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Influence of Substituents on NMR and Barriers to Rotation in *tert*-Benzyllithium Compounds

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Abstract: A series of para-substituted α-methyl-α-neopentylbenzyllithium compounds, **5a–i**, has been prepared by adding *tert*-butyllithium to the appropriate α-methylstyrene in hydrocarbon solvents containing 1–3 equiv of an amine or ether. Alternatively, species **5** have been obtained by cleavage of the trimethyltin derivatives in the presence of amines or ethers, but not with diethyl ether. Some exceptions to this general behavior are described. ^{1}H and ^{13}C NMR show the species to exist as loose ion pairs containing conjugated anions, since the ring shifts are independent of ligand and counterion. Comparison of the ^{13}C NMR shifts with those of neutral model compounds indicate a Hückeloid charge distribution. Development of negative charge in **5** brings about a total upfield shift of 160–167 ppm. Barriers to rotation in the series of benzyllithiums **5** depend slightly on ligand and critically on substituent. Rotation is concluded to proceed via a covalent transition state. It is concluded that variations in barriers largely reflect changes in ground-state energies of the anions and provide an empirical measure of the interaction of substituent with benzyl anion. Thus, *p*-Me$_3$Si increases the barrier (relative to *p*-H) by 4 kcal while for *p*-PhSiMe$_2$ and *p*-PhS the rates of rotation are too slow to measure; *p*-cyclopropyl lowers the barrier. Finally, with *p*-thiomethyl the benzyl anion is too unstable to study with NMR methods. The straightforward character of these results is ascribed to the heavy substitution on the benzyl carbon of **5**.

Introduction

Questions which concern the structure and behavior of π conjugated organolithium compounds include the charge distribution[1-6] as modified by the ionic character of the carbon–lithium bond[7,8] and, if ions are present, the nature of the ion pairs.[9,10] These matters have been extensively investigated with the methods of NMR spectroscopy.[1-6] NMR results for as seemingly innocuous a species as benzyllithium are complicated and hard to interpret. They vary with temperature, solvent, and concentration[11,12] apparently because the several effects, listed above, all contribute to the chemical shifts. As a result a bewildering array of structures have been proposed for benzyllithium under different conditions. For instance, the variation with solvent of the ^{13}C benzyl carbon NMR shift was ascribed to changes in hybridization.[11,12]

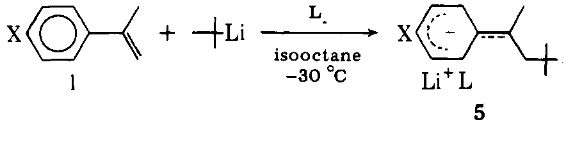
We were interested in finding a lithium compound which could be prepared in pure form and which behaves spectrally in a simply interpretable manner, i.e., one wherein a single effect dominates the shifts. The system which we decided to investigate in some detail is the series of hindered *tert*-benzyllithium compounds which may be prepared in high yields (see below) by the 1:1 addition of *tert*-butyllithium to α-methylstyrenes, essentially the initiation step of anionic styrene polymerization.[15] We previously found these species to behave spectrally like loose ion pairs, and their NMR line shapes were utilized to measure barriers to rotation about the ring benzyl bond.[13]

This paper concerns the preparation of some substituted *tert*-benzyllithium compounds, their chemistry, charge distributions, and barriers to rotation. The use of *tert*-benzyltin compounds was investigated. It will be shown how electron-accepting substituents increase the barriers to rotation via ground-state stabilization. Sulfur-bearing substituents show unusual effects. An example of steric acceleration of rotation will be given.

Results and Discussion

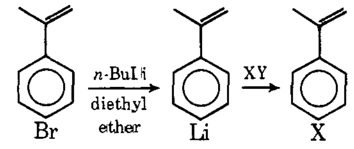
Substituted α-methylstyrenes were prepared by coupling 4-lithio-α-methylstyrene with the appropriate electrophile, Table I, or by dehydration of the corresponding cumyl alcohol, Table II. Precursors of these starting materials were prepared by standard methods; where these differ from the literature the procedure has been included in the Experimental Section. NMR data, both ^{1}H and ^{13}C, for the products are summarized in Table III. It is seen that the original assignment for ^{13}C chemical shifts in α-methylstyrene[19] has been reversed, based on new ^{13}C NMR data for 4-deuterio-α-methylstyrene. This has very weak absorption at 127.4 ppm (it is present in α-methylstyrene) and the resonance at 125.6 ppm appears as a 1:1:1 triplet, $J(^{13}C_oD) \simeq 1.0$ Hz. Since $J(^{13}C_oH_m)$ is ca. 7.4 Hz in benzene[20] and the corresponding value for α-methylstyrene is 7 ± 0.2 Hz, the assignment of the resonances at 125.6, 127.4, and 128.3 ppm to the ortho, para, and meta carbons, respectively, is unequivocal.

The central reaction utilized in this work is the 1:1 addition of *tert*-butyllithium to α-methylstyrenes in hydrocarbon solvents in the presence of amines and ethers, L, to form stable solutions of *tert*-benzyllithium compounds, **5**.[13,14] The course



(1)

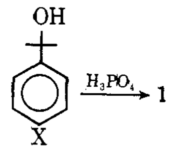
Table I



3 2 1

XY	X		ref
$(CH_3)_3SiCl$	$(CH_3)_3Si$	**1b**	16
$(CH_3)_3GeBr$	$(CH_3)_3Ge$	**1d**	16
$(CH_3)_3SnCl$	$(CH_3)_3Sn$	**1e**	16
CH_3SSCH_3	CH_3S	**1f**	17
PhSSPh	PhS	**1g**	

Table II



4

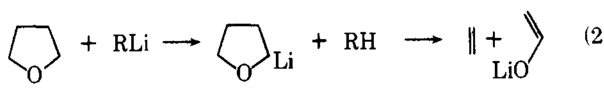
X		ref
cyclopropyl	1h	18
Ph	1i	17

of reaction was monitored with NMR as well as by GC separation of the products from silylation and hydrolysis of **5**. Typical results using a series of α-methylstyrenes are listed in Table IV.

The course of reaction 1 and the stability of the product are influenced by ligand and substituents. Generally, when reaction is incomplete, NMR indicates considerable metalation of ligand. However, *N*-methylpyrrolidine and 1,2-dipyrrolidylethane, both good catalysts for (1), were found to be unreactive to *tert*-butyllithium, even at 60 °C over 2 h.

In general the amine complexes of these *tert*-benzyllithium compounds are quite stable up to 100 °C, regardless of para substituent, but show wide differences in solubility, which does depend on substituent. The *N,N,N′,N′*-tetramethylpropylene-1,3-diamine and *N,N,N′,N′*-tetramethylmethylenediamine complexes of **5a** are insoluble in isooctane. These ligands evidently do not form cyclic bidentate complexes with lithium compounds, as does TMEDA,[21] producing instead insoluble polymeric complexes.

The THF complexes of *tert*-benzylic lithiums are all quite soluble in isooctane but vary greatly in stability. The more stable THF complexes with *p*-X = $(CH_3)_3Si$, $PhSi(CH_3)_2$, $Ge(CH_3)_3$, PhS, and Ph have half-lives at 90 °C of <40 min; those which deprotonated THF at lower temperature include *p*-X = H and cyclopropyl, $t_{1/2}$ ~45 min at 45 °C. A more quantitative order of carbanion stability comes from rotational barriers, to be described later. Where the THF complexes of *tert*-benzyllithiums are unstable, they decompose by deprotonating and cleaving THF, as can be observed in NMR spectra of the organometallic solutions, where RLi represents **5** or *tert*-butyllithium.

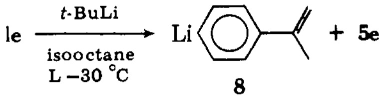


(2)

6 7

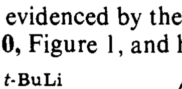
Compound **5b** is formed rapidly at −30 °C in the presence of dioxane. On warming to 0 °C, decomposition of **5b** was complete in a few minutes as observed by fading of the color and formation of hydrolysis product. Formation of **5b** is also rapid in the presence of 1,2-dimethoxymethane at −30 °C but on warming the solution to 0 °C (10 min) decomposition of **5b** was complete.

While the 1:1 addition of *tert*-butyllithium to α-methylstyrenes is quite general, there are exceptions. For example, *p*-trimethylstannyl **1** on treatment with RLi in the presence of TMEDA or THF underwent mainly cleavage of the Me_3Sn group with little addition. In contrast, addition to the acyclic double bond is the major reaction in the presence of diethyl ether. Compound **2**, as described above, was also prepared by halogen lithium exchange from 4-bromo-α-methylstyrene. In neither of these procedures has any lithium compound, **9**, been detected, i.e., not by addition to **2** nor by cleavage of **5e**. Evidently, **9** must be an unstable species.



8

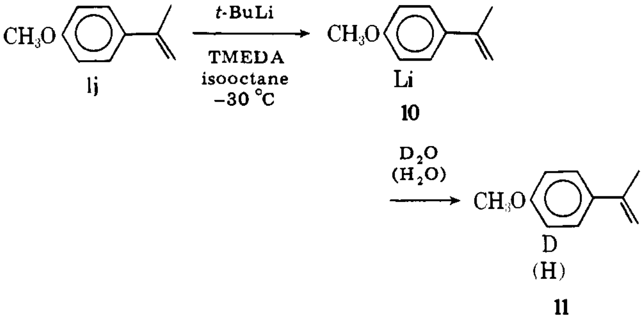
X = $(CH_3)_3Sn$
L = THF or TMEDA 80% 20%
L = diethyl ether 10% 90%



9

The preference for addition in the presence of ether also applies to **1f** (X = CH_3S). A *p*-CH_3S group would be expected to stabilize a benzyllithium compound.[23,24] Actually treatment of **1f**, X = CH_3S, with *tert*-butyllithium in the presence of TMEDA or THF gave only intractable gums. However, when ether was used as ligand, hydrolysis (D_2O) of the reaction mixture revealed that 75% addition to the double bond had taken place. Also, it is interesting that, while **5f** is stable in the presence of diethyl ether, addition of THF to this solution immediately gives hydrolysis products. These results for **5f** stand in stark contrast to the stabilizing influence of a *p*-thiophenyl in **5g**.

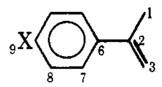
Finally, three α-methylstyrenes failed to undergo *tert*-butyllithium addition. They are *p*-bromo-, *p*-nitro-, and *p*-methoxy-α-methylstyrene, respectively. The first two compounds gave gums, while the latter underwent metalation at the meta position as evidenced by the NMR spectrum of the lithium compound **10**, Figure 1, and hydrolysates, Figure 2.



