STERIC EFFECTS IN THE METALATIONS OF 1,1-DI-*p*-TOLYLETHANE. KINETIC vs. EQUILIBRIUM CONTROL *

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Summary

The reactions of 1,1-di-*p*-tolylethane with metalating agents in tetrahydrofuran were examined. With lithio derivatives the nature of the anion formed depended upon the base. The ^{1}H and ^{13}C NMR spectra as well as the products of methylation of the anions are compared with those of *p*-xylyllithium and 1,1-diphenylethyllithium. Each anion is distinct in spectra and product of methylation. When a deficiency of 1,1-di-*p*-tolylethane was used, anion equilibration was effected.

Introduction

In previous work [1] we have studied the rotational barrier of 4,4'-dimethyldiphenylmethyllithium (I) generated from butyllithium and the corresponding hydrocarbon (II). To investigate the effect of substituents on this barrier we sought to prepare the corresponding 4,4'-dimethyldiphenylethyl anion (III). Initial experiments revealed two surprising features. First, anion generation was significantly more difficult and, second, it appeared that the expected anion was not obtained when more vigorous conditions were used.
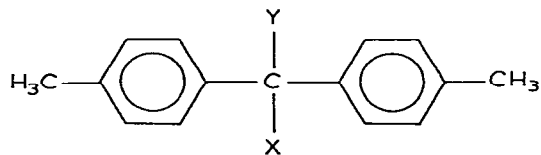
(I) X = Li , Y = H
(II) X = Y = H
(III) X = Li , Y = CH$_3$
(IV) X = H , Y = CH$_3$

* Dedicated to Professor H.C. Brown in recognition of his contributions to chemistry.

This seemingly small change in structure causing a large change in anion stability and formation suggested a steric effect. The quantitative understanding of steric effects is the result of elegant work of Brown [2]. Knowledge of these factors led to the suggestion that the present observation was of potential interest. Accordingly, we have investigated anion formation in this system in greater detail and compared it with select model anions. Included in this study are the ^{1}H and ^{13}C NMR of the anions and reactions of the anions with methyl iodide.

Results and discussion

The facile synthesis of 1,1-di-*p*-tolylethane (IV) and the prior successes of generating diphenylmethyl anions by metalation reactions in tetrahydrofuran (THF) [3] provided the basis for the expected generation of this substituted diphenylmethyl anion. Reaction of the aromatic hydrocarbon with commercial n-butyllithium in THF at temperatures from 0—25°C was very slow and the spectrum was complicated by significant acetaldehyde enolate and ethylene formation [4]. These products of reaction from THF with butyllithium [4] are observed in the absence of hydrocarbon or in its presence when metalation is not facile. To improve the extent of the desired metalation a stronger base was employed.

Reaction of IV with commercial t-butyllitium in THF at 0—25°C for 15 min produced a dark red color. The ^{1}H NMR spectrum (0.4 *M* in THF) did not reveal (Table 1 and Fig. 1) the expected AB pattern for the aromatic *ortho* and *meta* hydrogens of the diphenylmethyl anion. Additionally, the aromatic protons attributable to an anion resembled those of benzyl anion substituted in the *para* position (Table 1 and Fig. 1). Quenching of the anion with ethanol gave rise to the parent hydrocarbon IV as the only product. Finally, the anion solution was stable for several hours at room temperature and at least for 4 days at —10°C.
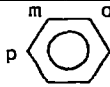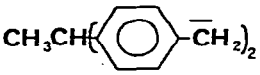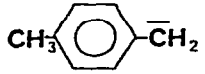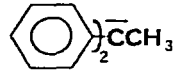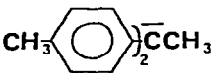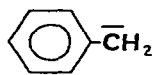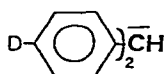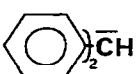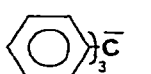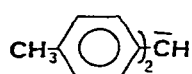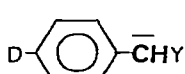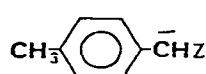
Two remarkable aspects of the reaction are the fact that t-butyllithium reacted with the methyl protons rather than central methine proton and the absence of aromatic protons ascribable to a neutral ring when reaction was complete. This could be explained by extensive formation of a dianion (V).

