Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.27; H, 9.32.

Birch Reduction of 15 to Give *anti*-5,13-Dimethyl[2.2]metacyclophane. A solution of 40 mg of [2.2.2](1,3,5)cyclophane (15) in 4 ml of tetrahydrofuran containing 50 mg of absolute ethanol was added slowly with stirring to a blue solution of 300 mg of sodium in 30 ml of liquid ammonia held at −78°. After 1 hr the ammonia was allowed to evaporate, water was added, and the mixture was extracted with ether. The residual solid, after concentration of the ether extracts, was chromatographed over silica gel using petroleum ether (30–60°) as eluent. The main eluate fraction afforded 20 mg (50%) of white crystals: mp 148.5–149.5; nmr (CDCl₃) τ 3.17 (s, 4 H, ArH), 5.86 (s, 2 H, ArH), 7.46 (AA′BB′, 8 H, ArCH₂), and 7.65 (s, 6 H, ArCH₃). The properties of these crystals were identical in all respects with a known specimen of *anti*-5,13-dimethyl[2.2]metacyclophane[34] and a mixture melting point showed no depression of melting point.

Transformation of [2.2.2](1,3,5)Cyclophane (15) to the Novel Cage Structure 24. To a mixture of 200 mg of anhydrous aluminum chloride in 5 ml of dichloromethane saturated with anhydrous hydrogen chloride a solution of 160 mg of [2.2.2](1,3,5)cyclophane

(15) in 5 ml of dichloromethane was slowly added (2 min). The resulting mixture was stirred an additional 10 min at 0° before adding 20 ml of cold, dilute aqueous hydrochloric acid. The organic layer was separated, washed with water, and concentrated to give 220 mg of an oil. This oil showed a positive Beilstein halogen test, a complex nmr pattern from τ 7.6–9.0, and a mass spectral pattern with peaks corresponding to molecular ions derived from $C_{18}H_{18}$-H_xCl_{6-x}, where x is an integer less than 6. This oil was then dissolved in 10 ml of tetrahydrofuran, 100 mg of lithium and a solution of 200 mg of *tert*-butyl alcohol in 4 ml of tetrahydrofuran were added, and the resulting mixture was boiled under reflux for 3 hr. The mixture was then filtered, 20 ml of ether was added to the filtrate, and the filtrate was washed with water. After the organic layer was dried and concentrated, the residual white solid was chromatographed over silica gel using pentane as eluent. The crystalline solid from the main eluate fraction was recrystallized from a pentane–ethanol mixture to give 81 mg (49%) of white crystals: mp 178–181°; ir (CCl₄) 2920, 2880, 1460, 1440, and 1304 cm⁻¹; nmr (CDCl₃) τ 8.33 (m, 6 H, >CH–), 8.43 (t, 12 H, *J* = 1.25 Hz, –CH₂–), and 9.01 (m, 6 H, >CH); mass spectrum, *m/e* 240 (M⁺).

Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 89.72; H, 10.18.

(34) V. Boekelheide and R. Griffin, *J. Org. Chem.*, **34**, 1960 (1969).

Nuclear Magnetic Resonance Studies of Structure and Hindered Rotation in Tertiary Benzylic Metal Compounds

Gideon Fraenkel,* John G. Russell, and Ying-Hsueh Chen

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received November 3, 1972

Abstract: A variety of α-methylstyrenes have been found to undergo nearly quantitative 1:1 addition with *tert*-butyllithium in isooctane-*N,N,N′,N′*-tetramethylethylenediamine, TMEDA. The ring proton shifts in several tertiary benzylic lithium and potassium compounds in ether, THF, tertiary amines, and TMEDA–isooctane, considerably shielded with respect to benzene, are independent of metal, solvent and substitution on the benzylic carbon. Also the proton–proton coupling constants differ greatly from those in covalently substituted benzyl compounds in that the J_m values are negative. These results indicate the benzylic moiety to be a planar conjugated anion within a solvent separated or loose ion pair. In the unsymmetrically substituted reagents all the ring hydrogens are magnetically nonequivalent. The shifts average at higher temperatures, 10–94°, and line-shape analysis yields rates of rotation about the ring–benzyl bond. These are first order in contained reagent but vary with both solvent and metal. In isooctane–TMEDA, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for a benzylic lithium compound are *ca.* 18.5 kcal and 5 eu. A solvent to carbon metal coordination transfer mechanism is proposed to account for the involvement of metal and solvent in the rotation process.

The molecular structure and dynamic behavior of π-conjugated carbanions have been the subject of extensive investigation. Problems which concern the structure and behavior of these species include the charge distribution, the ionic character of the carbon–metal bonds, and the various types of ion pairing involved. Further, many of these anions are not rigid, but undergo rotation about different π carbon–carbon bonds at rates conveniently within the nmr time scale.

The benzyl anion, one of the simplest conjugated carbanions, is important also for its role in the anionic polymerization of styrene.[1] Nmr studies have been reported on benzyllithium,[2] on substituted benzylpotassiums (cumyl, α-phenethyl, and benzyl),[3,4] and on

adducts of styrenes with *tert*-butyllithium.[4] All these authors have commented on the considerable shielding experienced by the ring hydrogens (compared to benzene) indicative of extensive conjugation.[3,4]

In unsymmetrically substituted benzyllithiums the ring hydrogens are all magnetically nonequivalent[3,4] confirming the coplanarity of the system, and this property has been exploited to measure barriers to rotation by means of the nmr line-shape method.[5]

Of related interest to the work described above are studies of molecular structure and hindered rotation in phenylallyl metal compounds[6] and in 1- and 2-naphthylmethyl metal reagents.[7]

In much of the work quoted here the shifts in the

(1) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968.

(2) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963); R. Waack, L. D. McKeever, and M. H. Doran, *Chem. Commun.*, 117 (1969).

(3) K. Takahashi, M. Takaki, and R. Asami, *Org. Magn. Resonance*, **3**, 539 (1971); *J. Phys. Chem.*, **75**, 1062 (1971).

(4) S. Bywater and D. J. Worsfold, *J. Organometal. Chem.*, **33**, 273 (1971).

(5) S. Brownstein and D. J. Worsfold, *Can. J. Chem.*, **50**, 1246 (1972).

(6) V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968).