Electrophilic Capture Processes. To characterize the 1:1 adducts of *tert*-butyllithium with α-methylstyrenes, we utilized their products with typical electrophile capture reagents such as D_2O, trimethylsilyl chloride, and trimethylstannyl chloride; see **12–14**. NMR data for three typical products are listed in Table V. An extensive list of shifts in all hydrolysates is found in Table VI. Ring shifts are assigned on the basis of the known effects of substituents on aromatic ring shifts.

The results described above led to an alternative route to *tert*-benzylic lithium compounds: cleavage[26] of the corresponding tin compounds with *tert*-butyllithium. The reaction, run typically in isooctane or cyclopentane at 25 °C, requires the presence of a ligand (see Table VII) but fails entirely with diethyl ether or lithium *tert*-butoxide. The deactivating in-

Table III. ^{13}C NMR Chemical Shifts of Styrenes[a]



1

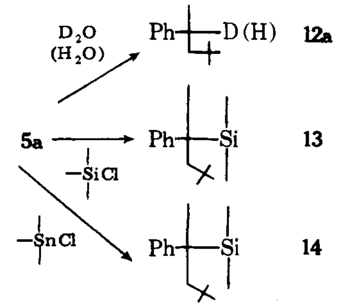
X no.	H **1a**	$(CH_3)_3Si$ **1b**	$PhSi(CH_3)_2$ **1c**	$(CH_3)_3Ge$ **1d**	$(CH_3)_3Sn$ **1e**	CH_3S **1f**	PhS **1g**	c-Pr **1h**	Ph **1i**	CH_3O **1j**	Br **1k**
1	21.8	21.8	21.7	21.8	21.7	21.7	21.7	21.8	21.7	21.8	21.6
2	143.3	143.3	143.2	143.3	143.3	142.5	142.5	143.3	142.8	142.6	142.2
3	112.4	112.6	112.7	112.4	112.4	111.9	112.7	111.4	112.5	110.6	113.0
6	141.4	141.7	141.9	141.6	141.4	138.1	140.1	138.5	140.2	133.8	140.1
7	125.6	124.9	124.9	125.1	125.1	126.5	126.3	125.4	125.9	126.6	127.1
8	128.3	133.4	134.2	132.9	135.8	125.9	130.9	125.5	126.9	113.6	131.3
9	127.4	135.9	137.2	141.3	141.2	137.7	134.7	143.0	140.1	152.9	121.4
X-CH_3		−1.1	−2.4	−1.8	−9.6	15.8				55.1	
X-10			138.2				135.9	15.2	140.8		
X-11			134.2				130.9	9.2	126.9		
X-12			127.8				129.2		128.8		
X-13			129.1				127.0		127.2		

[a] 22.63 MHz, $CDCl_3$ solution, 33 °C, ppm/Me_4Si.

Table IV. Formation of *tert*-Benzyllithium Compounds in Isooctane

compd	X	*n* × L[a]	sol[b]	yield, %	stability,[c] °C
a	H	1 × TMEDA[d]	S	95	90
a	H	1 × TMMDA[e]	I	90	90
a	H	1 × TMPDA[f]	I	90	80
a	H	2 × *N*-methyl-pyrrolidine	S	95	100
a	H	2 × THF	S	95	45
b	$Si(CH_3)_3$	1 × TMEDA	S	90	116
b	$Si(CH_3)_3$	2 × THF	S	90	107
b	$Si(CH_3)_3$	2 × diethyl ether	S	71	95
b	$Si(CH_3)_3$	dioxane	S	75	0
b	$Si(CH_3)_3$	$(CH_3O)_2CH_2$	S	95	0
c	$PhSi(CH_3)_2$	1 × TMEDA	S	95	>115
c	$PhSi(CH_3)_2$	1 × THF	S	95	>115
d	$Ge(CH_3)_3$	1 × TMEDA	S	95	>115
d	$Ge(CH_3)_3$	2 × THF	S	95	>100
e	$Sn(CH_3)_3$	2 × diethyl ether	S	90	
f	SCH_3	2 × diethyl ether	S	75	40
f	SCH_3	1 × TMEDA	S	<5	10
g	PhS	1 × TMEDA	S	95	90
g	PhS	2 × THF	S	90	25
h	cyclopropyl	1 × TMEDA	S	90	95
h	cyclopropyl	2 × THF	S	90	60
i	Ph	2 × THF	S	95	100
i	Ph	1 × TMEDA	S	97	95

[a] L = ligand. [b] Solubility. [c] Half-life of 40 min at given temperature. [d] *N,N,N′,N′*-Tetramethylethylenediamine. [e] *N,N,N′,N′*-Tetramethylmethylenediamine. [f] *N,N,N′,N′*-Tetramethyl-1,3-propylenediamine.



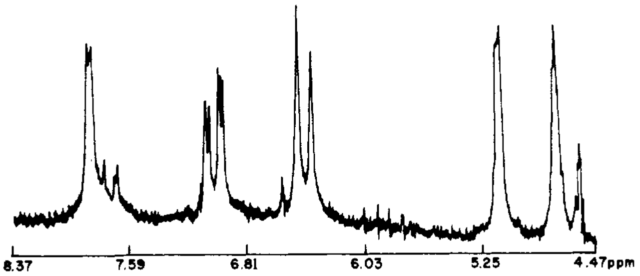


Figure 1. NMR spectrum, aromatic hydrogens of **10**, 1 M in TMEDA-isooctane, 90 MHz, 27 °C.

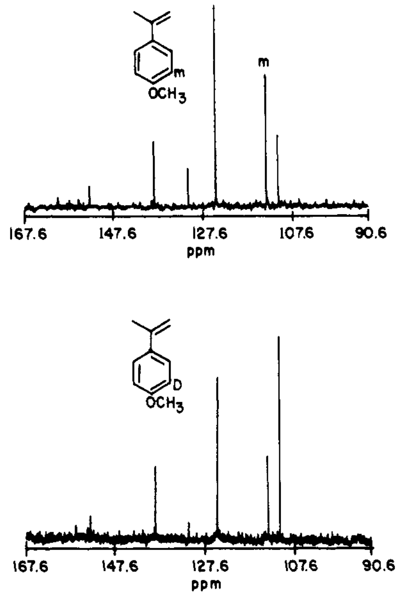
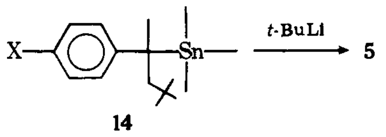


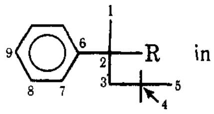
Figure 2. Carbon-13 NMR spectra, 22.63 MHz, 33 °C. Top: 4-methoxy-α-methylstyrene. Bottom: 3-deuterio-4-methoxy-α-methylstyrene, both 20% by volume in $CDCl_3$.



fluence of lithium alkoxides on alkyllithiums is already well known.

The benzylic lithium compounds generated by the cleavage reaction are identical with those produced by addition reactions to styrenes, as revealed by NMR of the resulting organometallic solutions and the results of electrophilic capture reactions.

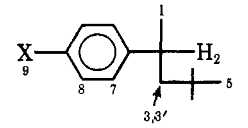
NMR Spectra of *tert*-Benzylic Lithium Compounds. In this section it is shown how NMR data for the benzylic lithium

Table V. NMR Parameters  in $CDCl_3$, δ ppm/Me_4Si, *J*, 33 °C

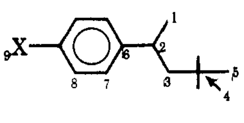
R, no.	D, **12a** δ $^1H^a$	D, **12a** δ $^{13}C^b$	$Si(CH_3)_3$, **13** δ ^1H	$Si(CH_3)_3$, **13** δ ^{13}C	$Sn(CH_3)_3$, **14** δ ^1H	$Sn(CH_3)_3$, **14** δ ^{13}C	$J(^{13}C,Sn)^c$
1	1.22	25.9	1.49	20.5	1.74	23.0	18.9
2		37.0		34.2		35.1	
3	1.50 1.73	52.3	1.59 2.21	46.3	1.80 2.68	50.3	15.8
4		31.3		31.6		36.0	66.0
5	0.80	30.2	0.79	32.6	0.74	32.3	
6		149.6		147.4		149.8	18.5
7	7.22	127.1	7.19	126.4	7.04	124.6	25.6
8		128.3		127.3	7.10	127.8	14.0
9		125.6		123.6	7.04	122.9	16.7
R			−0.15	−4.0	−0.10	−10.5	294.5^d 299.5
$J_{3,3'}{}^e$	−14.2		−14.9		−16.0		

[a] ^1H spectra obtained at 100 MHz. [b] ^{13}C spectra obtained at 22.63 MHz. [c] Average of $J(^{13}C, ^{117}Sn)$ and $J(^{13}C, ^{119}Sn)$ due to limited resolution. [d] Top, $J(^{13}C, ^{117}Sn)$; bottom, $J(^{13}C, ^{119}Sn)$. [e] Hertz.

Table VI. NMR Parameters[a]



12[c]



12[d]

X no.	H **a**	$(CH_3)_3Si$ **b**	$PhSi(CH_3)_2$ **c**	$(CH_3)_3Ge$ **d**	CH_3S **f**	PhS **g**	c-Pr[b] **h**	Ph **i**
				A. ^1H NMR				
δ(1)	1.22	1.19	1.22	1.20	1.19	1.21	1.19	1.20
δ(2)	2.78	2.77	2.79	2.76	2.78	2.80	2.78	2.77
δ(3,3′)	1.73 1.50	1.58	1.58	1.58	1.58	1.58	1.58	1.58
δ(5)	0.80	0.81	0.81	0.81	0.81	0.81	0.81	0.81
δ(7,8)	7.22	7.20–7.50	7.10–7.50	7.10–7.30	7.17	7.1–7.4	6.9–7.1	7.0–7.4
δ(9-CH_3)		0.24	0.53	0.34	2.39			
δ(9-Ph)			7.1–7.5			7.1–7.4		7.0–7.4
$J_{1,2}$	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
$J_{1,3}$								
$J_{3,3}$	−14.0	−14.0	−14.0	−14.0	−14.0	−14.0	−14.0	−14.0
				B. ^{13}C NMR[e]				
1	25.9	25.7	25.6	25.7	25.8	25.7	25.8	25.7
2	37.0	36.8	36.7	36.7	36.4	36.5	36.5	
3	52.3	52.1	52.1	52.1	52.1	52.0	52.4	52.3
4	31.3	31.3	31.3	31.3	31.3	31.3	31.3	31.3
5	30.2	30.2	30.2	30.2	30.2	30.1	30.2	30.2
6	149.6	150.3	150.6	149.8	146.9	149.2	147.0	148.4
7	127.1	126.5	126.6	126.7	127.3	128.0	127.0	127.5
8	128.3	133.4	134.1	132.9	127.6	129.8	125.9	126.9
9	125.6	137.0	134.6	139.0	134.9	134.1	141.0	138.7
$X(CH_3)_n$		−1.0	−2.2	−1.7	16.4			
X-10[f]			138.6			137.0	15.1	140.5
X-11			134.3			132.1	8.7	126.8
X-12			127.7			128.9		128.7
X-13			128.9			126.3		127.2

[a] Solvent $CDCl_3$, δ, ppm/Me_4Si; *J*, Hz. [b] Cyclopropyl CH, 0.65; CH_2, 1.78. [c] For ^1H NMR. [d] For ^{13}C NMR. [e] Hydrolysates, 23.63 MHz, $CDCl_3$ solution, 33 °C. [f] Phenyl numbered from ipso carbon.

