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# EFFECTS OF LIGANDS ON ION-PAIRING BEHAVIOR OF BENZYLIC LITHIUM COMPOUNDS

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## Summary

The 1/1 adduct of t-butyllithium and α-methylstyrene (II) has been generated in cyclopentane in the presence of a variety of ether and t-amine ligands as well as unsolvated, giving stable solutions in every case. NMR spectra of the solvated species are the same for all ligands but differ from that of the unsolvated compound. The results are consistent with a salt which contains a conjugated t-benzylic anion and exists as a loose ion-pair in the presence of ligands and as a tight ion-pair in cyclopentane alone. In contrast, benzyllithium behaves like a tight ion-pair in the presence of all ligands tried. Steric hindrance to tight ion-pairing at $C_\alpha$ of II is concluded to be responsible for the results observed.

A covalently-bonded dilithium compound, 4,4-dimethyl-2-lithio-2-(*p*-lithiophenyl)pentane has been generated.

## Introduction

Benzyl, allyl and pentadienyl are among the simplest conjugated anions. Organolithium compounds which contain these moieties exhibit a bewildering array of structures and modes of bonding which vary from mainly covalent, bridged carbon—lithium bonds to different kinds of ion-pairs [1]. It is already known that the mode of carbon—lithium bonding can depend entirely on which ligand is present, as in the case of the 1/1 adduct of t-butyllithium with butadiene, vide infra [2]. In general, ligands such as hexamethylphosphoramide, 12-crown-4, cryptate-2-1-1 and pentaglyme favor separated ion-pairs while t-amines and diethyl ether give mainly tight ion-pairs [3].

In this paper we consider the effects of ligands and substitution on the structure of benzyllithium compounds. For studies of this type it is desirable, though rarely achieved, to investigate organolithium compounds which are soluble in a variety of media including hydrocarbons. This condition has now been met in the case of 4,4-dimethyl-2-lithio-2-phenylpentane [4]. It will be

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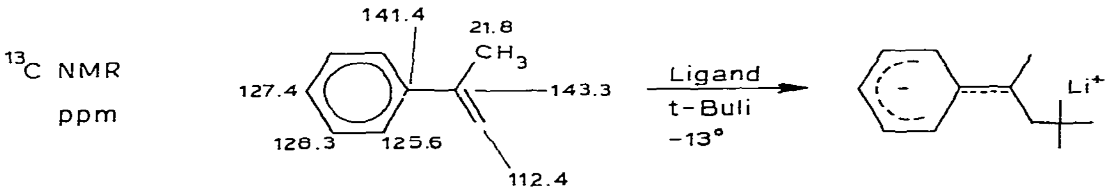
shown how this species retains its conjugated character in all solvents tried, in contrast to benzyllithium itself. Further an interesting dilithium species has been uncovered in this system.

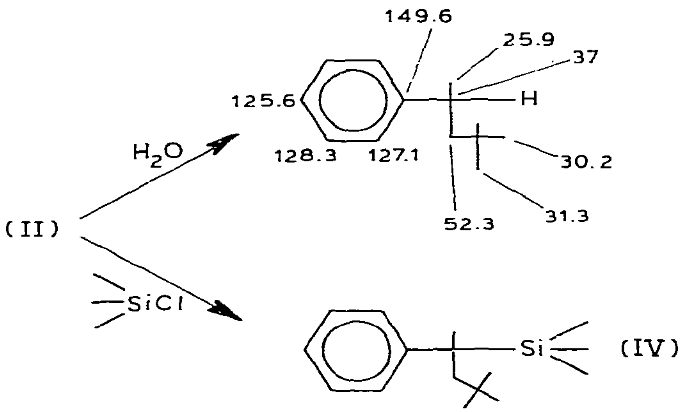
## Results and discussion

When α-methylstyrene (I) is treated with t-butyllithium at −78°C in hydrocarbon solvents in the presence of ethers or t-amines, the solution turns dark immediately on mixing the reactants [4]. The NMR spectrum of starting material becomes replaced immediately by that of the 1/1 adduct II, (see Figs. 1 and 2) as confirmed also by capture products III and IV.