(7) F. J. Kronzer and V. R. Sandel, *ibid.*, **94**, 5750 (1972).

organometallic compounds varied with metal as well as solvent.[2,6,7] Under these circumstances, structural interpretation of the nmr data is ambiguous since one cannot separate the electron density contributions[8] to the observed shifts from other effects such as ion pairing[9] or aggregation. Furthermore, in most of the examples referred to, the activation parameters for rotation varied with solvent as well as counterion.[7,8]

The question to which this paper is addressed concerns how bond rotation in benzyl metal compounds takes place. If it is the result of rotation in a free anion the rate should be independent of metal and solvent. If this is not the case then metal must be involved in some more complex molecular mechanism for rotation.
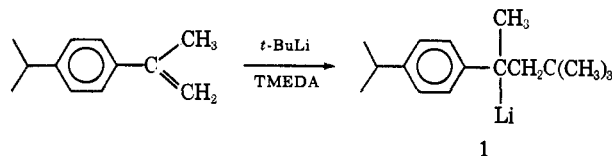
Below we describe an improved method to generate almost quantitatively 1:1 adducts of *tert*-butyllithium with α-methylstyrenes. The nmr spectra of these reagents are exceptionally well resolved allowing a precise determination of the nmr parameters, different from those reported elsewhere,[5] but which seem to be characteristic of conjugated anions. A consideration of the ring proton shifts in these tertiary benzyl metal compounds leads to some firm conclusions about their structures. Finally, the kinetics of rotation have been investigated. It will be shown that whereas the reagents behave like free anions in the ground state the mechanism for rotation involves the solvent as well as the cation.

Results and Discussion

Treatment of α-methylstyrene with *n*-butyllithium in hydrocarbons at 0° gave no indication of reaction as observed by nmr. Addition of a small amount of bases such as diethyl ether, THF, and N,N,N',N'-tetramethylethylenediamine (TMEDA) caused the solution to turn red. Now, nmr showed some resonance in the olefinic region indicative of benzylic lithium species but also much starting material as well as polymer.

It is well known that under conditions employed for anionic polymerization of dienes, for *n*-butyllithium propagation is at least as fast as initiation, whereas with secondary and tertiary lithium compounds initiation is several times faster than propagation and it is possible to obtain 1:1 adducts.[10]

On the basis of these results, it appeared that a tertiary alkyllithium reagent might undergo 1:1 addition to α-methylstyrene. Indeed when 0.015 mol of *tert*-butyllithium was allowed to react with 0.01 mol of *p*-isopropyl-α-methylstyrene in the presence of 0.015 mol of TMEDA at −30°, the mixture immediately turned red and the nmr spectrum of this solution indicated that at least 97% of the starting material had been converted to a species with resonance in the τ 3–5 region (Figure 1). Hydrolysis of this solution with

(8) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 82, 5846 (1960).
(9) G. Fraenkel and J. P. Kim, *ibid.*, 88, 4203 (1966).
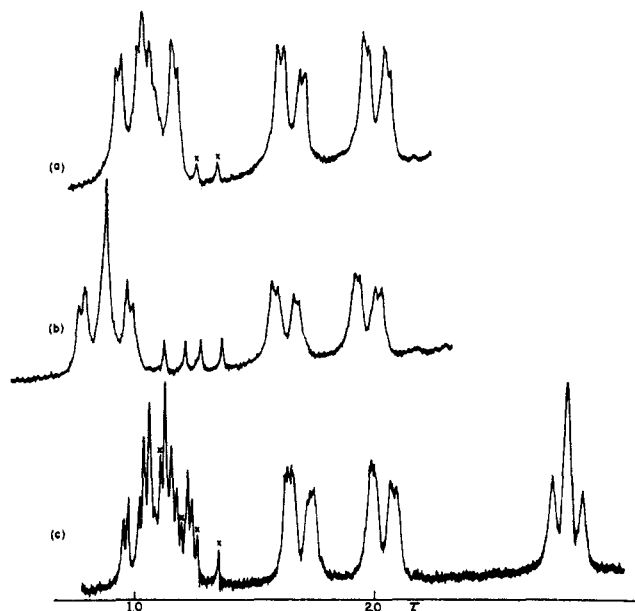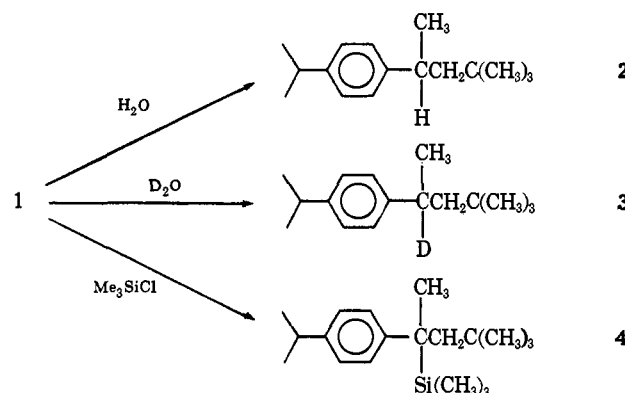(10) W. H. Glaze and P. C. Jones, *Chem. Commun.*, 1434 (1969).

Figure 1. Nmr spectra, 100 MHz, (a) 1, 16°; (b) 5, 16°; (c) 6, 40°; all 1 M in isooctane, 1 M TMEDA.

H_2O and D_2O gave the hydrocarbons 2 and 3, while reaction with trimethylsilyl chloride gave derivative 4. The structures of these compounds are confirmed by mass spectral (see Experimental Section) and nmr data (Table I). These results unequivocally establish the initial product, 1, to be 2-lithio-2-(4-isopropylphenyl)-4,4-dimethylpentane. It is formed, by nmr analysis, in nearly quantitative yield. In the same manner, by the reaction of the appropriate styrene with *tert*-butyllithium and TMEDA, three other benzylic lithium compounds were prepared: 2-lithio-2-(4-*tert*-butylphenyl)-4,4-dimethylpentane (5), 2-lithio-2-phenyl-4,4-dimethylpentane (6), and 2-lithio-2-(3,5-di-*tert*-butylphenyl)-4,4-dimethylpentane (7). Structures 6 and 7 are also assigned on the basis of nmr and mass spectral analysis of the hydrolysis products, 8–13, both from H_2O and D_2O (Table I).

Similar experiments to those described above with styrene and 4-vinylpyridine resulted only in polymers; 1:1 adducts could not be prepared from these olefins as described for α-methylstyrenes.

For purposes of comparison, several benzylic potassium compounds have been prepared by cleavage of the corresponding methyl ethers,[11] 14–16.