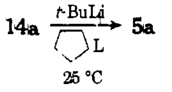
compounds provide significant information on interaction with substituents and the character of ion pairing.

^1H NMR data for the series of *tert*-benzylic lithium compounds in isooctane with TMEDA or THF are presented in Table VIII. These spectra were almost first order such that the shifts could be assigned by inspection. All spectra were analyzed using computer programs LACOON[27] and DNMR-3[28] and the NMR parameters iterated to fit the data.

The assignment of the ortho- and meta-ring resonances was established with decoupling experiments. Finally, it was assumed that the steric interaction between a neopentyl group and an aromatic proton contributes a deshielding increment[29] to the shift of the affected hydrogen. Thus, the downfield ortho and upfield meta resonances come from vicinal hydrogens on the same side as neopentyl.

The ring proton shifts for all the reagents listed in Table VIII

Table VII. Cleavage Reactions of Benzyltin Compounds



$$\mathbf{14a} \xrightarrow[\text{L, 25 °C}]{t\text{-BuLi}} \mathbf{5a}$$

L	equiv	yield **5a**, %
		<1
THF	2	>98
TMEDA	1	>98
diethyl ether	2	<1
diethyl ether	excess	<1
$(CH_3)_3COK$	1	80
$(CH_3)_3COLi$	1	<1

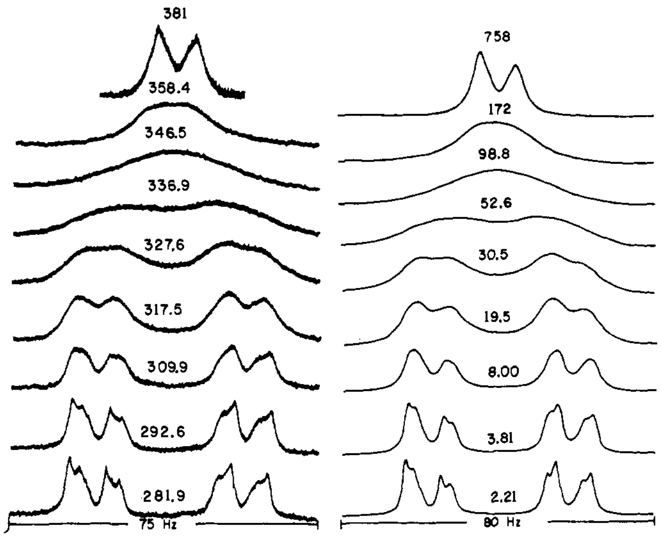


Figure 3. Left: NMR line shapes, ortho hydrogens of **5h**, 1 M in TMEDA-isooctane, at different temperatures. Right: calculated line shapes, with rate constants, s^{-1}.

are significantly shielded with respect to the corresponding hydrolysates, indicating effects due to increased electron density,[30] and follow the general order δ_p δ_o δ_m in the deshielding direction. Below 300 K within each reagent all four ortho and meta (with respect to the benzyl carbon) hydrogens are magnetically nonequivalent.

In general electron-acceptor para substituents cause measurable deshielding of the ortho hydrogens (phenyl, organosilyl, organogermanyl) compared to *p*-X = H, implying migration of charge into the substituents. This is most evident in the case of X = Ph from the proton shielding in the substituent (1.1 ppm at H_{13}) compared to hydrolysate. Such effects are discernible for X = $PhSi(CH_3)_2$ but not observed for **5g**, X = PhS.

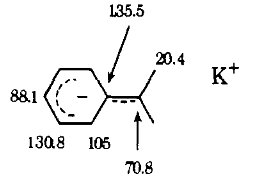
It is also interesting that substituents have less influence on the hindered ortho hydrogen shift compared to the unhindered hydrogen, possibly the result of neopentyl forcing the C-H bond from the molecular plane.

Below 300 K all these NMR parameters for the *tert*-benzylic lithium compounds appear to be independent of temperature, ligand, and concentration. This result supports our earlier proposal that the reagents exist as loose ion pairs.[13]

Since carbon-13 shifts are so sensitive to the π-electron density,[31] it was felt that the effects proposed from the ^1H NMR data could be clearly confirmed in a quantitative manner with ^{13}C NMR data. Some typical results displayed in Figure 3 show the wide range of π-carbon shifts observed for these benzylic lithium reagents, considerably shielded with respect to the neutral hydrolysates. Further, these spectra show all four ortho and meta carbons to be magnetically nonequivalent, as in the case of the ^1H NMR data; see Table IX.

Carbon-13 shifts were assigned using a combination of single-frequency off-resonance decoupling (SFORD) and selective proton decoupling experiments. In this way it was established that the low-field ortho and high-field meta carbon resonances represent carbons on the same side as neopentyl.

In general these ^{13}C NMR shifts in **5** do not vary significantly when different ligands are used. Furthermore, the results for **5a** in the presence of THF or TMEDA are even not much different from the ^{13}C NMR shifts of cumylpotassium in THF, **15**. This again argues strongly that the salts exist as loose ion pairs as indicated less clearly by the ^1H NMR data.



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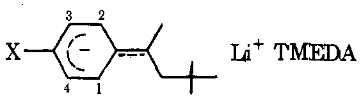
To assess the influence of charge on shift in an ion one must estimate neutral model shifts taken from a compound whose framework most closely resembles that of the ion in question. In this work, reasonable neutral model shifts for the ring carbons of **5a–d,g–i** are taken from those of the corresponding hydrolysates **12a–d,g–i**; a neutral sp^2 carbon shift for C_2 is chosen to be 143 ppm, close to the C_α shift in a variety of

Table VIII. ^1H NMR Parameters, in Isooctane, 33 °C

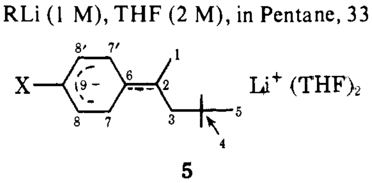


5

X compd	$(CH_3)_3Si$ **5b**	$PhSi(CH_3)_3$ **5c**	$(CH_3)_3Ge$ **5d**	$(CH_3)_3Sn$ **5e**[c]	PhS **5g**[d]	c-Pr **5h**[e]	Ph **5i**
$\delta(1)$[a]	5.39	5.39	5.33	5.36	5.20	5.16	5.43
$\delta(2)$	5.64	5.63	5.59	5.65	5.45	5.53	5.71
$\delta(3)$	6.17	6.17	6.11	6.11	6.00	5.99	6.51
$\delta(4)$	6.27	6.28	6.21	6.20	6.10	6.07	6.59
$J_{1,2}$[b]	2.56	2.49	2.62		2.5	2.35	2.40
$J_{1,3}$	−0.05	0.25	−0.25		−0.10	−0.07	−0.10
$J_{1,4}$	9.04	8.93	9.05		9.0	8.95	8.75
$J_{2,3}$	9.08	9.14	9.08		9.0	9.10	8.80
$J_{2,4}$	−0.25	−0.24	−0.25		−0.10	−0.07	−0.15
$J_{3,4}$	1.81	1.99	1.82		2.0	−2.34	1.94

[a] ppm/Me_4Si. [b] Hertz. [c] Ether-pentane, 27 °C. [d] THF-pentane. [e] 11 °C.

Table IX. ^{13}C NMR Shifts (ppm), Benzyllithiums RLi (1 M), THF (2 M), in Pentane, 33 °C



5

X	H	(CH$_3$)$_3$Si	PhSi(CH$_3$)$_2$	Ge(CH$_3$)$_3$	PhS	c-Pr	Ph	H[a]
no.	**5a**	**5b**	**5c**	**5d**	**5g**	**5h**	**5i**	**5a**
1	22.3	22.3	22.4	22.0	22.7	22.1	22.6	22.4
2	71.0	74.6	76.1	75.2	77.0	73.1	80.3	76.7
3	49.5	49.3	49.3	49.0	49.8	49.3	49.7	49.0
4	36.6	36.1	36.1	36.1	36.1	36.3	36.0	36.0
5	30.3	30.3	30.4	30.3	30.3	30.2	30.3	30.3
6	139.1	138.4	137.9	137.0	138.4	135.9	138.1	135.4
7	105.3	107.0	107.4	106.7	108.1	103.2	108.8	104.0
7'	107.4	108.5	108.8	108.0	109.9	105.3	110.5	106.0
8	128.1	131.8	133.3	132.4	135.9	127.3	124.3	128.2
8'	127.2	132.9	132.3	131.4	134.8	126.6	123.5	127.2
9	86.7	89.6	86.5	91.7	79.4	99.5	101.4	85.0
X(CH$_3$)$_n$		0.1	−1.5	−1.2				
X-10			144.5		150.8	14.2	142.6	
X-11			133.9		124.1	5.8	116.9	
X-12			126.9		127.4		127.8	
X-13			127.1		121.7		113.3	

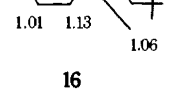
[a] With 1 M TMEDA.

α-methylstyrenes, as listed above. Compared to the neutral model shifts the ortho, para, and benzyl carbons in **5** are all considerably shielded while the meta carbons have shifts quite similar to those in the models.

Comparing ^{13}C NMR shifts in the para-substituted benzyllithium to those for *p*-X = H, one sees with few exceptions deshielding at the ortho, para, and benzyl carbons when the substituent is an electron acceptor. This implies some accumulation of electron density on the substituent. This is confirmed by the shifts in the substituents themselves. Comparing the lithium compounds, Table IX, with hydrolysates, Table VIB, in **5i** (*p*-X = Ph) there is shielding at the ortho, meta, and para carbons of *p*-Ph implying that 20% of the negative charge is located in the substituent phenyl. When *p*-X = PhSi(CH$_3$)$_2$ (**5c**) there is only 5.9-ppm deshielding at C$_{10}$, indicative of some negative charge on silicon. In **5g** (X = PhS), compared to hydrolysate, there is a downfield shift at C$_{10}$ of 13.8 ppm. This is similar to the increment at COH going from phenol to phenoxide, 13.8 ppm deshielding.[32] Deshielding is also observed in the CH$_3$Si and CH$_3$Ge ^{13}C NMR shifts in the lithium compounds **5b** and **5d** compared to hydrolysates.