(I)

(II) >98 %



(IV)

This procedure functions, using hydrocarbons as solvent, in the presence (separately) of 1 to 2 mol equivalents of *N,N,N′,N′*-tetramethylethylenedi-

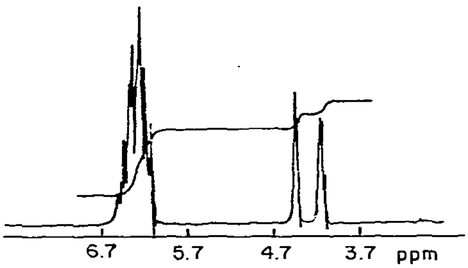


Fig. 1. Proton NMR spectrum, 60 MHz α-methylstyrene in chloroform-*d*.

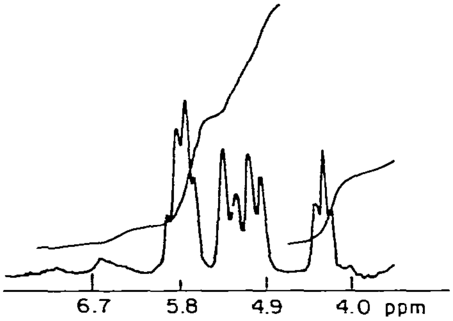
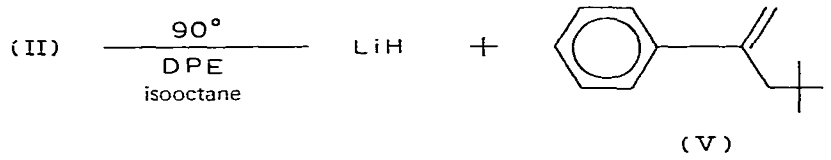


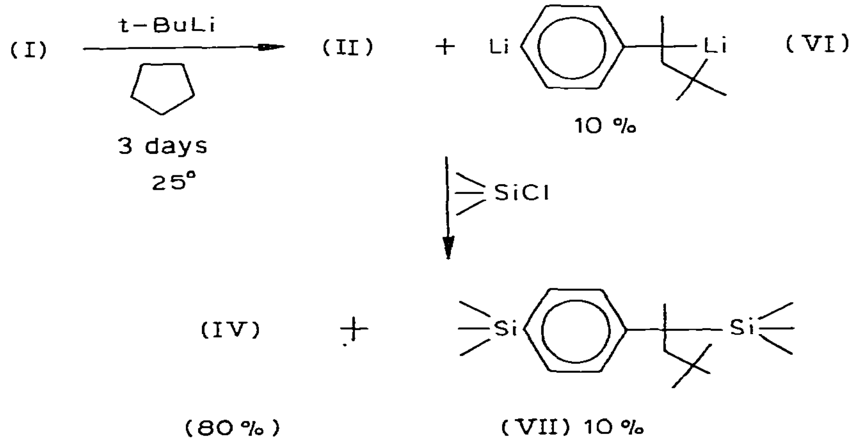
Fig. 2. Proton NMR spectrum 60 MHz of II, 1 $M$, with DPE, 1 $M$ in isooctane, 30°C.

amine (TMEDA) [4], 1,2-dipiperidylethane (DPE), *N*-methylpyrollidine (NMP), *N,N,N',N'*-tetramethylmethylenediamine (TMMDA), sparteine and diethyl ether in 95—98% yield, based on I.

The stability of salt II depends markedly on ligand. Thus at 80°C II is stable in the presence of TMEDA but rapidly deprotonates diethyl ether as shown by formation of hydrolysate III. Finally, on extended heating at 90°C in the presence of *N*-methylpyrollidine, or *N,N,N',N'*-tetramethylmethylenediamine or 1,2-dipiperidylethane. II undergoes loss of lithium hydride to give olefin V. These last-mentioned ligands are stable under the conditions of this reaction.



When the addition reaction I → II was tried at 25°C using cyclopentane as solvent, but without ligands, the mixture slowly turned red and viscous. After three days hydrolysis gave III in 85% yield and the rest was starting material. This indicates that 1/1 addition takes place without ligands. The silylation products from this reaction mixture revealed, in addition to the expected unsolvated II, a dilithium species VI in ca. 10% conversion as indicated by product VII.