The nmr spectra of the aromatic hydrogens in 1, 6,

(11) K. Ziegler and F. Dersch, *Chem. Ber.*, 62, 1833 (1929).

Table I. Nmr Data[a]

Y'	p-(CH₃)₂CH					p-t-Bu	3,5-(t-Bu)
X	H	D	Si(CH₃)₃	H	D	H	D
t-Bu	9.20	9.20	9.06	9.21	9.21	9.20	9.20
CH₃	8.33	8.33	8.35	8.81	8.81	8.82	8.79
H$_a$[b]	8.31_1	8.31_3	7.55	8.29_9	8.29_7	8.28_1	8.26_2
H$_b$	8.56_0	8.57_6	8.28	8.55_9	8.55_1	8.54_3	8.52_4
X	7.28		10.00	7.22		7.22	
Ring	2.99	3.00	2.73	2.90	2.90	2.68 o / 3.09 m	2.84 p / 3.00 (o)
YCH₃	8.81	8.81	8.62			8.74	8.71
CH	7.21	7.21	6.98				
J, Hz							
a, b	−14.02	−14.00	−14.90		−13.9	−14.0	−13.9
a, X	7.80			7.86	1.1	7.81	
b, X	5.71			4.54		4.72	
CH₃, X	6.9			7.0	1.03	7.0	
CH₃, H(Y)	6.9	6.9	7.0				
o, p						1.8	1.8

[a] τ scale. [b] Third place after decimal applies to internal shift.

5   **6**

7
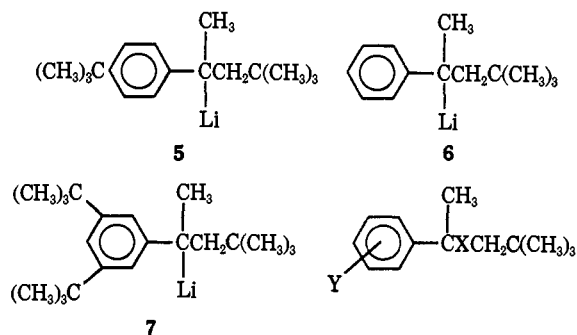
	X	Y
8	H	p-t-Bu
9	D	p-t-Bu
10	H	H
11	D	H
12	H	3,5-di-t-Bu
13	D	3,5-di-t-Bu

14   **15**   **16**
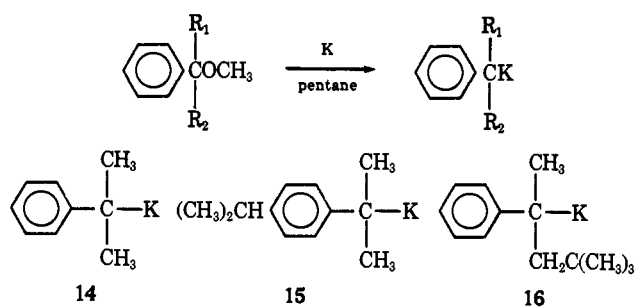
and **7**, illustrated in Figure 1, show no resonance for starting material. The peaks labeled with crosses come from the small amount of N,N-dimethylvinylamine produced by tert-butyllithium cleavage of TMEDA.

$(CH_3)_2NCH_2CH_2N(CH_3)_2$ + ⊥—Li ⟶

$(CH_3)_2CH_x = CH_2$ + $(CH_3)_2NLi$ + ⊥—H
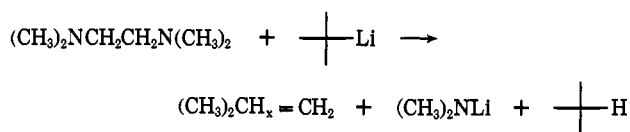
The hydrogen shifts in **1**, **5**, **6**, **7**, **14**, **15**, and **16** are considerably upfield of those in ordinary covalently substituted benzenes and quite widely separated. Fur-

thermore, in these spectra it is clear that all the ring hydrogens are magnetically nonequivalent. A detailed analysis of these spectra has been carried out by use of selective decoupling in conjunction with computer program LAOCOON.[12] Since the spectra are almost first order, trial values for chemical shifts and the ortho coupling constants can be obtained by inspection. Other parameters were estimated from the literature. The results are listed in Table II.

Table II. Nmr Parameters for Benzyllithium[a]

	Compd			
Shift[b]	6	1	5	7
H₂	2.04	2.00	1.96	1.75
H₃	1.16	1.12	0.93	
H₄	2.80			1.30
H₅	1.06	0.97	0.82	
H₆	1.70	1.65	1.62	1.75
	Coupling Constant, Hz ± 0.02			
2,3	9.20	8.98	8.97	
2,4	−1.31			
2,5	−0.10	−0.13	−0.22	
2,6	−2.83	−2.71	−2.70	
3,4	6.48			
3,5	−2.33	−2.61	−2.51	
3,6	−0.28	0.13	−0.23	c
4,5	6.51			
4,6	−1.22			
5,6	9.08	8.92	8.79	

[a] 1.0 M in isooctane–1 M TMEDA. [b] Shift in ppm with respect to benzene. [c] Not resolved.

For compound **6** the iteration error is smaller when the meta coupling constants (2,6), (3,5), (2,4), and (4,6)

(12) LAOCOON 3; A. A. Bothner-By and S. M. Castellano, Carnegie-Mellon University, Pittsburgh, Pa.

are negative. However, for the para-substituted reagents, **1** and **5**, the spectra do not depend on the signs of the meta coupling constants. They are assumed to be negative for all reagents.

It would be tempting to speculate whether these data actually apply to benzylic anions. To gain some insight into this question we obtained nmr spectra of some benzylic potassium compounds using three different solvents and these results are listed in Table III. Al-

Table III. Chemical Shifts for Cumylpotassiums

Solvent	Compd	Shifts[a]		
		2,6	3,5	4
THF	**14**	2.13	1.08	2.87
Ether	**14**	2.11	1.10	2.86
TMEDA	**14**	2.10	1.10	2.84
Bis(2-N-ethyl-N-methylethyl)-N'-methylamine	**14**	2.08	1.08	2.81
Ether	**15**	2.11	1.10	
Ether	**16**	2.20	1.27	2.83
		1.85	1.17	

[a] Shift in ppm with respect to benzene

though the spectra for the potassium compounds are nowhere nearly as well resolved as the lithium compounds they are nearly first order and shifts can be accurately measured. It is clear in Table III that the shifts in cumylpotassium are almost independent of the solvent. The chemical shifts for compound **6** and the potassium derivative **16** are so similar that the shifts are essentially *unperturbed by the counterion*. Furthermore, this conclusion really applies to the results for all the tertiary benzyllithium compounds described here as well as those reported previously.[3,4] These include cumylpotassium in five solvents, **6** in isooctane–TMEDA and THF, and **16** in ether. In spite of differences in substituents at C_α and in solvent, their shifts are so similar that they must be due to the anion alone; also in a tight ion pair ring shifts would be influenced by the electric field due to the counterion.[9] As this is not observed the ion pairs (or aggregates thereof) must be fairly loose and/or solvent separated.