Subtracting the benzyllithium ^{13}C NMR shifts, Table IX, from the neutral model shifts, Table VIB, gives the values in Table X. Summing these shift increments provides the total shift which attends the addition of one negative charge to the hypothetical neutral model. For all but the last anion the values are quite close to the 160–165 ppm/e observed previously.[31] The last case, *p*-X = Ph, could be in error owing to an incorrect choice of the neutral model compound. In particular, the rings are probably not coplanar in the hydrolysate **12i** used as model.

Altogether, the above treatment cannot be used to obtain the charges in the anion since the model need not be uniformly neutral. If it is indeed neutral, then the shifts imply a Hückeloid π-electron distribution, say for **5a**, as shown by **16**.



16

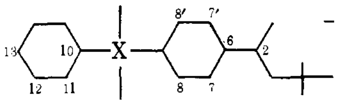
In the above procedure, we started by assuming that the shifts come from a linear combination of increments due to substituents in the neutral models and contributions due to charge. The changes in shifts (substituted vs. unsubstituted) are qualitatively in accord with electron accumulation on the stabilizing substituent. The total change in shift (from neutral model to anion) is consistent with most known experimental relationships of charge with shift.[31] This means that the benzyl carbon is also part of the π system and does not undergo changes in hybridization as proposed for benzyllithium itself.[11,12] Thus, we would like to suggest that the simpler behavior of the *tert*-benzyllithium compounds, compared to benzyllithium, arises from the heavy substitution at *C*-benzyl. This has the effect of rendering formation of a tight ion pair or carbon–lithium covalency energetically prohibited in the ground state.

Barriers to Rotation in Benzylic Lithium Compounds. In this section it will be shown how NMR line shapes for benzyllithium compounds provide rate data for rotation and ultimately information on ground-state energies.

Figure 3 displays the ortho proton NMR line shapes for **5h** (*p*-cyclopropyl) in isooctane containing 1 equiv of TMEDA. Below 280 K the ortho hydrogens give rise to the AB part of an ABXY system. Further cooling below 280 K causes very little change in the ^{1}H NMR spectrum; i.e., the NMR parameters are essentially invariant with temperature. With increasing temperature the system exhibits the typical behavior associated with progressively faster rotation[13,14] about the benzyl-ring bond; i.e., the ortho proton resonance broadens, coalesces, and sharpens to become the AA' part of an AA'XX' spectrum. Varying the concentration of **5h** gave essentially the same results as before. One can conclude that the rotation process is first order in contained *tert*-benzyllithium compound. All species studied behaved in this way.

NMR line shapes for the ring hydrogens of **5h** (*p*-cyclopropyl) were calculated using the parameters given above as a function of the rate of rotation[28,33,34] using the **PI** method.[34] Comparison of experimental with theoretical spectra (see Figure 3, right side) gave rate measurements and activation parameters. When these experiments were carried out at different concentrations of **5h**, the results were essentially unchanged within experimental error. Figure 4 shows a typical

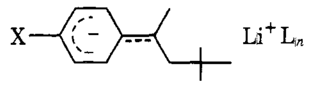
Table X. $\delta^{model} - \delta^{anion}$ (ppm)[a]



subst carbon	H	$(CH_3)_3Si$	$(CH_3)_3Ge$	$PhSi(CH_3)_2$	PhS	c-Pr	Ph
2	72	68.4	67.8	66.9	66	69.9	62.7
6	10.5	11.9	12.8	12.7	10.8	11.1	10.3
7	21.8	19.5	20	19.2	19.9	23.8	18.7
7′	19.7	18.0	18.7	17.8	18.1	21.7	17.0
8	2.0	1.6	0.5	0.8	−6.1	−1.4	2.6
8′	1.1	0.5	1.5	1.8	0.7	−0.7	3.4
9	38.9	47.4	47.3	48.1	54.7	41.5	37.3
10				−5.9	−13.8		−2.1
11				0.4	6.0		9.9
12				0.8	1.5		0.9
13				1.8	2.2		13.9
$\sum^b$	162.3	167.3	168.6	165.6	167.6	165.9	185.3

[a] Positive increments are shielded. [b] Sum of shift increments at all sp^2 carbons.

Table XI. Activation Parameters for Rotation, *tert*-Benzyllithiums in Isooctane



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X	L (equiv)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{300K}, s^{-1}
H[a]	TMEDA (1)	18.7 ± 0.4	0.3 ± 1	0.11
$(CH_3)_2CH$[a]	TMEDA (1)	18.5 ± 0.4	4.6 ± 1.3	2.1
$(CH_3)_3C$[a]	TMEDA (1)	18.5 ± 0.5	5.2 ± 1.3	1.7
$(CH_3)_3Ge$	TMEDA (1)	18.2 ± 0.7	4.7 ± 0.7	0.027
cyclopropyl	TMEDA (1)	11.8 ± 0.5	−15.5 ± 5	7.1
$(CH_3)_3Si$	TMEDA (1)	22.0 ± 1.5	3.4 ± 1.5	8×10^{-5}
$PhSi(CH_3)_2$	TMEDA (1)	>26		
PhS	TMEDA (1)	>26		
Ph	TMEDA (1)	>26		
18	TMEDA (1)	15.4 ± 0.5	−5.2 ± 1.6	2.5
18	THF (2)	11.9 ± 0.4	−10.0 ± 1.1	80

[a] Reference 13.

Eyring plot. All activation parameters for rotation in the species **5** studied in this work and elsewhere are collected in Table XI.

Before commenting on the above results it is useful to describe a possible mechanism to account for the rotational behavior of the benzyllithiums, **5**.

All existing molecular-weight data show benzyllithium to be monomeric in the presence of tertiary amines[35] or ethers.[8,36] One can assume that this applied also to salts **5**.

It has already been noted that rotation in some benzyllithiums,[13] phenylallyl,[37] and naphthylmethyl[38] metal compounds, respectively, depends on the nature of the counterion. That implies that the counterion is involved in the transition state for rotation. As discussed above, in the ground state these species, **5**, exist as separated ion pairs (most likely monomeric) containing conjugated anions, and lithium is complexed to the ligand. For rotation to occur the benzyl carbon must acquire tetrahedral character. The system would be stabilized by simultaneous development of partial covalency from benzyl carbon to lithium. This would be accompanied by some decrease in the interaction of lithium with ligand. Thus, it is proposed that rotation in the separated pairs, **5**, is assisted by electrophilic attack of lithium at the benzyl carbon. The system rotates via a covalent transition state, Scheme I. The process described in Scheme I would be critically influenced by substituents on the ring, by different ligands, and by steric effects due to the structure about the benzyl carbon.

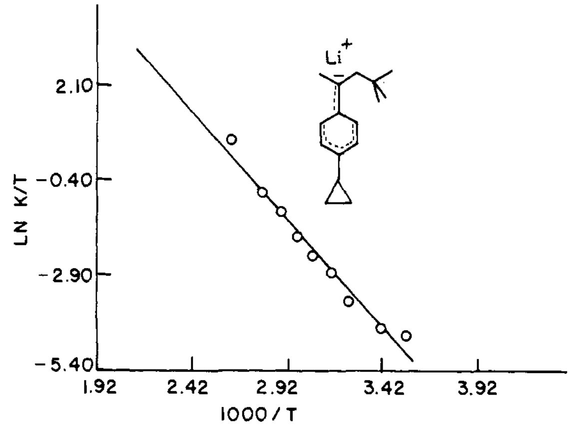


Figure 4. Eyring plot for rotation of **5h**, 1 M in TMEDA.

As seen in Table XI, $\Delta H^{\ddagger}$ for rotation in **18** (prepared from 1-phenylcyclopentene and *tert*-butyllithium) in the presence of THF is 3.5 kcal/mol less relative to **18** complexed to TMEDA. In similar fashion Brownstein and Worsfold[14] reported the barrier of **5a**-THF to be 14 kcal/mol compared to 18 kcal/mol reported by using TMEDA.[13] Effects of different ligands on rotational rates in **5b** at 38 °C are listed in Table XII. These rates vary with ligand to a small but measurable

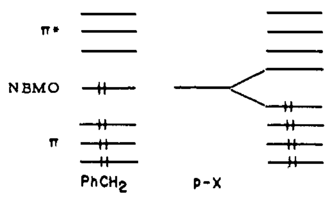
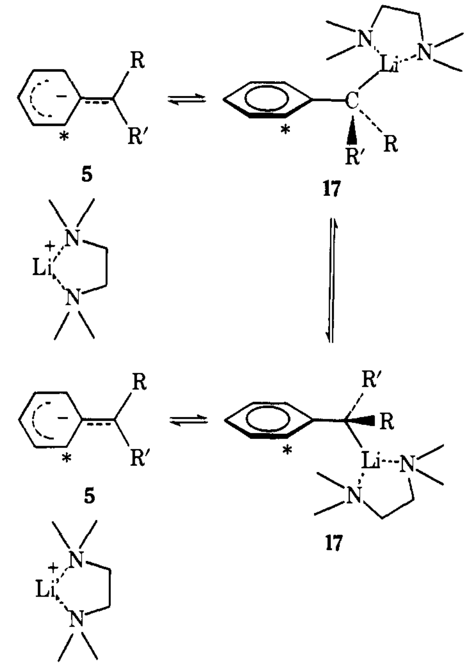
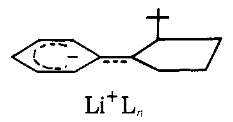


Figure 5. Interaction of para-electron-deficient substituent with benzyl anion.

Scheme I



degree, a result which might arise from small differences in ion pairing.



18

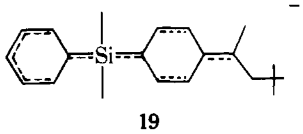
Substituents at the 4 position of **5** exert significant effects on $\Delta H^{\ddagger}$ for rotation. When *p*-X is alkyl or $(CH_3)_3Ge$, the barriers differ little from that for **5a** (X = H). The substituents, first mentioned, are concluded to interact weakly with the rings in both the ground state (benzyl anion) and the transition state (phenyl) for rotation.