This reaction has also been run in cyclopentane in the presence of equimolar amounts of aromatic compounds and olefins including benzene, toluene, *m*-xylene and tetramethylethylene. These showed no effect on the rate of t-butyl addition to $\alpha$-methylstyrene compared to I in cyclopentane. Addition of *N*-methylpyrollidine to the reaction mixture I $\rightarrow$ II + VI gave a non-viscous solution whose NMR spectrum is almost identical to that obtained above for the sample from $\alpha$-methylstyrene and t-butyllithium reacted in the presence of *N*-methylpyrollidine.

Carbon-13 NMR of salt II, see for example Fig. 3, formed in the presence of different ligands, Table 1, shows marked shielding at the benzyl (2) *ortho* (7) and *para* (9) carbons, compared to starting material or hydrolysate [5], see I and III. The magnetic non-equivalence of the *ortho* as well as *meta* carbons at room temperature shows rotation about the ring—benzyl bond to be slow on the NMR time scale. As seen in Table 1 the ring and benzyl shifts of II vary relatively little in the presence of different ligands implying the effect of ligand and lithium ion on the ring shifts to be about the same and possibly too small to measure.

A comparison of the ring and benzyl $^{13}C$ shifts of solvated II with shifts of neutral carbons in structurally similar environments reveals a change in total shift of +150 ppm on going from neutral model shifts to the solvated species II. This is close to the 160 ppm shift per electron observed for $\pi$-systems by several investigators [6]. The neutral ring shifts used here came from hydrolysate III and C(2), neutral, is chosen as 143 ppm as in a 1,1-dialkylolefin [7]. Taken together, these results imply that the solvated salts behave as if they contain conjugated benzylic anions and the counterion is too far from the organic moiety to influence its ring and benzyl shifts. Interestingly, the $^{13}C$ ring shifts for solvated II are very similar, also, to those of cumylpotassium [5], implying solvated II to consist of loose ion pairs.

The NMR shifts for unsolvated II, see Table 1, while qualitatively consistent for a conjugated anion, are noticeably different from those of solvated II, especially at $C(7, 7')_{ortho}$, $C(2, \alpha)$ and $C(6)_{ipso}$. This could result from tighter

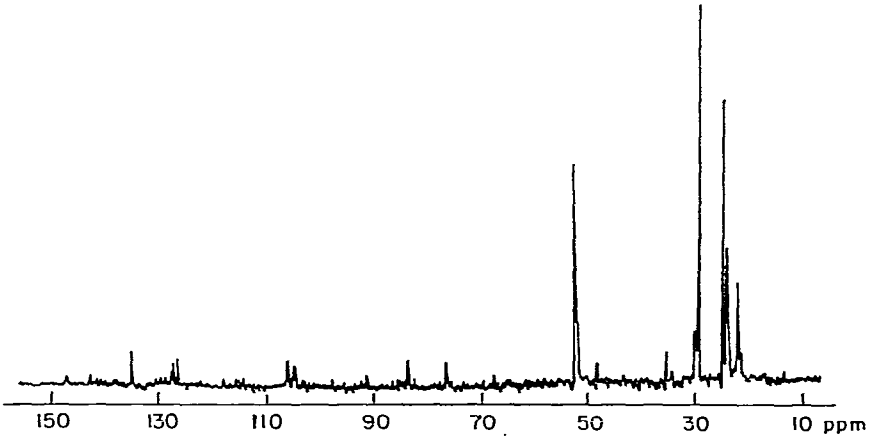
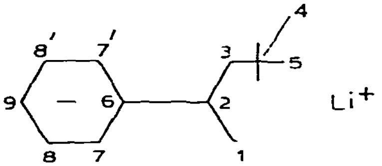


Fig. 3. $^{13}C$ NMR spectrum, 15.09 MHz, of II, 1 *M*, with DPE, 1 *M*, in isooctane.