(V)
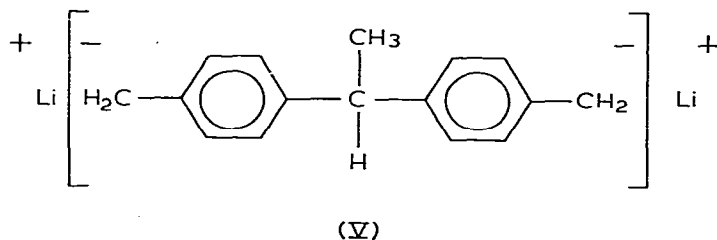
This possibility was of considerable interest and merited further attention. Anion formation from two model hydrocarbons was investigated for comparison. The first of these *p*-xylene could only provide a *para*-substituted benzyl anion (VII) whereas the second, 1,1-diphenylethane (VIII) could only provide a

TABLE 1

NMR DATA OF AROMATIC PROTONS OF LITHIOARYLMETHYL ANIONS IN THF

p〈ring〉m o –$\bar{\text{C}}$	H_o [a]	H_m [a]	J_{om} (Hz)	H_p [a]	J_{pm} (Hz)	Ref.
$CH_3CH(\text{C}_6H_4-\bar{C}H_2)_2$	6.14	6.36	8.3			This work
$CH_3-\text{C}_6H_4-\bar{C}H_2$	6.12	6.24	8.0			This work
$(\text{C}_6H_5)_2\bar{C}CH_3$	6.84	6.51	7.8	5.60	6.5	This work
$(CH_3-\text{C}_6H_4)_2\bar{C}CH_3$	6.79	6.38	8.3			This work
$\text{C}_6H_5-\bar{C}H_2$	6.09	6.30	8.0	5.50	6.2	[13]
$(D-\text{C}_6H_4)_2\bar{C}H$	6.50	6.50	8.1			[1,3b]
$(\text{C}_6H_5)_2\bar{C}H$	6.51	6.54	8.2	5.65	6.9	[13]
$(\text{C}_6H_5)_3\bar{C}$	7.31	6.52	7.9	5.96	6.6	[13]
$(CH_3-\text{C}_6H_4)_2\bar{C}H$	6.52	6.52	8.1			[1,3b]
$D-\text{C}_6H_4-\bar{C}HY$	6.42	6.42	8.1			[1,3b]
$CH_3-\text{C}_6H_4-\bar{C}HZ$	6.42	6.42	8.1			[1,3b]

[a] ppm downfield from Me_4Si (internal). [b] Y = p-methylphenyl, Z = p-D-phenyl.

substituted diphenylmethyl anion IX. In turn then each serves as a model for the possible metalation sites in IV.

Reaction of VI with t-butyllithium in THF at —60 to —70°C for 15 min produced a dark orange color which was stable when warmed to room tempera-

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(VI) X = H
(VII) X = Li

(VIII) X = H
(IX) X = Li
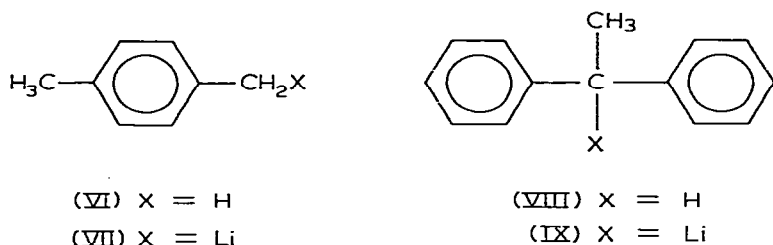
ture. The proton NMR spectrum (1.7 M in THF) (Table 1 and Fig. 1) revealed aromatic protons at 6.12 and 6.24 ppm corresponding to that expected for a *para*-substituted benzyl anion. Similarly, the ^{13}C NMR spectrum (Table 2) was consistent with the expected anion structure. Finally, quenching the anion solution with methyl iodide provided *p*-ethyltoluene.

Reaction of VIII with t-butyllithium in THF at −60 to −70°C for 15 min produced a red color which was stable when warmed to room temperature. The proton NMR (Table 1 and Fig. 1) revealed the expected pattern for the aromatic protons on a substituted diphenylmethyl anion. Additionally, the ^{13}C NMR, (Table 2) was consistent with the expected structure. Finally quenching the anion solution with methyl iodide gave rise to 2,2-diphenylpropane.