In contrast to the first three entries in Table XI, when X = $(CH_3)_3Si$, $\Delta H^{\ddagger}$ increases by 4 kcal/mol compared to X = H while thiophenyl, phenyldimethylsilyl,[39] and phenyl all cause the rates of rotation to be too slow to measure using NMR line shape methods. Since these species all carry electron acceptors, they would be expected to substantially stabilize the ground state, benzyl anion. This would result from mixing substituent orbital, X, with the NBMO of benzyl anion (see Figure 5), stabilization being twice the matrix element $H_{\mathrm{X,NBMO}}$. By comparison, the interaction of substituent with transition state (modeled as a substituted benzene) would be much weaker. Therefore, the increases in barrier where X is an electron acceptor, compared to X = H, alkyl, are due mainly to *ground-state stabilization*. Since these NMR line shape measurements were almost all carried out with the same solvent and ligand, one can assume a similar degree of benzyl carbon-lithium covalency in the transition states for rotation throughout the series. Then the increased barriers for **5b,c,g,i** should be proportional to the matrix elements $H_{\mathrm{X,NBMO}}$, just described, where X is the electron-deficient substituent, Si, S, or C_1 of phenyl.

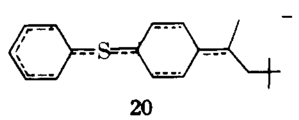
Table XII. Effect of Ligand on the Rate of Rotation of **5b**

ligand	k, s^{-1}	ligand	k, s^{-1}
triethylamine	3.5 ± 1	THF	40 ± 8
trimethylamine	15 ± 4	diethyl ether	20 ± 4
TMEDA	10 ± 3		

The slow rotation in **5e**, X = $PhSi(CH_3)_2$, compared to **5b**, X = $Si(CH_3)_3$, implies conjugation into the substituent phenyl ring, **19**. In similar fashion the stability of **5g**, X = PhS, and its slow rate of internal rotation compared to **5f**, X = CH_3S, which is quite unstable, implies conjugation in **5g** through sulfur, **20**.



19



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Compared to the other systems studied, **5h** (X = cyclopropyl) exhibited a lower barrier to rotation than **5a** (X = H). From its para σ value (Hammett)[18,40] it appears that a *p*-cyclopropyl group slightly inhibits the ionization of benzoic acid. Cyclopropylcarbinyl anions are known to be unstable with respect to their rearrangement products.[41] The reason for this is not widely understood. However, the ground state of **5h** is a vinylogous analogue of cyclopropylcarbinyl anion. It is probably destabilized, thus lowering the barrier to rotation. Possible interactions between the cyclopropyl group and aromatic ring in the transition state could stabilize the latter, thereby contributing further to a lower barrier of rotation.

Inspection of Table XI also shows that *p*-alkyl substituents increase the rate of rotation relative to **5a** (*p*-H). A similar effect was observed for 4-methyl-4'-deuteriodiphenylmethyllithium, wherein rotation of the tolyl group was observed to be faster than that of 4-deuteriophenyl.[42]

Compound **18**, a benzylic lithium nested in a five-membered ring, provides further insight into the rotation process. Inspection of models, following the mechanism for rotation proposed above, shows steric effects in the ground and transition states for rotation of **5a** and **18** to be nearly the same save for one major difference: compound **18** has severe steric interactions between *tert*-butyl and the π structure of the aromatic ring in the ground state. The lower barrier to rotation in **18** is consistent with destabilization of the ground state from steric interactions.

General Conclusions

The *tert*-benzyllithium compounds prepared and studied in this work behave like separated ion pairs. ^{13}C NMR shows the organic moiety in the ion pairs to be a conjugated benzyl with a near-Hückeloid charge distribution. In distinct contrast data for benzyllithium itself under different conditions show this species to exist within several different kinds of ion pairs. The simple uniform behavior of the set of species, **5**, can be best ascribed to the heavy substitution about *C*-benzyl which effectively renders tight ion pairing or bridged C, Li bonds energetically inaccessible.

The rotation about the ring-benzyl bond is concluded to proceed via a species or transition state with partial covalency from *C*-benzyl to lithium. A similar process was proposed to account for rotational rates in phenylallyl metal compounds.[37] The set of *tert*-benzyllithium compounds thus can assume two forms: the loose ion pair in the ground state and the covalently bonded transition state or high-energy intermediate. Variations among the barriers to rotation can be traced to differences in ground-state energies.

Experimental Section

Solvents. Tetrahydrofuran, ethyl ether, and dimethoxymethane were dried by preparing a Grignard, usually *n*-butylmagnesium bromide, solution. When the commerical ethers were too wet to allow Grignard preparation directly, prior distillation from calcium hydride eliminated this problem. Dioxane, glyme, and diglyme were distilled from calcium hydride and stored over lithium aluminum hydride. They were distilled from this reagent directly before use. *N,N,N′,N′*-Tetramethylethylenediamine, *N,N,N′,N′*-tetramethyl-1,3-propylenediamine, triethylamine, diethylcyclohexylamine, and *N*-methylpyrrolidine were fractionally distilled from potassium hydroxide pellets. The center cut was stored over calcium hydride and distilled from this reagent directly before use. Trimethylamine was generated from its hydrochloride salt by stirring the salt with potassium hydroxide pellets in mesitylene. The liberated amine was passed through two 10 by 1 cm cylindrical columns containing potassium hydroxide pellets and oxide lumps, respectively, then trapped in a calibrated cold finger at −78 °C. Pentane, cyclopentane, and 2,2,4-trimethylpentane (isooctane) were washed with concentrated sulfuric acid, water, and 10% bicarbonate solution, dried over anhydrous potassium carbonate, stored over lithium aluminum hydride, and distilled from this reagent directly before use. Benzene was dried by distilling 10% of its volume, discarding the distillate, adding calcium hydride, and distilling from calcium hydride directly before use. All solvents used in anion preparations and organometallic reactions were distilled under argon either directly into the reaction vessel or into a dry side-arm flask and transferred through syringes equipped with stopcocks and stainless steel needles. This equipment was baked at 120 °C for at least 1 h prior to use.

Apparatus. Syringes were Becton-Dickenson and Co. multifits or Hamilton gas tight. Stainless steel needles were from W. A. Butler. Syringe stopcocks were Becton-Dickenson MS01. NMR tubes were Wilmad 507-PP 5-mm o.d. for ^{1}H NMR and Wilmad 513-7PP 10-mm o.d. for ^{13}C NMR. Some carbon spectra of benzylic lithiums were obtained using Wilmad 513A-7PP 8-mm o.d. tubes. All product mixture analyses and separations by vapor-phase chromatography were done on a Varian Aerograph A-700. Columns were either a 5 ft by 0.5 in. 20% SE-30 on firebrick (column A) or a 15 ft by 0.25 in. 20% SE-30 on Chromosorb P (column B). Operations requiring an inert atmosphere were carried out in either a Kewaunee Scientific Equipment 2C281-20 glovebox or a Vacuum Atmospheres HE-43 glovebox. Continuous-wave proton spectra were obtained on the Varian A-60A (60 MHz), HA-100 (100 MHz), and Bruker HX-90 (90 MHz) NMR spectrometers. Some proton spectra were obtained in the Fourier transform mode on the Bruker HX-90 spectrometer. Carbon spectra were obtained on the Bruker HX-90 spectrometer at 22.63 MHz in the Fourier transform mode. Auxiliary equipment used in obtaining the Fourier transform spectra included a Nicolet BNC-12 computer containing 20 480 20-bit words of memory and a Diablo movable-head disk-storage unit. Disks were IBM low-density, 600K word capacity.

Variable-Temperature NMR Spectra of Benzylic Lithiums. NMR spectra used for the kinetic analysis of rotation in benzylic lithiums were obtained on the HA-100 or HX-90 spectrometers. The temperature of the gas stream was regulated by the Varian V-6040 temperature controller for the former instrument and the Bruker BS-100/700 temperature controller for the latter. The temperature in the probe was determined from the chemical-shift difference of ethylene glycol (temperature >40 °C) or methanol (temperature <40 °C) using the standard equation. At each temperature, three to five spectra were obtained. The homogeneity was maximized before each scan. The sweep width was 1 Hz/cm and the sweep time was 500 s. The spectra for **5h** were obtained using an 80-Hz sweep width (1.6 Hz/cm) generated by a Wavetek frequency unit. The temperature was determined before and after each set of measurements. If a temperature variation of greater than 2 °C had occurred, the spectral measurements were repeated.

Carbon-13 Spectra of Benzylic Anions. Solutions of benzylic lithiums were syringed into 8-mm o.d. NMR tubes fitted with stopcocks bearing ground-glass joints, degassed on the vacuum line by three freeze–thaw cycles and sealed off with a torch under dynamic vacuum. Teflon tape was wrapped around the 8-mm o.d. tube so that it fitted snuggly inside a 10-mm o.d. tube. Care was taken so that the smaller tube was centered inside the larger one. The annulus contained CDCl$_3$ for field-frequency lock. With these precautions the assembly spun inside the NMR probe with no discernible wobble. The experimental acquisition parameters were sweep width 5000 Hz (sampling interval 100 μs), delay time 200 μs (interval between pulse and acquistion of first data point), data table 16 384 points, and pulse width 4.0 μs (corresponds to a flip angle of 25°). All the carbon spectra of benzylic lithiums displayed in this work were the result of 1024 scans. Full proton decoupling was obtained with a center-band frequency of approximately 89.999 800 MHz modulated into a band-pass of greater than 1000 Hz and amplified to 10 W of power. Before Fourier transform each point of the free-induction decay was multiplied by the exponential function $e^{iTC/N}$, where i is the index of the point, TC is a constant (−1.6 was used), and N is the size of the data table (16 384), in order to improve the signal-to-noise ratio of the transformed spectrum. This technique is sometimes referred to as digital filtering, exponential multiplication, or sensitivity enhancement. Fourier transformation resulted in a 8192 data point spectrum yielding a computer resolution of 0.610 Hz/data point. All chemical shifts, intensities, and integrals were obtained using the Nicolet T1-PRGM II Fourier transform program.

Preparation of Benzylic Lithium Compounds from α-Methylstyrenes. All glassware used in benzylic lithium preparations was baked out at 120 °C for at least 1 h, assembled, and flamed with a microburner under a current of argon. If the density of a liquid was known, quantitative transfer was effected via a tared syringe. The reactions were carried out under a positive argon pressure. All reagents were transferred via syringes equipped with stopcocks except where noted.