Although association numbers are not available for compounds **1**, **5**, **6**, and **7** in isooctane–TMEDA, it is known that triethylenediamine forms a 1:1 complex[13] with benzyllithium and that benzyllithium is a monomer in donor solvents such as ether or THF.[2] Hence it is probable that the benzyllithium compounds **1**, **5**, **6**, and **7** are also monomers under the conditions used in this work.

The shifts in the benzyllithiums are all considerably upfield of those in ordinary benzylic compounds indicating extensive delocalization of charge around the rings, as noted for benzyllithium itself.[2,14] While in general proton shifts in aromatic compounds are not as reliable an index of electron density as carbon-13 shifts[15] they still follow the electron densities in a qualitative manner.[8] Using the observed proportionality of +10 ppm/electron,[8] charge distributions from chem-

(13) S. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965).
(14) R. Waack and M. H. Doran, *ibid.*, **85**, 1651 (1963).
(15) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); T. Tokuhiro and G. Fraenkel, *J. Amer. Chem. Soc.*, **91**, 5005 (1969).
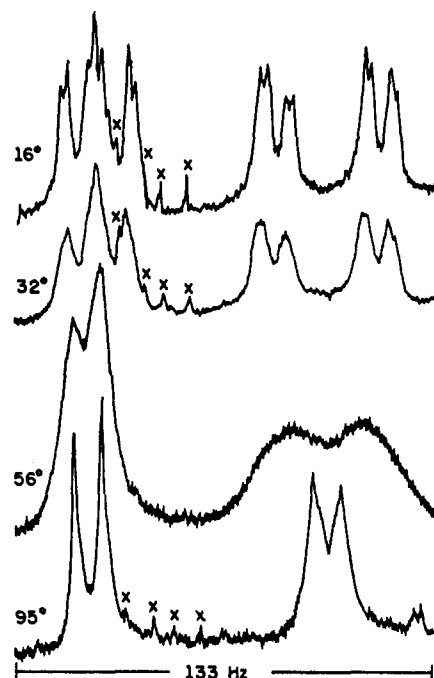

Figure 2. Nmr spectra, 100 MHz for 1 ring hydrogens, of 1, 1 M in isooctane–1 M TMEDA at different temperatures.

ical shifts for several benzyllithiums are compared with values calculated from molecular wave functions in Table IV. It is seen that the shifts most closely follow

Table IV. Charge Distribution in Benzyl Metal Compounds

	$6^{a,b}$	$1^{a,b}$	5^a	14^a	$PhCH_2^-$ Hückel	$PhCH_2^-$ SCF
o	−0.185	−0.183	−0.179	−0.211	−0.14	−0.14
m	−0.111	−0.105	−0.088	−0.110	0.0	−0.07
p	−0.280			−0.286	−0.14	−0.23

[a] From nmr data. [b] o and o' shifts are averaged as are m and m'.

charges calculated from SCF wave functions.

Up to this point, the principle conclusion to be derived from these results concerns the structure of the benzylic lithium and potassium compounds in solution. Taken together, the nonequivalence of the ring hydrogens (*viz.* **1**, **5**, **6**, and **16**), their positive shielding with respect to benzene, and the observed insensitivity of shifts to solvent and cation strongly implicate a largely conjugated structure, **17**, being the negative

$$Li^+ \quad \overset{CH_3}{\underset{CH_2C(CH_3)_3}{\diagdown\diagup}}$$

17
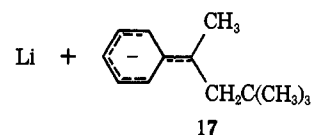
moiety in a loose or solvent separated ion pair. Rotation about the C_{ring}–C_{benzyl} bond must be slow on the nmr time scale.

At temperatures above 40° for **1** and 15° for **5** and **6** the nmr spectra undergo changes indicative that some exchange process is averaging the shifts among the ortho hydrogens and also those among the meta hydrogens. With increasing temperature, the resonance for the ortho protons (2 and 6) broadened and then coalesced to a doublet at their center. Similar changes
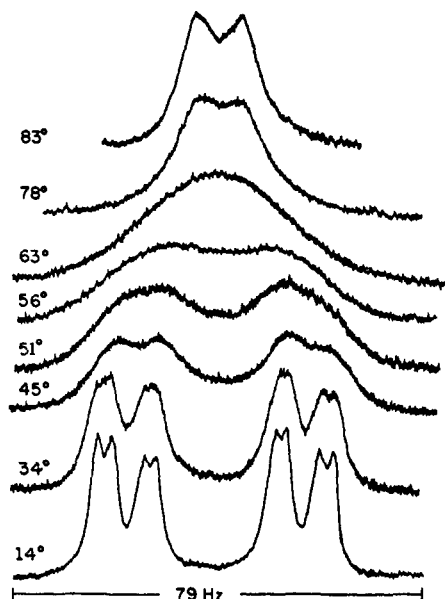
Figure 3. Nmr spectra, 100M Hz, ortho hydrogens in 5, 1 M iso-octane–1 M TMEDA at different temperatures.

Figure 4. (a) Nmr spectra, 100 MHz, ortho hydrogens, 6, 1 M in isooctane–TMEDA at different temperatures. (b) Calculated nmr line shapes for ortho hydrogens of 6 at different values of τ.

were observed for the meta protons (3 and 5). The aromatic resonances of **5** and **6** change from ABXY to AA′XX′ while **1** changes from ABMNX to AA′MM′X. Figures 3 and 4 reproduce the aromatic resonances of **1** and **6**, respectively, 0.90 M in isooctane and TMEDA as a function of temperature. The temperature-dependent nmr spectra for the ring protons only in compounds **1**, **5**, and **6** are shown in Figures 2, 3, and 4a.