The ^{1}H NMR (Table 1 and Fig. 1) of the anion solution prepared by reaction of IV under these same conditions is similar to that of VII and distinct from that of IX. Most significantly, however, methylation of the anion solution with methyl iodide provides 1,1-bis(4-ethylphenyl)ethane (X). Accordingly, it is rea-

(X)
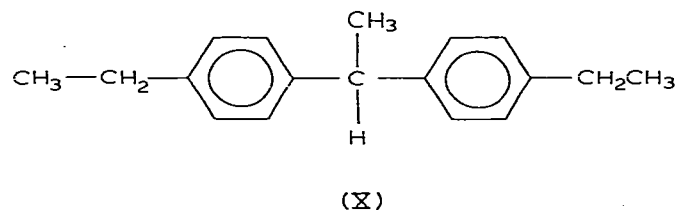
sonable that under the conditions of this experiment anion V was indeed formed.

The nature of the anion produced from IV was found to depend upon the metalating agent and the diarylmethyl anion (III) was formed when benzyllithium was used. Accordingly, reaction of toluene with t-butyllithium in THF for 15 min at −60 to −70°C produced a characteristic anion color. Reaction of this anion with IV in THF was followed by proton NMR. After 15 and 45 min the spectrum of the benzyl anion was essentially replaced by that of a diphenylmethyl type anion δ 6.79 (*ortho*), 6.38 (*meta*) ppm, J_{om} = 8.3 Hz (Table 1 and Fig. 1). These shifts agree quite well with those of anion IX and are distinct from those of anions V or VII. Confirmation of the anion structure was obtained by reaction with methyl iodide. Reaction of the anion solution gave rise to the isolation of 2,2-di-*p*-tolylpropane. Accordingly, metalation and subsequent methylation of IV takes two distinct paths which depend upon the nature of the base used. A reasonable explanation of these results is that the benzyl type anion is the product of kinetic control and that the diarylmethyl
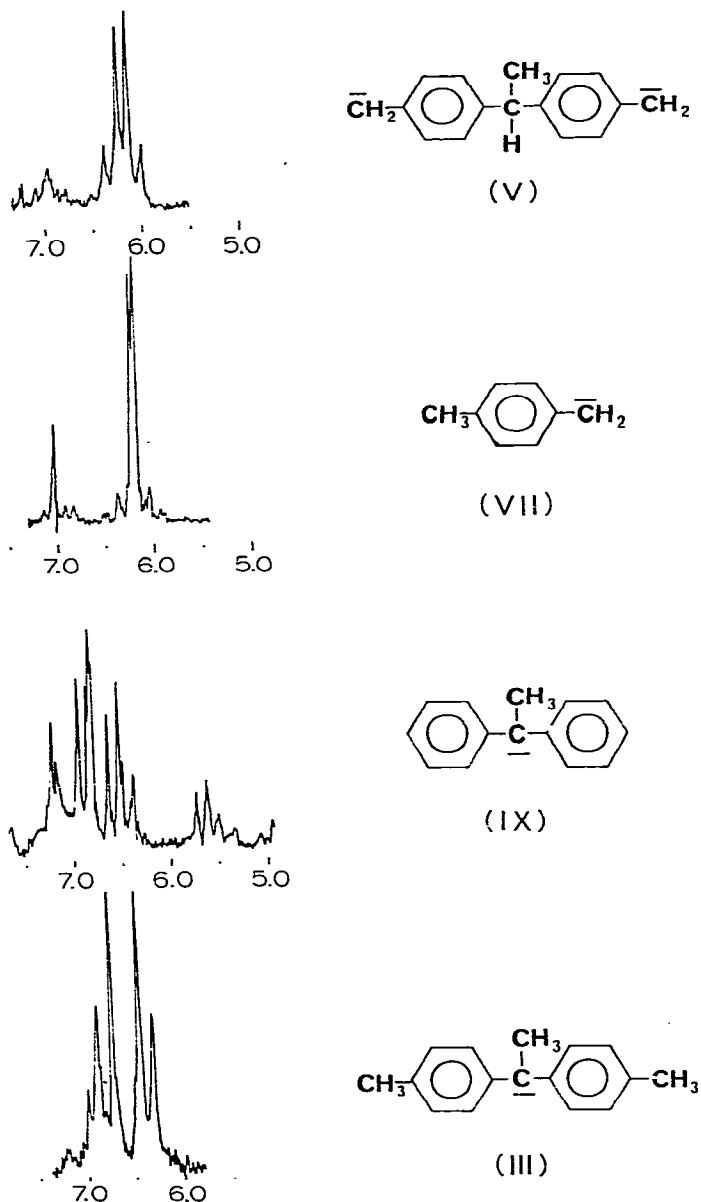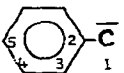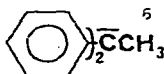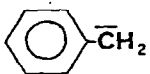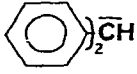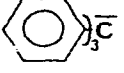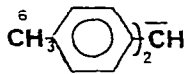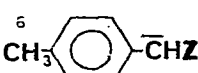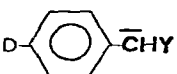
Fig. 1. Aromatic proton NMR spectra of arylmethyl anions in THF.

