_2B_2C_3$ spin system. See: Cavanaugh, J. R.; Dailey, B. P. *J. Chem. Phys.* **1961**, *34*, 1094. Chamberlain, N. F. "The Practice of NMR Spectroscopy"; Plenum Press: New York, 1974; p 367.

An Important Limitation in the Reactions of 1-Chloro-1-alkenes with *n*- or *sec*-Butyllithium

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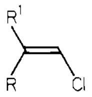
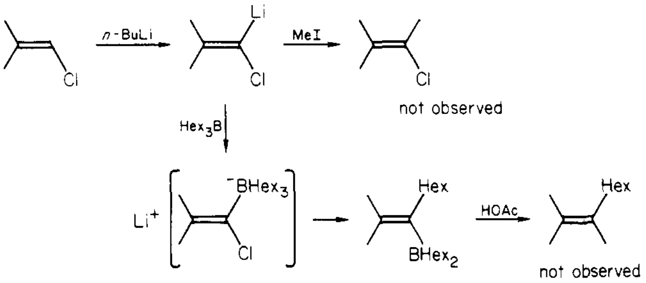
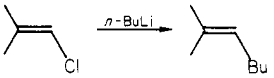
It has been reported that the low-temperature reaction of *n*-butyllithium with 1-chloro-1-alkenes yields stable lithium derivatives that can then be converted into a variety of compounds with overall retention of stereochemistry.[1-3] Often, it was stated that the reaction takes place for R = R^1 = alkyl.[2,4] However, a thorough literature search reveals that these reactions have been reported only for the compounds in which one or both of R and R^1 are groups capable of conjugating with the double bond (such as Ar, Ph, and Cl),[1,2,4,5] and not for compounds in which both R and R^1 are typical alkyl groups. Thus, the literature is somewhat misleading for one desiring to carry out this reaction with compounds in which R and R^1 are aliphatic. Therefore, we report our results for the reactions of representative compounds of this type with *n*- or *sec*-BuLi in order to identify an important limitation of this reaction.



On the basis of statements in the literature,[2,4] one might predict that the reaction of 1-chloro-2-methyl-1-propene (1) with *n*- or *sec*-butyllithium would yield a lithium derivative stable at low temperatures and useful in succeeding reaction steps. However, we find no evidence for that stable intermediate in this reaction over a wide range of temperatures (−110 °C to room temperature).



At 0 °C, equimolar amounts of 1 and *n*- or *sec*-BuLi followed by addition of either methyl iodide or trihexylborane as electrophile do not lead to the products one might predict. Instead, both reactions give 2-methyl-2-heptene in low yields.[6] Thus, while these electrophiles quench apparently stable anions of 1-chloro-1-alkenes bearing groups such as phenyl (vide supra), they fail in our system. To ascertain whether there was any involvement of the added electrophiles in formation of the 2-methyl-2-heptene, we ran a blank reaction. This reaction of equimolar amounts of 1 and *n*-BuLi also produced 2-methyl-2-heptene. Evidently, if any of the lithium derivative is formed, it reacts relatively rapidly with a second equivalent of *n*-BuLi.



We observe such formation of 2-methyl-2-heptene at temperatures as low as −23 and −45 °C. At lower temperatures (−78 or −110 °C) where the lithium derivative should be more stable, the reaction of equimolar amounts of 1 and *n*- or *sec*-BuLi followed by addition of 1 equiv of the electrophile yields predominantly polymerization products.

One might argue that the failure of the use of MeI to yield 2-chloro-3-methyl-2-butene could be due to problems inherent in the reactivity of MeI toward organolithiums, although this is unlikely since the use of 1 equiv of this electrophile has been shown to give good results in such cases.[7] However, the failure of Hex_3B to quench the anion is not due to any such problems with the electrophile, since the spontaneous rearrangement undergone by such borate complexes has been well-demonstrated.[8] This reaction probably involves initial metalation α to chlorine, similar to the *cis*- or *trans*-1-chloro-2-methylstyrene system.[9] However, at any of the temperatures investigated, the anion of the aliphatic system evidently is not sufficiently long-lived to be useful in succeeding reaction steps, as is that of the aromatic system. We find no evidence for deprotonation γ to chlorine which has been reported to be the major reaction of some 1-chloro-2-methylcycloalkenes.[10]

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