TABLE 1

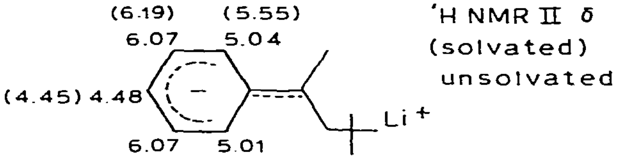
$^{13}$C NMR SHIFTS FOR II (1 *M*) IN ISOOCTANE WITH DIFFERENT LIGANDS (1 *M*) AT 30°C



| site | shifts δ (ppm) [a] | | | | | |
|---|---|---|---|---|---|---|
| | | TMEDA | DPE | TMMDH | $^{-}$O$^{-}$ [b] | NMP |
| 1 | 22 | 22.4 | 22.3 | 22.0 | 21.8 | 22.3 |
| 2 | 87 | 76.7 | 77.4 | 78.1 | 78.2 | 80.0 |
| 3 | 48.2 | 49.0 | 49.3 | 49.0 | 48.7 | 49.1 |
| 4 | 36.1 | 36.0 | 36.3 | 36.0 | 36.1 | 36.6 |
| 5 | 30.9 | 30.3 | 30.5 | 30.6 | 30.6 | 30.4 |
| 6 | 131.0 | 135.4 | 135.9 | 134.5 | 134.7 | 134.9 |
| 7 | 102 | 104.0 | 105.6 | 106.0 | 104.3 | 104.2 |
| 7' | 106 | 106.0 | 106.6 | 106.3 | 106.4 | 107.1 |
| 8 | 127.3 | 128.2 | 128.1 | 128.7 | 127.9 | 129.5 |
| 8' | 127.0 | 127.2 | 127.3 | 127.6 | 127.2 | 128.3 |
| 9 | 83.3 | 85.0 | 84.3 | 85.4 | 85.3 | 84.9 |

[a] From tetramethylsilane. [b] 2 *M*.

ion-pairing and a probably higher state of aggregation in unsolvated II compared to solvated II. The proton NMR data lead to similar conclusions, there is one set of shifts for the solvated salt II and another for unsolvated salt, see VIII.



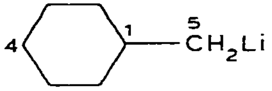
(VIII)

Interestingly, the *ortho* carbon resonance for unsolvated II is very broad at 35°C, the only broad line in the spectrum, indicating rotation about the ring—benzyl bond to be much faster (ca. ×200) than in the case of solvated II. Cooling this sample of unsolvated II caused precipitation of the salt, so the *ortho* $^{13}$C resonance could not be observed under conditions of slow rotation.

It is instructive to compare NMR data for II with those for benzyllithium (IX) itself. Benzyllithium was prepared by treatment of toluene or trimethylbenzyltin with n-butyllithium in the presence of different ligands. The $^{13}$C NMR data listed in Table 2 show how in contrast to solvated II the $^{13}$C shifts of benzyllithium vary considerably with ligand, especially at C(α). Furthermore the shifts of benzyllithium in different media cannot be rationalized as due to charge effects alone. Comparing the average shifts in Table 3 with neutral model shifts gives a total change in shift from model to benzyllithium of only

TABLE 2

$^{13}$C SHIFTS IN BENZYLLITHIUM, 25°C



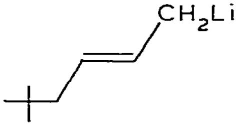
(IX)

| Solvent (ligand X equiv) | C(1) | C(2) | C(3) | C(4) | C(5) |
|---|---|---|---|---|---|
| Diethyl ether [a] | 152.7 | 116.3 | 130.2 | 109.7 | 30.8 |
| Diethyl ether [b] | 153.2 | 116.9 | 130.2 | 110.5 | 29.3 |
| Diethyl ether [a] (TMEDA X 1) | 157.5 | 116.6 | 129.2 | 107.0 | 35.4 |
| Diethyl ether [a] (DPE X 1) | 158.9 | 118.0 | 128.7 | 109.3 | 34.7 |
| THF [10] | 160.5 | 116.4 | 128.2 | 105.5 | 36.7 |
| THF [10] (TMEDA X 1) | 159.0 | 117.2 | 128.2 | 105.5 | 36.3 |

[a] By metallation of toluene using n-butyllithium. [b] From benzyltrimethylstannane and n-butyllithium.

ca. +98 ppm. This is far less than the +160 ppm/electron reported for $^{13}$C shifts in cyclic $\pi$-species [6]. The neutral model shifts used for benzyl are (in ppm) $C(\alpha)$ 112, $C(2)_{ortho}$ 128, $C(3)_{meta}$ 128, $C(4)_{para}$ 128, $C_{ipso}$ 142. Thus in benzyllithium effects due to tight ion-pairing, or even some partial carbon lithium covalency at $C(\alpha)$, contribute to the $^{13}$C shifts. Note that the structure of the benzyllithium-DABCO complex, from X-ray crystallography, shows lithium to be close to $C(\alpha)$ and the edge of the ring [8].