Method A. Preparation of Benzylic Lithiums in TMEDA–Isooctane. A 10-mL pear-shaped flask equipped with a "stopcock adapter" (2-mm straight-bore stopcock attached to a male ground-glass joint) protected with a rubber serum cap, was charged with 5 mmol of the appropriate α-methylsytrene and 3 mL of isooctane. The solution was outgassed by passing argon through it via a stainless-steel needle. The reaction vessel was a 50-mL round-bottom flask equipped with a "stopcock adapter", a side arm fitted with a 2-mm straight-bore stopcock, both protected by rubber serum caps and a magnetic stirring bar. The reaction vessel was charged with *tert*-butyllithium in pentane (1.33 M, 3.7 mL, 5.5 mmol, 10% excess). The pentane was removed by passing a current of argon over the rapidly stirred solution and 3 mL of isooctane added. The reaction vessel was immersed in a dry ice–isopropyl alcohol bath at −50 °C, and TMEDA (0.64 g, 5.5 mmol) was added. The bath temperature was allowed to rise to −30 °C, and the deoxygenated styrene-isooctane solution prepared as described above was added dropwise to the rapidly stirred *tert*-butyllithium–TMEDA slurry over a 30 min to 1 h time period. The temperature of the bath was maintained at −30 ±5 °C during the addition. The resulting dark-red solution was allowed to warm to 0 °C and stirred at this temperature for 30 min, completing the reaction. This method allowed the preparation of the following tertiary benzylic lithiums in greater than 95% yield: 2-lithio-2-phenyl-4,4-dimethylpentane (**5a**); 2-lithio-2-(*p*-trimethylsilylphenyl)-4,4-dimethylpentane (**5b**); 2-lithio-2-(*p*-trimethylgermylphenyl)-4,4-dimethylpentane (**5d**); 2-lithio-2-(*p*-thiophenylphenyl)-4,4-dimethylpentane (**5g**); 2-lithio-2-(*p*-phenyldimethylsilylphenyl)-4,4-dimethylpentane (**5c**); 2-lithio-2-(*p*-cyclopropylphenyl)-4,4-dimethylpentane (**5h**).

Method B. Preparation of Benzylic Lithiums in THF–Pentane. A 10-mL pear-shaped flask equipped with a "stopcock adapter" protected with a rubber serum cap was charged with 5 mmol of the appropriate α-methylstyrene and 3 mL of tetrahydrofuran. The solution was outgassed for at least 10 min by passing argon through it using a stainless-steel needle.

The reaction vessel (same as in method A) was charged with *tert*-butyllithium in pentane (1.33 M, 3.7 mL, 5.5 mmol, 10% excess) and immersed in a dry ice–isopropyl alcohol bath at −50 °C. THF (1.0 mL) was added and the temperature of the bath allowed to rise to −30 °C. The deoxygenated styrene–THF solution prepared as described above was added dropwise to the rapidly stirred *tert*-butyllithium–THF solution over a 30–60-min period. The temperature of the bath was maintained at −30 ±5 °C during the addition. The resulting dark-red solution was allowed to warm to 0 °C and stirred at this temperature for 30 min, completing the reaction. This method allowed the preparation of the following tertiary benzylic lithiums in greater than 95% yield: **5a–d,g–i.**

Using method A, **5a** was prepared in a greater than 90% yield when the following ligands were substituted for TMEDA: *N*-methylpyrolidine (0.94 g, 11.0 mmol), diethylcyclohexylamine (1.71 g, 11.0

mmol), *N,N,N′,N′*-tetramethyldiaminomethane (0.56 g, 5.5 mmol), and *N,N,N′,N′*-tetramethyl-1,3-propylenediamine (0.72 g, 5.5 mmol).

Using method A, **5b** was prepared in greater than 90% yield when the following ligands were substituted for TMEDA: tetrahydrofuran (0.79 g, 11.0 mmol), ethyl ether (0.82 g, 11.0 mmol), dioxane (0.48 g, 5.5 mmol), dimethoxymethane (0.42 g, 5.5 mmol), 1,2-dimethoxyethane (0.50 g, 5.5 mmol), and triethylamine (1.11 g, 11.0 mmol).

2-Lithio-2-(*p*-thiomethylphenyl)-4,4-dimethylpentane (5f) in Ethyl Ether–Isooctane. A stock solution of *p*-thiomethyl-α-methylstyrene (**1f**) in ethyl ether was prepared as follows. A 25-mL volumetric flask equipped with a 2-mm straight-bore stopcock and ground-glass joint was charged with **1f** (5.7 g, 34.7 mmol) and filled to the mark with ethyl ether (concentration 1.36 M). The solution was degassed on the vacuum line (three freeze–thaw cycles) and filled with argon.

A 50-mL round-bottom flask equipped with two 2-mm straight-bore stopcocks protected with rubber serum caps and a magnetic stirring bar was charged with a solution of *tert*-butyllithium in pentane (1.33 M, 4.1 mL, 5.5 mmol). The pentane was removed by passing a current of dry argon through the reaction vessel, and 6 mL of isooctane was added. The reaction vessel was immersed in a dry ice–isopropyl alcohol bath at −30 °C. The **1f**–ether solution prepared as described above (3.7 mL, 5.08 mmol) was added dropwise to the rapidly stirred *tert*-butyllithium–isooctane solution over a 10-min period. A light-red precipitate formed immediately as the solution was added. Hydrolysis of the heterogeneous reaction mixture (see section on capture reactions) and subsequent NMR analysis of the product mixture indicated that **5f** had formed in 75% yield.

2-Lithio-2-(*p*-trimethylsilylphenyl)-4,4-dimethylpentane (5b) in Trimethylamine–Isooctane. A three-neck round-bottom flask was equipped with an argon gas inlet, a magnetic stirring bar, and a condenser. The top of the condenser was attached at an angle of 90° to two 10 by 1 cm drying tubes containing potassium hydroxide pellets and calcium oxide lumps, respectively. The second drying tube was attached to a "T", one end of which was equipped with a 2-mm straight-bore stopcock and attached to an argon line, the other attached to a calibrated cold finger. All connections were made by $^{14}/_{20}$ ground-glass joints. The exit from the cold finger was attached via a short piece of Tygon tubing to one side arm of a 50-mL round-bottom flask equipped with a magnetic stirring bar and two side arms protected by 2-mm straight-bore stopcocks. The second side arm was protected with a rubber serum cap. The entire assembly was flushed with argon for 1 h. The cold finger and 50-mL round-bottom flask were flamed with a microburner several times during this period.

The 100-mL round-bottom flask was charged with trimethylamine hydrochloride (9.6 g, 0.10 mol), a magnetic stirring bar, and 50 mL of mesitylene; the cold trap was cooled to −78 °C with a dry ice–isopropyl alcohol bath, and ca. ten KOH pellets were added to the 100-mL round-bottom flask. The reaction mixture was stirred at room temperature until the pellets were almost totally consumed; then ca. ten more KOH pellets were added. The process was repeated twice more. After the fourth addition, the amount of precipitated KCl made it difficult to stir the reaction mixture and to monitor the disappearance of the KOH pellets. By this time ca. 6 mL of liquid had condensed in the cold finger.

The 50-mL round-bottom flask was charged with a solution of *tert*-butyllithium in pentane (5.7 mL, 1.0 M, 5.7 mmol) and cooled to −78 °C. With the argon still flushing the system, the dry ice–isopropyl alcohol bath was removed from the cold finger until 1.5 mL of trimethylamine (0.99 g, 16.5 mmol) had been transferred from the cold finger to the reaction flask; then the cold finger was reimmersed in the dry ice–isopropyl alcohol bath and held at −70 °C. The reaction flask was warmed to ca. −50 °C, and a solution of *p*-trimethylsilyl-α-methylstyrene (**1b**, 1.0 g, 5.2 mmol) in 3 mL of isooctane was added dropwise via syringe over a 45-min period. After the addition was completed, the reaction mixture was warmed to 0 °C and stirred at that temperature for 30 min. Most of the pentane and excess trimethylamine were removed by allowing the reaction mixture to warm to 20 °C while passing a current of argon over the solution. Additional isooctane (5 mL) was added to the reaction mixture prior to the preparation of a sealed, degassed NMR sample. The NMR analysis of the reaction mixture showed that a 90% conversion of **1b** to **5b** had occurred.

2-Lithio-2-(*p*-trimethylstannylphenyl)-4,4-dimethylpentane (5e). Using method A, a solution of *p*-trimethylstannyl-α-methylstyrene (**1e**, 0.86 g, 3.1 mmol) in 3 mL of isooctane was reacted with a solution of *tert*-butyllithium (3.4 mmol) in isooctane (5 mL) in the presence of ethyl ether (0.7 g, 9.5 mmol) at −30 °C. NMR analysis revealed that the 1:1 adduct **5e** had formed in greater than 90% yield.

1-Lithio-1-phenyl-2-*tert*-butylcyclopentane (18). Using method A, a solution of 1-phenylcyclopentene (1.3 g, 9.0 mmol) in 5 mL of isooctane was reacted with *tert*-butyllithium (0.95 M, 10.0 mL, 9.5 mmol) in the presence of TMEDA (1.16 g, 10.0 mmol) at −30 °C. The yield of **18** was 95% (NMR analysis). Using method B, a solution of 1-phenylcyclopentene (1.3 g, 9.0 mmol) in 3 mL of tetrahydrofuran was reacted with *tert*-butyllithium (0.95 M, 10.0 mL, 9.5 mmol) at −30 °C to give **18** in 95% yield.

Capture Reactions. 2-(*p*-Cyclopropylphenyl)-4,4-dimethylpentane (12b). A rapidly stirred solution of 2-lithio-2-*p*-cyclopropylphenyl-4,4-dimethylpentane (5 mmol) in TMEDA–isooctane (prepared as described above) was treated with water (2.0 g, 11.1 mmol) added by syringe at room temperature (exothermic reaction). The organic phase was diluted with 50 mL of pentane and washed with 5% aqueous hydrochloric acid (25 mL, five times), water (25 mL, once), and saturated aqueous sodium bicarbonate (25 mL, once). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of solvents, and distillation through a short-path distillation head gave 2-(*p*-cyclopropylphenyl)-4,4-dimethylpentane (**12h**, bp 90–97 °C (0.1 Torr), 1.05 g, 98%). This method was used to prepare the following hydrocarbons: **12a**, bp 50–60 °C (0.5 Torr), 95%; **12b**, bp 80–90 °C (0.5 Torr), 90%; **12d**, bp 95–115 °C (0.5 Torr), 85%; **12c**, molecular distillation, 120 °C (0.5 Torr), 81%; **12g**, molecular distillation, 120 °C (0.5 Torr), 76%; **12f**, bp 75–90 °C (0.5 Torr), 75%; **12i**, sublimed, 75 °C (0.5 Torr), 71%, mp 87 °C. See Table VI for NMR parameters.