On the basis of the preceding discussion it is most likely that the process responsible for averaging shifts in compounds **1**, **5**, and **6** is rotation about the C_{ring}–C_{benzyl} bond. Nmr line shapes for benzyllithium compounds **1**, **5**, and **6** have been calculated as a function of the rate of rotation about the C_{ring}–C_{benzyl} bond using computer program DNMR.[16] The output from this calculation was plotted with an IBM-1130. Such calculated line shapes for the ortho protons of **6** in isooctane–TMEDA at different values of τ, the mean life-time between rotations, are shown in Figure 4b. Comparison of experimental with theoretical line shapes gave rates of rotation in the various benzylic lithium compounds.

The simplest explanation for the results obtained so far is that rotation in the benzyl anion is responsible for the changes in the nmr line shapes. However, some molecular processes in organometallic compounds are not first order and involve more complicated mechanisms. For instance, inversion in primary Grignard reagent proceeds via a bimolecular transition state.[17] Therefore, we have undertaken kinetic studies of rotation in **1**, **5**, and **6**.

Using the definition of τ

$$1/\tau \equiv R/[G] \tag{1}$$

where R is the total rate of exchange and [G] is the concentration of exchanging substance, and assuming a simple rate law

$$R = k[G]^n \tag{2}$$

(16) Computer program based on G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969). We thank Professor Binsch for giving us a copy of this program.

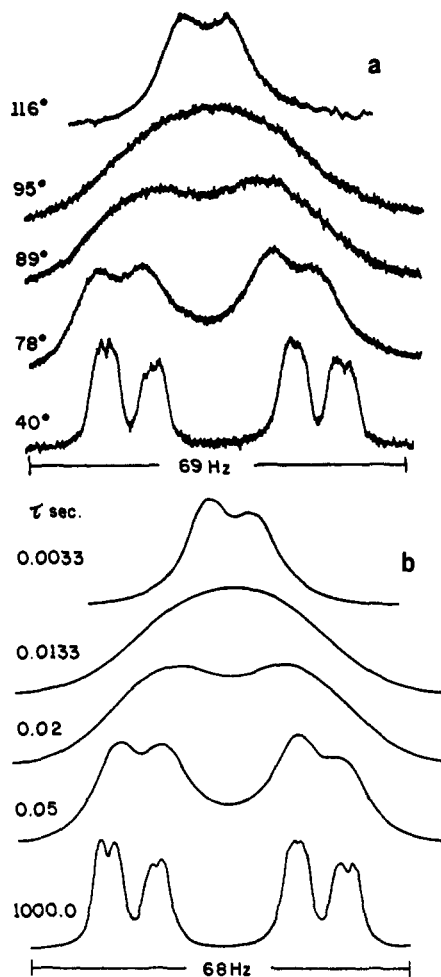(17) G. Fraenkel, C. E. Cottrell, and D. T. Dix, *ibid.*, **93**, 1704 (1971).

we have

$$1/\tau = k[G]^{n-1} \tag{3}$$

If eq 2 applies, a plot of log $1/\tau$ vs. log [G] will have a slope of $n - 1$. The results of these studies at different temperatures are summarized in Figures 5a–c for compounds **1**, **5**, and **6**, respectively. Values of n determined by a least-squares analysis of the data, which are labeled on the figures, come out close to 1 in all cases, indicating the rate of rotation to be first order in contained benzyllithium reagent. Since **1**, **5**, and **6** are probably monomers in isooctane–TMEDA, this result implies a unimolecular transition state for rotation.

The kinetic data from different temperatures have been plotted in Figure 6 to give the activation parameters listed in Table V.

Table V. Activation Parameters for Rotation in Benzyllithiums[a]

Compd	$E_a \pm 0.6$ kcal	$\Delta H^{\ddagger} \pm 0.6$ kcal	$\Delta S^{\ddagger} \pm 1.2$ eu	$\Delta G^{\ddagger}_{298°K} \pm 0.6$ kcal
6	19.4	18.7	0.3	18.6
1	19.1	18.4	4.6	17.1
5	19.2	18.5	5.2	17.0

[a] Solvent TMEDA (1 M)-isooctane.

The activation parameters for rotation vary little among the systems studied; $\Delta S^{\ddagger}$ is close to zero and
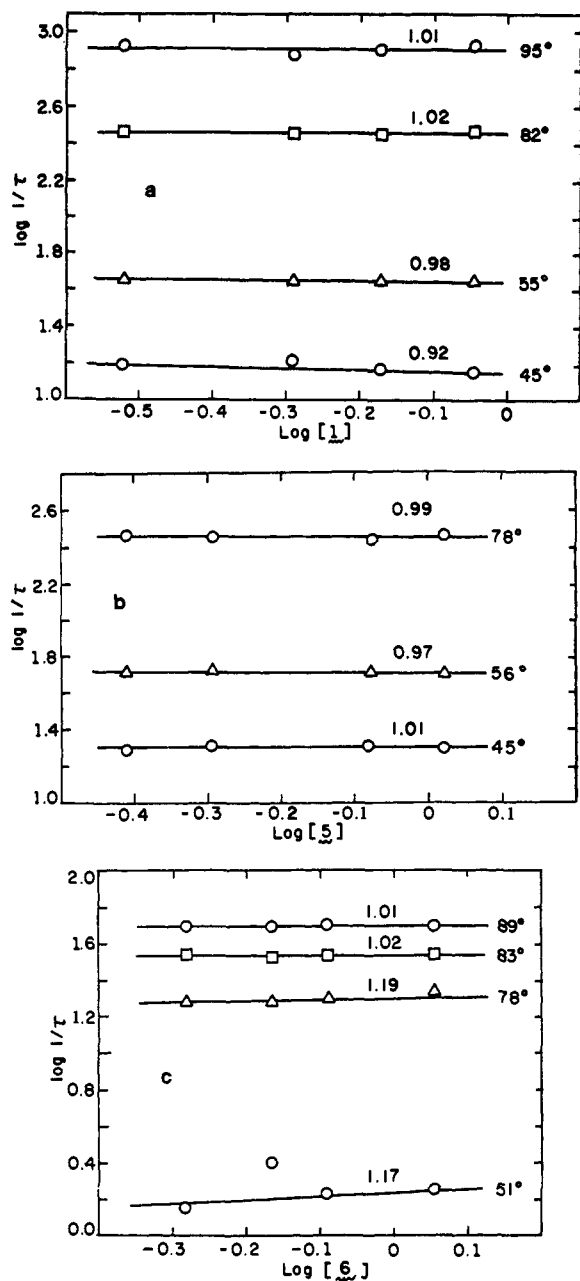
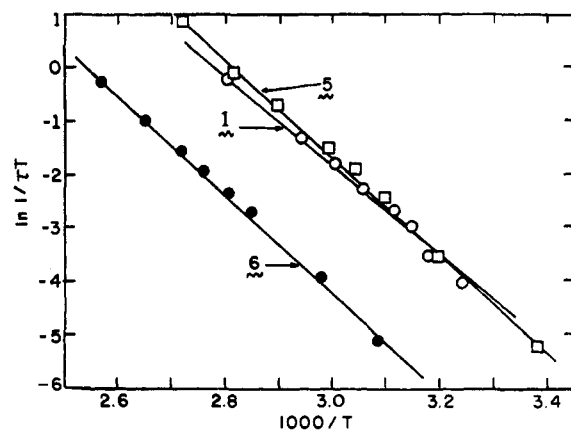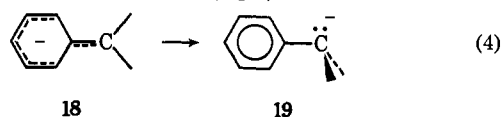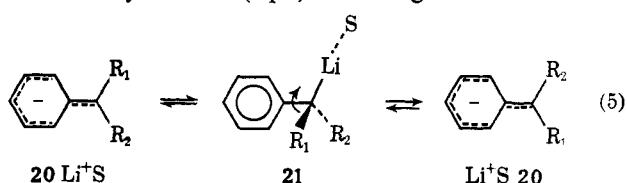Figure 5. Kinetic plots for rotation, with reaction orders for (a) 1, (b) 5, and (c) 6.