anion is the product of thermodynamic control. In reaction with an excess of lithium reagent rapid metalation at a benzyl site should strongly affect the position for further metalation. The methine position is now far less acidic due to the presence of the negative charge in one of the aromatic rings. On the other hand, the kinetic and thermodynamic acidity of the other *para* methyl group is largely unaffected. Confirmation of kinetic vs. thermodynamic control was provided by reaction of an excess of 1,1-di-*p*-tolylethane with t-butyllithium and following the reaction as a function of time.

TABLE 2

CARBON-13 CHEMICAL SHIFTS OF LITHIOARYLMETHYLLANIONS IN THF[a]

$\overset{5}{\underset{4}{\bigcirc}}\overset{2}{\underset{3}{}}\overset{}{\bar{C}}_{1}$	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Ref.
$\overset{7}{CH_3}\overset{6}{CH}(\bigcirc-\bar{CH_2})_2$	32.80	158.4	117.1	127.7		44.1	44.7	This work
$\overset{6}{CH_3}\bigcirc-\bar{CH_2}$	33.6C	158.7	117.6	129.1	113.3	20.9		This work
$(\bigcirc)_2\overset{6}{\bar{C}CH_3}$	81.40	147.0	116.9	127.8	106.8	19.3		This wcrk
$\bigcirc-\bar{CH_2}$	36.9	161.5	117.0	128.6	104.7			[14]
$(\bigcirc)_2\bar{CH}$	78.8	147.7	117.8	128.4	107.2			[14,15]
$(\bigcirc)_3\bar{C}$	91.0	150.5	124.4	128.3	113.3			[14,15]
$\overset{6}{CH_3}(\bigcirc)_2\bar{CH}$	72.1	145.8	117.4	128.9		20.9		[1,3b]
$\overset{6}{CH_3}\bigcirc-\bar{CH}Z^{b}$	75.7	145.2	117.8	128.8		21.0		[1,3b]
$D-\bigcirc-\bar{CH}Y$	75.7	147.3	116.9	128.0				[1,3b]

[a] ppm downfield from Me_4Si (internal).   [b] Y = p-methylphenyl, Z = p-D-phenyl.