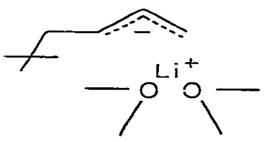
Another system whose NMR data are critically dependent on lithium ligand is the 1/1 adduct of t-butyllithium with 1,3-butadiene [2]. In hydrocarbon solvents the spectral data are most consistent with the covalent structure 5,5-dimethyl-1-lithio-2-hexane, *trans* and *cis* (Xa and Xb), respectively, while in



(Xa)

(Xb)

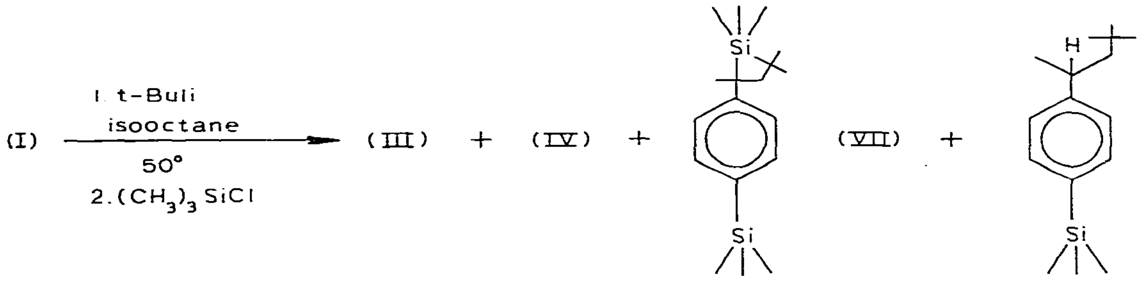
the presence of ethers the properties fit best for a tight ion-pair, XI.



(XI)

The explanation for this difference in behavior of II compared to IX and X, XI could be that heavy substitution about the benzyl carbon of II, renders bridged carbon—lithium bonds energetically inaccessible. Hence II contains a conjugated anion even when unsolvated, while the other species listed above are subject to varying degrees of C, Li covalency as well as tight ion-pairing.

The addition reaction of t-butyllithium to α-methylstyrene was also investigated at 50°C using isooctane as solvent.



The yield of dilithium species increases with temperature and t-butyllithium concentration, see Table 3. This reaction produces a red viscous solution together with some precipitate. Proton and $^{13}C$ NMR of these samples show mainly unsolvated II and a small amount of starting material.

In addition there is a broad line at δ 7 ppm in the proton spectrum, Fig. 4, and peaks at 123, 127 and 169 ppm in the $^{13}C$ spectrum. These are best ascribed to dilithium species VII. Furthermore, 169 ppm is close to the shift of carbon-bound lithium in phenyllithium (in ether) [9]. Then the resonances at 123 and 127 ppm must be due to $C_{ortho}$ and $C_{meta}$ of VI. These are evidently shifts for neutral carbons. In this way we are led to conclude that both lithiums in VI are covalently bound. One might argue that substitution about C(α) in VI should preclude covalent bonding to lithium as is the case of II. However a resulting 4-lithiobenzyl anion could be destabilized, relative to VI, by the accumulation of charge at $C_{para}$, XIII.