2-Deuterio-2-(*p*-trimethylsilylphenyl)-4,4-dimethylpentane. Using the same procedure as described above, 5 mmol of 2-lithio-2-*p*-trimethylsilylphenyl-4,4-dimethylpentane was reacted with deuterium oxide to give the title compound in 97% yield, bp 90–105 °C (0.5 Torr). The carbon and proton magnetic resonance data showed that deuterium had been incorporated at the benzylic position, $J(^{13}\mathrm{C}, \mathrm{D}) = 19.2 \pm 0.6$ Hz, deuterium isotope shift 0.05 ppm upfield.

2-Phenyl-2-trimethylsilyl-4,4-dimethylpentane (13a). A solution of 2-lithio-2-phenyl-4,4-dimethylpentane (10 mmol) in tetrahydrofuran–isooctane (prepared using method B, doubling all quantities) was treated with freshly distilled trimethylsilyl chloride (1.2 g, 11 mmol), added dropwise via syringe at 0 °C. The resulting white precipitate (lithium chloride) was dissolved by the addition of 25 mL of water. The organic phase was diluted with 50 mL of pentane and washed with saturated sodium chloride solution (25 mL). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of solvents, and distillation yielded **13a** (1.6 g, bp 80–85 °C (0.2 Torr), 65%). The NMR parameters are given in Table V.

2-Phenyl-2-trimethylstannyl-4,4-dimethylpentane (14a). A solution of 2-lithio-2-phenyl-4,4-dimethylpentane (10 mmol) in tetrahydrofuran–pentane (prepared as described by method B with doubling of all quantities) was treated with a solution of trimethylstannyl chloride (20.0 g, 10.0 mmol) in 25 mL of tetrahydrofuran at 0 °C. The same workup as described directly above yielded **14a** (19.4 g, 58%, bp 95–105 °C (0.5 Torr)). The NMR parameters are given in Table V.

Cleavage of Benzylic Tin Compounds. Reaction of 2-Phenyl-2-trimethylstannyl-4,4-dimethylpentane (14a) with *tert*-Butyllithium. A standard solution of **14a** was prepared as follows. A 25-mL volumetric flask equipped with a 2-mm straight-bore stopcock fitted with a ground-glass joint was charged with 5.5 g of **14a** (25 mmol) and filled to the mark with cyclopentane (concentration of 1 M). The solution was degassed on the vacuum line (three freeze–thaw cycles, pressure >1 μm) and filled with argon.

A 25-mL round-bottom flask equipped with a "stopcock adapter" protected by a rubber serum cap and magnetic stirring bar was charged with 3.5 mL of sublimed *tert*-butyllithium in pentane (0.88 M, 3.1 mmol) and 3.0 mL (3 mmol) of the **14a**–cyclopentane solution described above. At room temperature TMEDA (0.17 g, 3.0 mmol) was added dropwise. A dark-red, homogeneous solution resulted immediately. NMR analysis indicated that the formation of 2-lithio-2-phenyl-4,4-dimethylpentane (**12a**) was greater than 90%.

The following experimental variations occurred in examining the effect of various ligands on the above reaction. Using the same procedure but substituting tetrahydrofuran (0.43 g, 6 mmol) or ethyl ether (0.45 g, 6 mmol) gave the results listed in Table VII. The reaction of 3.0 mmol of **14a** with a mixture of 6.2 mmol of *tert*-butyllithium and 3.1 mmol (0.2 g) of *tert*-butyl alcohol was accomplished by adding the *tert*-butyl alcohol to the *tert*-butyllithium at room temperature before the addition of **14a**. Sublimed alcohol-free lithium *tert*-butoxide (0.25 g, 3.1 mmol) was placed in the round-bottom flask inside a drybox. The flask was removed from the drybox and the reaction completed by adding the *tert*-butyllithium in pentane (7.0 mL, 6.2 mmol) followed by the **14a** cyclopentane solution. The reaction involving potassium *tert*-butoxide was performed in the same manner. See Table VII.

Preparation of Benzylic Lithium Precursors. 2-(*p*-Bromophenyl)-2-propanol (21). A 1-L round-bottom three-neck flask was fitted with pressure-equalizing dropping funnel, mechanical stirrer, and condenser. The entire apparatus was flamed out under a current of argon and allowed to cool. Magnesium turnings (9.0 g, 0.37 g-atom) were placed in the flask and the dropping funnel was charged with a solution of *p*-dibromobenzene (75 g, 0.32 mol) in anhydrous ethyl ether (400 mL). Approximately 50 mL of the ether-bromine solution was discharged from the dropping funnel and a small crystal of iodine was added to the flask. The stirrer was started and within 2 min a vigorous reflux had commenced. The reaction was controlled with an ice bath until the reflux had subsided, the ice bath was removed, and the remainder of the ether-bromide solution was added at such a rate as to maintain a steady reflux. The total addition time was approximately 1.25 h. The flask was then heated so that the ether maintained a steady reflux for 4 h, the head removed, and the flask immersed in an ice bath. A solution of acetone (19.8 g, 0.35 mol) in anhydrous ethyl ether (50 mL) was added via the dropping funnel while stirring vigorously. The ice bath was removed and the resultant white slurry was stirred at room temperature for 2 h. The flask was again immersed in an ice bath and a saturated aqueous solution of ammonium chloride was added via the dropping funnel with vigorous stirring until the magnesium salts settled to the bottom of the flask in large clumps, and a clear, light-yellow ether solution was evident. The stirrer was stopped, the ice bath removed, and the contents of the flask allowed to further settle for 30 min. The ether solution was decanted from the magnesium salts, and the salts were washed with additional portions of ether (50 mL, five times). The combined ether extracts were dried over anhydrous magnesium sulfate overnight. Subsequent filtration, flash evaporation of ether, and distillation using a short-path distillation head yielded 2-(*p*-bromophenyl)-2-propanol (53.2 g, 78%, bp 75-85 °C (0.1 Torr), lit.[43] 99-102 °C (2.5 Torr)).

2-(*p*-Bromophenyl)propene (3) A. A 500-mL round flask equipped with a magnetic stirring bar, Dean-Stark trap, and condenser was charged with 2-(*p*-bromophenyl)-2-propanol (32.5 g, 0.15 mol), benzene (300 mL), and phosphoric acid (85%, 1 mL). Refluxing the mixture for 5 h resulted in the separation of 1 equiv of water (3.0 mL) in the trap. After cooling to room temperature, the reaction mixture was poured into a separatory funnel containing ethyl ether (150 mL). The ether-benzene solution was washed twice with water (100 mL), once with a saturated aqueous solution of sodium bicarbonate (50 mL), again with water (100 mL), and once with saturated aqueous sodium chloride (100 mL), then dried over anhydrous magnesium sulfate overnight. Filtration, evaporation of volatile solvents, and distillation through a short-path distillation head yielded 2-(*p*-bromophenyl)propene (25.4 g, 83%, bp 55-65 °C (2.3 Torr), lit.[43] 58-60 °C (2 Torr)).

2-(*p*-Bromophenyl)propene (3). B. A 25-mL round-bottom flask equipped with a magnetic stirring bar was charged with 2-(*p*-bromophenyl)-2-propanol (10.5 g, 49 mmol) and potassium bisulfate (6.8 g, 50 mmol). Distillation of the mixture through a 2-in. Vigreux column at water aspirator pressure (ca. 20 Torr) yielded the title compound (6.5 g, 68%, bp 110-120 °C).

2-(*p*-Trimethylsilylphenyl)propene (1b). Into a flame-dried 500-mL round-bottom three-neck flask equipped with a magnetic stirring bar, "stopcock adapter" protected with a rubber serum cap, and adapter for maintaining a positive argon pressure was added via syringe a solution of *n*-butyllithium in hexane (1.4 M, 20 mL, 28 mmol). The solution was cooled by immersion in a dry ice-isopropyl alcohol bath at −50 °C, and 100 mL of diethyl ether was added via syringe. The bath temperature rose to ca. −15 °C while a solution of 2-(*p*-bromophenyl)propene (5.0 g, 25 mmol) in 50 mL of ethyl ether was added dropwise to the vigorously stirred solution. The bath temperature was maintained at −15 °C for 1 h. Analysis by vapor-phase chromatography on a hydrolyzed aliquot showed that the formation of 2-(*p*-lithiophenyl)propene was quantitative. Then freshly distilled trimethylsilyl chloride (4.2 g, 38 mmol) was added in a thin stream from a syringe. The reaction mixture was warmed to room temperature, and 50 mL of water was added to dissolve the lithium salts. The organic layer was diluted with pentane (200 mL) and washed with water (50 mL, twice) and saturated aqueous sodium chloride (50 mL, once). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of solvents, and distillation through a short-path distillation head yielded 2-(*p*-trimethylsilylphenyl)propene (4.1 g, 85%, bp 78-80 °C (1.1 Torr), lit.[16] 68-70 °C (0.7 Torr)). NMR data are listed in Table III.

2-(*p*-Trimethylgermylphenyl)propene (1d). A solution of 2-(*p*-lithiophenyl)propene (76 mmol) in ethyl ether-hexane prepared as described above was treated with trimethylgermyl bromide (15 g, 76 mmol) at −15 °C to yield after similar workup and two distillations 2-(*p*-trimethylgermylphenyl)propene (6.8 g, 30%, bp 65-72 °C (0.5 Torr), lit.[16] 55-57 °C (0.3 Torr). NMR data are listed in Table III.

2-(*p*-Trimethylstannylphenyl)propene (1e). A solution of 2-(*p*-lithiophenyl)propene (40 mmol) in ether-hexane prepared as described above was treated with a solution of trimethylstannyl chloride (10.2 g, 51 mmol) in 50 mL of ethyl ether at −15 °C. The same workup as described above and one distillation yielded 2-(*p*-trimethylstannylphenyl)propene (8.5 g, 75%, bp 59-63 °C (0.1 Torr), lit.[16] 49-51 °C (0.0003 Torr)). The carbon magnetic resonance data were in accord with the expected structure, Table III.

2-(*p*-Thiomethylphenyl)propene (1f). A solution of 2-(*p*-lithiophenyl)propene (40 mmol) in ethyl ether-hexane prepared as described above was treated with dimethyl disulfide (5.3 g, 57 mmol) added neat via syringe at 0 °C. After a similar workup to that for the *p*-silyl derivative (*caution—extremely malodorous reaction*) the yield of 2-(*p*-thiomethylphenyl)propene was 85% (5.7 g, bp 85-89 °C (0.7 Torr), lit.[17] 85 °C (1.0 Torr)). The product solidified in the receiving flask (mp 45-47 °C, lit.[17] 51 °C). NMR data are listed in Table III.

2-(*p*-Thiophenylphenyl)propene (1g). A solution of 2-(*p*-lithiophenyl)propene (26 mmol) in ethyl ether-hexane prepared as described above was treated with a solution of diphenyl disulfide (6.0 g, 27.5 mmol) in 25 mL of ethyl ether at 0 °C. The reaction mixture was stirred at room temperature for 24 h. After the normal workup and distillation, the yield of 2-(*p*-thiophenylphenyl)propene was 4.1 g, 71%, bp 115-122 °C (0.1 Torr). Table III lists the carbon magnetic resonance data.