Figure 6. Eyring plots for rotation in 1, 5, and 6.

molecular process to reflect mainly changes in solvation. Suppose the rotation process involved transforming a planar delocalized benzylic anion to the twisted tetradedral species with the negative charge concentrated on the α carbon (eq 4). The solvation re-

$$
\text{(4)}
$$

18   19

quirements for the two species would be expected to be quite different. This effect would appear in $\Delta S^{\ddagger}$, but, in fact, the entropies are all quite close to zero. Then, some effect is responsible for neutralizing the solvation requirements of the localized anion, 19. This could happen if there were a much closer association of the lithium with the α carbon, involving some increase in covalency, in the transition state for rotation, compared to the ground state. It is envisaged that as the C_{ring}–C_{benzyl} bond in 20 begins to twist lithium ion approaches the benzyl carbon to form the more covalent structure 21. One or more rotations followed by loss of lithium ion brings about the exchange of the two substituents on the benzyl carbon (eq 5). In reagents such as those

$$
\text{(5)}
$$

20 Li$^+$S   21   Li$^+$S 20

$\Delta H^{\ddagger}$ *ca.* 18.5 kcal. It is pertinent to inquire whether this actually represents the barrier to rotation in the benzyl anion or whether some other more complex process is responsible for the rotation observed. To this end the ring nmr absorption of potassium compound 16 was monitored from 16 to 94°. The spectrum did not change throughout this entire temperature range. There was no sign of exchange broadening, indicating the rate of rotation to be slow on the nmr time scale up to 94°. At this temperature the reagent slowly deprotonated the solvent. Since 16, the potassium derivative, rotates very much more slowly than 1, the metal ion must participate in the rotation process at least in one and possibly in both of these compounds, that is, some molecular mechanism operates to produce rotation.

This conclusion just discussed also comes from consideration of the entropies of activation for rotation in 1, 5, and 6 (Table V). We assume $\Delta S^{\ddagger}$ for this uni-

studied here, TMEDA (S) is surely coordinated to lithium. The transformation 20 → 21 would be accompanied by some reduction in the bidentate coordination of lithium with TMEDA (S) and at the same time an increase in its covalent interaction with C_{benzyl}. The rate of such a coordination transfer process should be extremely sensitive to the nature of the ligand and the metal ion as is observed. Thus while the ring shifts for 6 in isooctane–TMEDA and in THF are almost the same, implying a similar electronic structure, the rates of rotation are quite different. At 40° in the former solvent k_1 is 0.7 sec^{-1} while in THF the value is 100 sec^{-1}.[5] Brownstein and Worsfold reported E_a of 14 kcal ($\Delta H^{\ddagger}$ = 10 kcal, $\Delta S^{\ddagger}$ = 5 eu) for rotation of 6 in THF,[5] quite different from the result obtained with isooctane–TMEDA. Evidently lithium coordination transfer from THF to carbon is faster than with TMEDA, the better ligand. The most extreme mani-

Fraenkel, Russell, Chen / Hindered Rotation in Benzylic Metal Compounds

festation of this effect takes place with the potassium compound, 16, where electronegativity considerations render a carbon–metal covalent interaction less favorable than with lithium; hence rotatiòn is too slow to measure. Note that this mechanism just described was invoked by Sandel, McKinley, and Freedman to account for the dependence on metal of rotation rates in phenylallyl metal compounds.[6]

In sum what we have found is that while nmr data for tertiary benzylic lithium and potassium compounds fit a planar conjugated loose or solvent separated ion pair, the rotation process which is detected does not take place in the free anion by itself. Instead, rotation results from a rearrangement within the ion pair whereby lithium coordination transfer from TMEDA to carbon produces a thermally excited less ionic benzyl metal compound. Because the process is promoted by the metal ion, rotation in the free anion is too slow to observe. The involvement of complex molecular mechanisms to bring about fast exchange, inversion, and rotation processes in organometallic compounds at equilibrium appears to be quite general.

The results described here are in distinct contrast to similar studies of rotation and chemical shifts in phenylallyl[6] and naphthylmethyl[7] metal compounds, respectively, where both the ground-state properties and the activation parameters were found to depend on solvent and metal. Possibly due to steric effects, the alkyl substituents at the benzyl position in 1, 5, and 6 cause these species to exist as loose ion pairs.

Experimental Section

Instruments. Mass spectra were obtained with an AEI Model MS-9 instrument. Vapor chromatography was performed on a Varian Aerograph Model A-700 automatic preparative gas chromatograph using a SE-30 column.