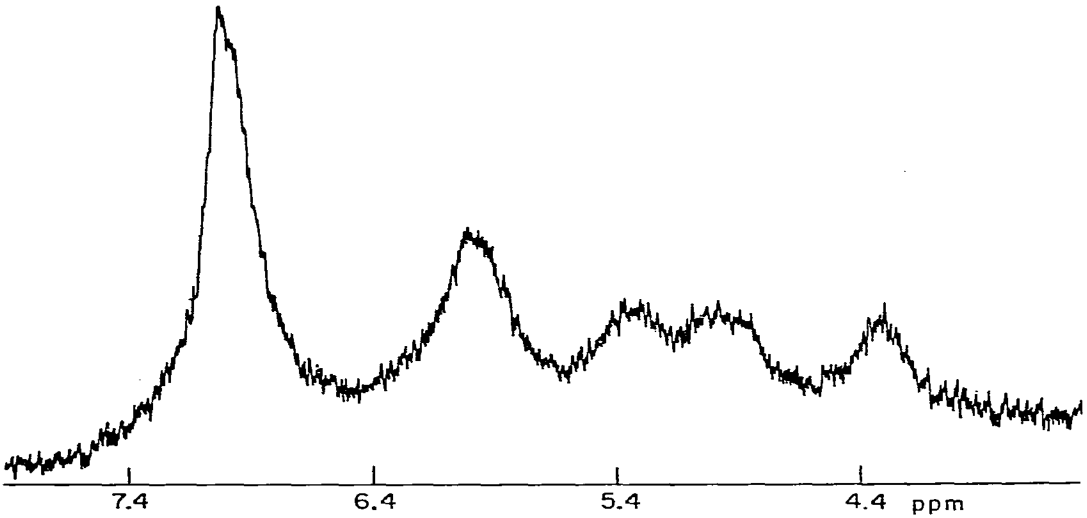
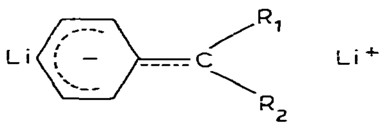


Fig. 4. Proton NMR spectrum, 90 MHz, of II (1 M) and VI (0.3 M) in isooctane, 30°C.

TABLE 3

| I | n X t-Buli<br>50°, 30 min<br>isooctane | II + VI |
|---|---|---|
| $n$ | Yield of II (%) [a] | Yields of VI (%) [a] |
| 1.0 | 68 | 17 |
| 1.5 | 55 | 41 |
| 2.0 | 24 | 73 |
| 2.5 | 14 | 81 |

[a] Based on I.



(XIII)

## Conclusions

It has been shown that substitution of alkyl groups at $C_\alpha$ of benzyllithium favors the formation of loose ion pairs containing conjugated anions unpertubed by ligand. In comparison, benzyllithium behaves like a tight ion pair. The role of steric effects at $C_\alpha$ is to render tight ion pairing energetically inaccessible.

## Experimental

### *Solvents*

Grignard reagents, mainly n-butylmagnesium bromide, were prepared in diethyl ether, tetrahydrofuran, and dimethoxyethane. Dry solvent was distilled from these solutions as needed. *N,N,N′,N′*-Tetramethylethylenediamine, *N,N,N′,N′*-tetramethylmethylenediamine, *N*-methylpyrolidine, 1,2-dipiperidylethane, and triethylamine were fractionally distilled from potassium hydroxide pellets. The center cut was stored over calcium hydride and distilled directly before use. Cyclopentane and 2,2,4-trimethylpentane (isooctane) were washed with concentrated sulfuric acid, water, and 10% bicarbonate solution, dried over anhydrous magnesium sulfate, stored over lithium aluminum hydride and distilled from this reagent prior to use. Benzene, toluene, *m*-xylene, and tetramethylethylene were dried by distilling 10% of its volume, discarding the distillate, adding calcium hydride and distilling from it directly before use. Naphthalene was recrystallized from a 9/1 chloroform/ethanol solution, then carefully sublimed and stored under argon. All solvents used in benzyllithium preparations and organometallic reactions were distilled under argon into a dry sidearm flask and transferred through syringes equipped with stopcocks and stainless steel needles. This equipment was baked at 135°C for at least one hour prior to use.

### *Apparatus*

Syringes were Becton-Dickenson and Co. multifits. Stainless steel needles were from W.A. Butler. Syringe stopcocks were Becton-Dickenson MSO1. NMR tubes were Wilmad 507-PP five millimeter o.d. for proton NMR and Wilmad 513-7PP ten millimeter o.d. for carbon NMR. All separations by vapor phase chromatography were done using a Varian Aerograph A-700 instrument equipped with a fifteen foot by $\frac{1}{2}$ inch 20% SE-30 on Chromosorb P column. Operations requiring an inert atmosphere were carried out in either a Kewaunee Scientific Equipment 2C281-20 glove box or a Vacuum Atmospheres HE-43 glove box.