2-(*p*-Biphenylyl)-2-propanol (21). A solution of *p*-phenylmethyl benzoate (20 g, 0.095 mol) in diethyl ether (400 mL) was slowly added to a refluxing solution of 0.2 mol of methylmagnesium iodide in 200 mL of ether. The addition took 5 h and was followed by 5 h of reflux, then stirring at room temperature overnight. The flask was immersed in an ice-water bath and stirred vigorously, and a saturated solution of aqueous ammonium chloride was added via the dropping funnel until the magnesium salts settled to the bottom of the flask in large clumps. The stirrer was stopped and the contents of the flask allowed to settle for 30 min. The ether was decanted through a glass-wool plug, the magnesium salts were washed with three 100-mL portions of ethyl ether, and the combined ether solutions were dried over anhydrous magnesium sulfate for 8 h. Flash evaporation of ether left 19.5 g (95%) of a yellow-orange solid which displayed no carbonyl absorption in the infrared.

2-(*p*-Biphenylyl)propene (1i). Into a 500-mL round-bottom flask equipped with a magnetic stirring bar, Dean-Stark trap, and condenser were added 2-(*p*-biphenylyl)-2-propanol (19.0 g, 0.09 mol), dry benzene (200 mL), and 85% phosphoric acid (1 mL). The solution was refluxed until no more water was observed separating from the condensate (1.5 h, 1.4 mL of water collected, 87.5%). After cooling to room temperature, the contents of the flask were poured into a separatory funnel containing 200 mL of pentane, washed with water (50 mL, three times), saturated aqueous sodium bicarbonate (50 mL, three times), water (50 mL, once), and saturated aqueous sodium chloride (50 mL, once), and dried over anhydrous magnesium sulfate overnight. The solution was concentrated by rotary evaporation until the volume was approximately 30 mL, poured onto a column of alumina (Woelm, activity 1, basic, column dimensions 3 by 20 cm), and eluted with pentane. The first 500 mL of eluate was evaporated to leave a slightly yellow solid (17.3 g) which was recrystallized three times from 1:1 ether-hexane to yield 2-(*p*-biphenylyl)propene (8.5 g, 49%, mp 114-118 °C, lit.[17] 115 °C). Table III lists the ^{13}C NMR parameters.

2-(*p*-Cyclopropylphenyl)propene (1h). Into a 500-mL round-bottom flask equipped with a magnetic stirring bar, Dean-Stark trap, and condenser were added 2-(*p*-cyclopropylphenyl)-2-propanol (4.5 g, 0.0256 mol), benzene (300 mL), and phosphoric acid (1 mL, 85%). Refluxing the solution for 1 h resulted in the separation of 1 equiv of water. Workup in the same manner as already described for the previous tertiary carbinol dehydrations yielded 2-(*p*-cyclopropylphenyl)propene (2.07 g, 51%, bp 72-78 °C (0.75 Torr), lit.[18] 84-85 °C (1-2 Torr)). See Table III for NMR data.

2-(*p*-Nitrophenyl)propene (23).[44] 2-Bromo-2-(*p*-nitrophenyl)propane (75 g, 0.03 mol) was dissolved in 50 mL of 10% potassium hydroxide in ethanol in a 100-mL round-bottom flask and stirred at room temperature for 3 days. The solution was filtered to remove potassium bromide, reduced to one-half of its volume, and diluted with 200 mL of water. This ethanol-water solution was extracted with three 100-mL portions of ethyl ether. The combined ether extracts were washed with water (50 mL, five times). The ether solution was neutral to litmus paper. The ether solution was washed with saturated aqueous sodium chloride (50 mL, once) and filtered through a cone of anhydrous magnesium sulfate. Flash evaporation of ether and distillation through a 2-in. Vigreux column gave a yellow oil which solidified in the receiver (2.46 g, 50%, mp 41-46°C). A 1.5-g portion was recrystallized from anhydrous ethanol, then dried in a vacuum desiccator over anhydrous calcium chloride to give 0.92 g (19%) of 2-(*p*-nitrophenyl)propene (mp 54-55 °C, lit.[44] 54-55 °C).

2-(*p*-Dimethylphenylsilylphenyl)propene (1c). To a solution of 2-(*p*-lithiophenyl)propene (50 mmol) prepared as described previously was added a solution of dimethylphenylchlorosilane (8.5 g, 50 mmol) in 25 mL of ethyl ether at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The precipitated lithium chloride was dissolved by adding 100 mL of water. Separation of the two phases followed by the normal workup [see preparation of 2-(*p*-trimethylsilylphenyl)propene] gave 2-((*p*-dimethylphenylsilyl)phenyl)propene (7.6 g, 60%, bp 110-125 °C (0.1 Torr)). Table III displays the NMR parameters.

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References and Notes

(1) Bywater, S; Worsfold, D. J. *J. Organomet. Chem.* **1971**, *33*, 273–279.
(2) van Dongen, J. P. C. M.; van Dijkman, H. W. D.; de Bie, M. J. A. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 29–32.
(3) Szwarc, M. "Carbanions, Living Polymers and Electron Transfer Processes"; Interscience: New York, 1968.
(4) Takahashi, K.; Takaki, M.; Asami, R. *Org. Magn. Reson.* **1974**, *6*, 580–582.
(5) Takahashi, K.; Takaki, M.; Asami, R. *Org. Magn. Reson.* **1971**, *3*, 535–537.
(6) Takahashi, K.; Takaki, M.; Asami, R. *J. Phys. Chem.* **1971**, *75*, 1062–1067.
(7) McKeever, L. D.; Waack, R. *J. Organomet. Chem.* **1971**, *28*, 145–151.
(8) Waack, R.; McKeever, L. D.; Doran, M. A. *Chem. Commun.* **1967**, 1291–1293.
(9) Patterman, S. P.; Karle, I. L.; Stuckey, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150–1157.
(10) Hammons, J. H. *J. Org. Chem.* **1968**, *33*, 1123–1127.
(11) Waack, R.; Doran, M. A.; Baker, E. B.; Olah, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 1272–1275.
(12) Waack, R.; McKeever, L. D.; Doran, M. A. *Chem. Commun.* **1969**, 117.
(13) Fraenkel, G.; Russell, J. G.; Chen. Y. H. *J. Am. Chem. Soc.* **1973**, *95*, 3208–3215.
(14) Brownstein, S.; Worsfold, D. J. *Can J. Chem.* **1972**, *50*, 1246–1248.
(15) Hsieh, H. L. *J. Polym. Sci., Part A* **1965**, *3*, 153–161, 163–172, 173–180.
(16) Noltes, J. A.; Budding, H. A.; van der Kerle, A. J. M. *Recl. Trav. Chim. Pays-Bas* **1960**, *79*, 1076–1084.
(17) Bachman, G. B.; Carlson, C. L. *J. Am. Chem. Soc.* **1951**, *73*, 7857. Hopff, H.; Luessi, H. *Makromol. Chem.* **1963**, *62*, 31–39.
(18) Hahn, R. C.; Corbin, T. F.; Shechter, H. *J. Am. Chem. Soc.* **1968**, *90*, 3404–3415.
(19) Dhami, K. S.; Stothers, J. B. *Can J. Chem.* **1965**, *43*, 510–520.
(20) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 2967–2969.
(21) Brooks, J. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7333–7338.
(22) Lettre, H.; Jungman, P. J.; Salfeld, J. C. *Chem. Ber.* **1952**, *85*, 397–407. Fraenkel, G.; Dayagi, S.; Kobayashi, S. *J. Phys. Chem.* **1968**, *72*, 955–961.
(23) Oae, S.; Tagaki, W.; Ohno, A. *Tetrahedron* **1964**, *20*, 425–436.
(24) Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M. M.; Wolf, S. *J. Am. Chem. Soc.* **1975**, *97*, 2209–2218.
(25) Shirley, D. A.; Johnson, J. R., Jr.; Hendrix, J. P. *J. Organomet. Chem.* **1968**, *11*, 209–216.
(26) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. *J. Organomet. Chem.* **1964**, *2*, 431–433.
(27) Bothner-By, A. A.; Castellano, S. M. *J. Chem. Phys.* **1964**, *41*, 3863–3869.
(28) Steigel, A.; Sauer, J.; Kleir, D. A.; Binsch, G. *J. Am. Chem. Soc.* **1972**, *94*, 2770–2778.
(29) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2; Pergamon Press: Oxford, 1965; p 721.
(30) Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5486–5488.
(31) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468–472. Lauterbur, P. C. *J. Am. Chem. Soc.* **1961**, *83*, 1838–1846. Tokuhiro, T.; Fraenkel, G. *Ibid.* **1969**, *91*, 5005–5013. O'Brien, D. H.; Hart, H. J.; Russell, C. R. *Ibid.* **1975**, *97*, 4410–4412.
(32) Maciel, G. E.; James, R. V. *J. Am. Chem. Soc.* **1964**, *86*, 3893–3895. Maciel, G. E.; Natterstad, J. J. *J. Chem. Phys.* **1965**, *42*, 2427–2434.
(33) Binsch, G. *J. Am. Chem. Soc.* **1969**, *91*, 1304–1309.
(34) Kaplan, J. I.; Fraenkel, G. *J. Am. Chem. Soc.* **1972**, *94*, 2907–2913.
(35) Screttas, C. G.; Eastham, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 3276–3277.
(36) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 2328–2330.
(37) Kronzer, F. J.; Sandel, V. R. *J. Am. Chem. Soc.* **1972**, *94*, 5750–5759.
(38) Sandel, V. R.; McKinley, S. V.; Freedman, H. H. *J. Am. Chem. Soc.* **1968**, *90*, 495–497.
(39) The rate of rotation is 3 ± 1 s^{-1} at 93 °C. Boiling of the NMR sample makes measurement at higher temperatures impractical.
(40) Hansch, C. *J. Med. Chem.* **1973**, *16*, 1207–1216.
(41) Landgrebe, J. A.; Shoemaker, J. D. *J. Am. Chem. Soc.* **1967**, *89*, 4465–4472.
(42) Bushweller, C. H.; Sturges, J. S.; Cipullo, M.; Hoogasian, S.; Gabriel, M. W.; Bank, S. *Tetrahedron Lett.* **1976**, 1359.
(43) Seymour, D.; Wolfstirn, K. B. *J. Am. Chem. Soc.* **1948**, *70*, 1177–1179.
(44) Brubacher, G.; Suter, E. *Helv. Chim Acta* **1950**, *33*, 256–261.