Unless otherwise specified, all nmr spectra were obtained with a Varian HA-100 high-resolution nmr spectrometer equipped with a variable-temperature probe. The sample temperature was controlled with the Varian V-6040 variable-temperature controller. The temperature reading, taken both before and after the spectrum was recorded, was determined from the temperature-dependent chemical shifts of methanol (low-temperature range) and ethylene glycol (high-temperature range). The homogeneity was optimized before each scan. Line shapes were recorded at a sweep time of 500 sec and at sweep width of 100 Hz (0.2 Hz/sec). At each temperature, three scans were recorded and the results averaged.

Purification of Reagents and Solvents. All olefins were dried with calcium hydride and fractionally distilled using proper provisions for exclusion of moisture. N,N,N',N'-Tetramethylethylenediamine was treated in the same way. Isooctane was shaken with 96% sulfuric acid, and the organic layer was washed with water, dried over potassium carbonate, and then distilled. Purified isooctane was stored over sodium. Dimethoxyethane and diglyme were refluxed over calcium hydride and then distilled. A second distillation from lithium aluminum hydride completed purification. Diethyl ether and THF were distilled from lithium aluminum hydride before use.

4-*tert*-Butyl-α-methylstyrene. A solution of methyl *p-tert*-butylbenzoate (179 g, 0.93 mol) in 400 ml of anhydrous ether was added dropwise to 2.3 mol of methylmagnesium iodide in 80 ml of ether at such a rate as to maintain a steady reflux. After refluxing for 2 hr the reaction mixture was worked up with 2 N hydrochloric acid. The ether solution of the product was washed with distilled water and dried over anhydrous MgSO₄. After evaporation of ether, the residue was distilled at reduced pressure from KHSO₄. The distillate was dried and redistilled giving 86.7 g (54%) of product, bp 85° (3 mm) (lit.[18] bp 98° (5 mm)). The nmr spectrum agreed with the predicted structure.

3,5-Di-*tert*-butyl-α-methylstyrene. 3,5-Di-*tert*-butylbenzoic acid[19] was converted to the methyl ester. The latter was treated with 3 equiv of methylmagnesium bromide, giving after work-up a 96% yield of (3,5-di-*tert*-butylphenyl)dimethylcarbinol. Dehydration with phosphoric acid yielded 79% of 3,5-di-*tert*-butyl-α-methylstyrene, bp 94–95° (1.8 mm) (lit.[20] bp 127–128° (12 mm)).

4,4-Dimethyl-2-phenyl-2-pentanol. 4,4-Dimethyl-2-pentanone (45 g, 0.4 mol) in 50 ml of dry ether was added to 500 ml of a 0.75 M solution of phenyllithium (0.4 mol) in ether. The reaction mixture was refluxed overnight and then hydrolyzed with saturated ammonium chloride. The ether layer was washed with water and dried with magnesium sulfate. Ether was removed and the residue distilled at 104–105° (4.2 mm) to give 60.1 g of the title compound in 78% yield.

4,4-Dimethyl-2-methoxy-2-phenylpentane. Under an argon atmosphere at room temperature, 1-phenyl-2,3,3-trimethylbutanol (19.2 g, 0.1 mol) was added slowly to a stirred suspension of potassium hydride (10 g, 0.12 mol) (50% oil mixture). Heat was evolved and the mixture first turned pink and then yellow. The reaction mixture was allowed to stand overnight. Then 30 ml of dry THF was added and the mixture stirred for 2 hr at room temperature. Methyl iodide, 28.4 g (0.2 mol), was added to the stirred reaction mixture. Heat evolved and the color changed from yellow to white. This mixture was stirred for 0.5 hr and allowed to stand overnight. Finally, hydrolysis with aqueous sodium chloride followed by drying of the ether layer with potassium carbonate and then removal of the ether gave after distillation at 123–126° (14.4 mm) 18 g of the ether in 87% yield.

2-Potassio-4,4-dimethyl-2-phenylpentane. Under an argon atmosphere a solution of 4,4-dimethyl-2-methoxy-2-phenylpentane (1.03 g, 0.005 mol) in 10 ml of dry pentane was stirred overnight with potassium (0.5 g, 0.013 mol) in small pieces. The resulting black precipitate was washed with four 10-ml portions of dry pentane and then dissolved in diglyme, forming a *ca.* 0.9 M solution.

Benzylic Lithium Compounds. All the α-methylstyrene–*tert*-butyllithium reactions were carried out in a 50-ml, round-bottomed flask closed with a 2-mm straight bore glass stopcock which was protected by a serum cap. Prior to use, all glassware was flamed out in a current of argon.

In a drybox, the reaction flask was charged with 0.015 mol (7.5 ml) of a 2.0 M solution of *tert*-butyllithium in pentane. After the apparatus was removed from the drybox, the pentane was evaporated by a stream of argon, and 3 ml of purified isooctane was added. The solution was stirred and cooled to −40 to −50° with a Dry Ice–acetone mixture. To the vigorously stirred solution of *tert*-butyllithium-isooctane at −50°, N,N,N',N'-tetramethylethylenediamine (TMEDA) (1.75 g, 0.015 mol) was added dropwise using a syringe equipped with a styringe stopcock. A light yellow slurry was obtained. At this time, using a syringe, a solution of 0.01 mol of α-methylstyrene in 1.5 ml of isooctane was added dropwise to the vigorously stirred slurry of *tert*-butyllithium–TMEDA at −30°. A deep red solution was immediately obtained. When the addition was complete, the stopcock was closed and the solution left stirring at −15° for 0.5 hr before a sample was removed. In this way solutions were prepared of 2-lithio-2-(4-isopropylphenyl)-4,4-dimethylpentane (1), 2-lithio-2-phenyl-4,4-dimethylpentane (6), 2-lithio-2-(4-*tert*-butylphenyl)-4,4-dimethylpentane (5), and 2-lithio-2-(3,5-di-*tert*-butylphenyl)-4,4-dimethylpentane (7). The last compound precipitated from the reaction mixture as a red-orange solid. It dissolved in ether and this solution was used for nmr analysis.

The benzyllithium compounds listed above were stored at −20° in vials protected by straight bore stopcocks.

Determination of Benzyllithium Concentration. A sample of the benzyllithium solution to be analyzed was hydrolyzed and the hydrolysate vapor chromatographed using a Varian Aerograph Model A-700 instrument equipped with a SE-30 column. The absorption area for 2,2-dimethyl-4-phenylpentane was compared with those obtained under identical conditions from standard solutions of this hydrocarbon with TMEDA in isooctane. Interpolation using the data from the standard solutions yielded concentrations of 2,2-dimethyl-4-phenylpentane, hence the orginal benzyllithium concentration. Nmr analysis of the organometallic solutions showed less than 1% (relative to the lithium compounds) of hydrolysate to be present.