### *NMR spectra*

Proton NMR spectra were obtained using Varian A-60A (60 MHz), EM-360L (60 MHz), or Bruker HX-90 (90-MHz) spectrometers. Carbon spectra were obtained on a "home-made" instrument at 15.0898 MHz in the Fourier transform mode. It consists of a Bruker chassis equipped with a B-SV3B decoupler, and B-SN 15 field stabilizer, an Ortec 416A gate and delay generator and 4610 program control unit, Teletronix 602 display unit, Hewlett Packard 5105A frequency synthesizer and Varian Associates electromagnet (60 MHz). The data system includes a Nicolet BNC 1080E computer with 20,480 20-bit words of memory and a Diablo movable head disk storage unit.

### *Carbon-13 NMR spectra of benzyllithium compounds*

Solutions of benzylic lithiums were syringed into 10 mm o.d. NMR tubes fitted with stopcocks bearing ground glass joints. These were attached to the vacuum line by two freeze-thaw cycles and sealed off by flame with pumping. The NMR acquisition parameters were: sweep width 3000 Hz, delay time 166 microseconds, pulse width 3.0 microseconds (corresponds to a flip angle of 19°), and either 2048 or 4096 scans depending on the concentration of species. Full proton broad-band decoupling was accomplished with a center-band frequency of approximately 60 MHz modulated into a band pass of 3000 Hz and amplified with 3 watts of power. A spectrum of 4096 data points was obtained with resolution 0.735 Mz/data point.

### *Quench reactions of benzyllithium compounds*

Dimethyl sulfate and trimethylchlorosilane were distilled from molecular sieves and the center cut was stored under argon. A dry test tube fitted with a serum cap was flushed with argon and approximately 1 ml of either dimethyl sulfate or trimethylchlorosilane was added via syringe. The test tube was cooled with an ice-water bath and 0.4 ml of the appropriate benzyllithium solution added dropwise by means of a syringe. Distilled water (1 ml) and diethyl ether (1 ml) were then added and the organic layer separated. The products were separated by vapor chromatography.

### *Reaction of α-methylstyrene with t-butyllithium, Method A at 50°C*

The reaction vessel consisted of a 25 ml round bottomed flask equipped with two sidearms with attached 3 mm straight-bore Teflon stopcocks, both protected with serum caps. This assembly, containing also a glass covered magnetic stir-bar, was flamed out while flushing the system with a current of dry argon. The flask was charged via syringe with t-butyllithium (Aldrich) in pentane (3.8 ml, 2.65 *M*, 10 mmol). Pentane was removed by passing a current of argon over the rapidly stirred solution and replaced by 3 ml of dry degassed isooctane, using a syringe. After warming the reaction vessel to 50° C with stirring, a solution of α-methylstyrene (0.65 ml, 5 mmol) in 3 ml isooctane (both dry and free of oxygen) was rapidly syringed in. The reaction mixture was heated for an additional half hour with stirring. The viscous red solution which resulted was cooled to 0° C and treated with trimethylchlorosilane (1.1. g, 10 mmol), distilled from triethylamine. This product mixture was taken up in water and isooctane, 5 ml each, the organic layer dried over $MgSO_4$ and the organic components separated using a Varian Aerograph A-700 gas chromatograph equipped with a fifteen foot by $\frac{1}{2}$ inch 20% SE-30 on Chromosorb P column. There ensued: 2,2-dimethyl-4-phenylpentane (III), 10%, *m/e* found 176.1565, calcd. 176.1568; 2,2-dimethyl-4-phenyl-4-trimethylsilylpentane (IV), 36%, *m/e* found 248.1962, calcd. 248.1964; 2,2-dimethyl-4(4-trimethylsilylphenyl)pentane, 13%, *m/e* found 248.1693, calcd. 248.1964; and 2,2-dimethyl-4(4-trimethylsilylphenyl)-4-trimethylsilylpentane (VII), 33%, *m/e* found 320.2362, calcd. 320.2364. All but the last compound were compared to authentic samples prepared by alternate routes. NMR data are collected in Table 2. Other preparations of II and VI in solution differed from the foregoing only in the temperature and time of reaction as well as the amount of t-butyllithium used.