Hydrolysis Reactions of Benzyllithiums. 2,2-Dimethyl-4-(4-iso-

(18) H. K. F. Hermans, A. C. Knaeps, and C. A. M. Van der Eycken, *Ind. Chim. Belge*, 24, 1467 (1959).

(19) W. Van Hartingveldt, P, E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 75, 301 (1956).

(20) H. D. Scharf and F. Doering, *Chem. Ber.*, 100, 1761 (1967).

propylphenyl)pentane. 2-Lithio-2-(4-isopropylphenyl)-4,4-dimethylpentane, prepared from *p*-isopropyl-α-methylstyrene (0.05 mol) as described above, was allowed to react with a tenfold excess of water.

The reaction mixture was extracted with diethyl ether and the extract washed subsequently with 1 *N* HCl until the aqueous layer was acidic in order to remove TMEDA and then washed with distilled water several times. The ether layer was separated, dried over MgSO₄, and concentrated on a rotary evaporator under vacuum. The 1:1 adduct, 2,2-dimethyl-4-(*p*-isopropyl)phenylpentane, was obtained by vacuum distillation, yield 7.37 g (67.7%), based on *p*-isopropyl-α-methylstyrene, bp 103–104° (4.3 mm). The mass spectrum showed M⁺ 218.

2,2-Dimethyl-4-phenylpentane. This compound was obtained in 68% yield, according to the above procedures starting from 0.05 mol of α-methylstyrene followed by hydrolysis, bp 77–77.5°(6.3 mm), M⁺ 176.

2,2-Dimethyl-4-(*p-tert*-butylphenyl)pentane. From 8.7 g of *p-tert*-butyl-α-methylstyrene, according to the above procedure, was obtained 9.4 g, 81% yield, of the title compound, bp 103–105° (2.2 mm), M⁺ 232.

2,2-Dimethyl-4-phenylpentane-*4-d*. The procedure was identical with that described above except the benzyllithium solution was hydrolyzed with D₂O. Vacuum distillation gave 5.2 g, 58.6% yield, of product, bp 78–78.5° (6.7 mm), M⁺ 177.

2,2-Dimethyl-4-(*p*-isopropyl)phenylpentane-*4-d*. The procedure was identical with that described above except the benzyllithium solution was hydrolyzed with D₂O. Vacuum distillation gave 8.0 g, 73.2% yield, bp 106–107° (4.9 mm), M⁺ 219.

2,2-Dimethyl-4-(3,5-di-*tert*-butyl)phenylpentane-*4-d*. The α-methyl-α-neopentyl-(3,5-di-*tert*-butyl)benzyllithium solution was prepared from the reaction of 6.9 g of 3,5-di-*tert*-butyl-α-methylstyrene with *tert*-butyllithium. The red solution containing some orange precipitate was hydrolyzed with D₂O and worked up with diethyl ether as usual. Distillation under reduced pressure gave 6.6 g (76.2%) of product, bp 113.5–115° (1.5 mm), M⁺ 289.

2,2-Dimethyl-4-(*p*-isopropyl)phenyl-4-trimethylsilanylpentane. The appropriate benzyllithium solution prepared as described above was allowed to react with 1 equiv of trimethylchlorosilane. The work-up procedure was the same as that described above. Vacuum distillation gave 10.6 g (73.1%), bp 90–91° (0.1 mm). The mass spectrum showed M⁺ 290.

An Electron Spin Resonance Study of the Phosphorescent States of Some 4- and 4,4'-Substituted Biphenyls

Harriet V. Taylor,[1] **A. L. Allred,* and Brian M. Hoffman**[2]

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received August 21, 1972

Abstract: Substituent effects on the unpaired spin distribution of the phosphorescent state for a series of 4- and 4,4'-substituted biphenyls were studied by epr and phosphorescence spectroscopy. No net differences in either epr or phosphorescence results are seen among the various alkyl substituents. Examination of zero-field splitting parameters suggests partial transfer of π-electron spin density from aromatic rings to silyl and germyl groups. Line-width variation among CH₃, CD₃, and CF₃ derivatives is explained by hyperfine interaction with substituent nuclei. The triplet state epr and phosphorescence results are supported by previously reported polarographic and uv data and by MO theory.

The influence of substituents on an aromatic π-electron system has been the subject of study for many years among organic chemists. Several orderings of electron donating and withdrawing effects have been proposed for many substituents based on studies of acidity or reactivity.[3–8] It is also of interest to determine the effect of these groups when the molecules are not undergoing reaction, since in many cases the influences on reactivity can be attributed to steric interactions or solvation effects.

Substituent effects are here reported for the first excited triplet state of several 4- and 4,4'-substituted biphenyls. Similar studies have been reported for methyl-substituted naphthalenes.[9] Triplet state energies are obtained from phosphorescence spectra. Electron paramagnetic resonance is used to obtain a measure of the changes in the triplet state spin density distribution caused by substituents on biphenyl and also to obtain triplet state lifetimes. Changes in the triplet spin density are reflected by changes in the zero-field splitting (ZFS) parameters *D* and *E* which characterize the dipolar spin Hamiltonian. With the addition of an isotropic Zeeman interaction, the Hamiltonian can be expressed as[10]

$$\hat{H}_D = g\beta H \cdot S + DS_z^2 + E(S_x^2 - S_y^2)$$

The parameter *D* is a measure of the distance between unpaired triplet spins averaged over the triplet wave function ($D \propto \langle r_{12}^{-3}\rangle$), and thus *D* gives a measure of

(1) National Institutes of Health Predoctoral Research Fellow.
(2) Alfred P. Sloan Fellow.
(3) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.
(4) J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).
(5) W. M. Schubert, J. M. Craven, R. G. Minton, and R. B. Murphy, *Tetrahedron*, 5, 194 (1959).
(6) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959.
(7) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, 74, 3120 (1952).
(8) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, 90, 4328 (1968).

(9) B. Smaller, E. C. Avery, and J. R. Remko, *J. Chem. Phys.*, 46, 3976 (1967).
(10) J. E. Wertz and J. R. Bolton, "Electron Spin Resonance: Elementary Theory and Practical Applications," McGraw-Hill, New York, N. Y., 1972.