Reactions monitored with NMR were run in sealed 10 mm o.d. NMR tubes.

### *Solvated 4,4-dimethyl-2-lithio-2-phenylpentane, Method C*

In this procedure [4] α-methylstyrene (0.65 ml, 5 mmol) is slowly added at —50° C to an equivalent of t-butyllithium and one or two molar equivalents of ligand in 3 ml of isooctane. The mixture is stirred at —50° C for 2 h and allowed to warm to room temperature over ca. 4 h. Silylation and hydrolysis indicated >97% conversion to II based on starting material.

### *Preparation of solvated 4,4-dimethyl-2-lithio-2-phenylpentane, Method B*

The apparatus and method for isolating the t-butyllithium are as described in procedure A. Thus α-methylstyrene (0.65 ml, 5 mmol) was slowly added to t-butyllithium (5.5 mmol) in 3 ml isooctane at room temperature under an atmosphere of argon. The mixture was stirred overnight, ca. 10 h, then the appropriate ligand (5.5 mmol) was added to the resulting red viscous solution and the mixture stirred for one more hour. Ligands used were 1,2-dipiperidylethane (Reilly), *N,N,N',N'*-tetramethylethylenediamine, diethyl ether, and 1,2-dimethoxyethane. Vapor phase chromatography of the hydrolysates of these reactions showed them to run at least 95% completion, based on α-methylstyrene.

### *4,4-Dimethyl-2-phenyl-1-pentene (V)*

The solution obtained from α-methylstyrene (0.65 ml, 5 mmol) and t-butyllithium (5.5 mmol) and *N,N,N',N'*-tetramethylmethylenediamine, as in Method B was heated at 90° C for 4 h. Treatment with $D_2O$ followed by gas chromatographic separation of the organic phase gave 0.15 g 2-deuterio-4,4-dimethyl-2-phenylpentane (17%), identified by comparison with an authentic sample [4] and 0.7 g of 4,4-dimethyl-2-phenyl-1-pentene (80%); NMR data given in Table 1; *m/e* found 174.1412, $C_{13}H_{18}$ calcd. 174.1408. Repeating the experiment with 1,2-dipiperidylethane gave similar results.

*Preparation of benzyllithium*

(a) A reaction vessel (as in A) was charged with n-butyllithium in cyclopentane (3.6 *N*, 1.4 ml, 5.5 mmol, 10% excess) and either diethyl ether (1.4 ml, 11 mmol) or DPE (1.2 ml, 5.5 mmol) was added at room temperature. Toluene (0.53 ml, 5.0 mmol) was added within minutes and the yellow solution stirred for 1 h. The reaction was monitored by vapor phase chromatography of the methylated derivatives using dimethyl sulfate; at least 90% conversion to the benzyl salt occurred within 1 h.

(b) Toluene (1.1 ml, 10 mmol) was added to a solution of TMEDA (1.66 ml, 11 mmol) and n-butyllithium in isooctane (1.7 *N*, 6.5 ml, 11 mmol, 10% excess) at room temperature. An immediate yellow precipitate formed. To dissolve this solid, 1.0 ml of diethyl ether was added, and the reaction followed just as previously described.

*Reaction of benzyltrimethyltin with n-butyllithium*

The reaction vessel (as in A) was charged with n-butyllithium in cyclopentane (1.55 *N*, 3.55 ml, 5.5 mmol, 10% excess), and benzyltrimethyltin (1.27 g, 5.0 mmol) was added via syringe at room temperature within minutes. Diethyl ether (1.14 ml, 11 mmol) was then added by syringe at room temperature, producing a bright yellow solution. After stirring ca. 3 h, a yellow precipitate formed, then redissolved within 30 minutes. A carbon-13 NMR sample was prepared as previously described and vapor phase chromatography of a methylated aliquot showed 95% yield of benzyllithium as ethylbenzene.

## Acknowledgment

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