Reaction of IV with a deficiency of t-butyllithium in THF at —70°C for 10 min followed by 1 h at —20°C gave rise to the anions whose spectrum is shown in Fig. 2b. This spectrum reveals the presence of both the substituted benzyl anion (Fig. 2a) as well as the substituted diphenylmethyl anion in ratios of 1/1 with ~70% of the unreacted aromatic. After 1.5 h at room temperature, the anion spectrum (Fig. 2c) reveals, an absence of the benzyl type anion, a corresponding increase in the substituted diphenylmethyl anion and no further increase or decrease in unreacted hydrocarbon. Additionally, this anion solution was significantly more stable at room temperature than the benzyl type
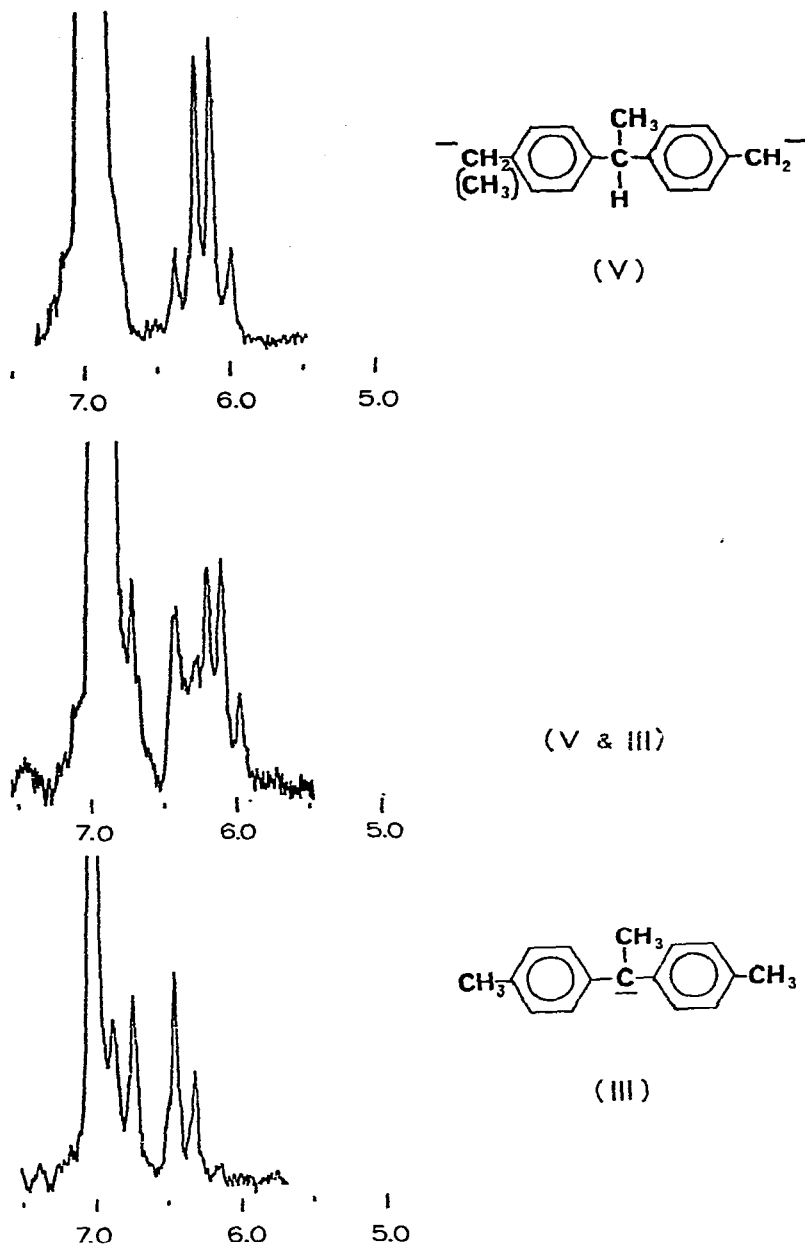
Fig. 2. Aromatic proton NMR spectra of anion equilibration.

anion. Thus the benzyl anion formed in the initial stages of reaction is converted to the more stable substituted diphenylmethyl anion.

Further confirmation of the anion interconversion was obtained via an independent experiment with toluene. After generation of the benzyl anion in ~75% yield, a deficiency of toluene was added and the reaction mixture was followed by proton NMR. Within several hours the toluene had disappeared and this was followed by the appearance of the peaks due to the anion III. The

final solution showed a reappearance of toluene, an absence of the anion V, and the anion III in amounts indicating some overall anion quenching. Accordingly, the anions V and III are equilibrated via the benzyl anion formed *in situ* from V and toluene. This leads to the order of anion stability, V < benzyl < III, in full accord with expectations.

Possibly several factors contribute to the reversal of kinetic and thermodynamic acidity of the two reaction sites. First the reference base is considerably more basic than the base formed by reaction at either site [5]. Additionally, for the reacting hydrocarbon acid there is considerably greater F strain [2] for attack at the single methine position than at the six methyl positions. Importantly, the steric bulk of the reacting base is large and aggregation which is likely would increase the size even more [6]. The increased steric demands of the base will serve to increase the relative steric requirements at the two sites. As demonstrated so clearly by Brown, the magnitude of steric effects in acid base reactions are a function of the steric requirements of the reference acid or base [7]. Accordingly, an exceedingly potent and large base selects the sterically less hindered site. The less powerful and smaller base, benzyllithium, selects the thermodynamically more favorable site.

Turning attention to the NMR of the anions in this study and some of those previously studied, several patterns emerge. For the proton NMR, the chemical shifts of the *ortho* and *meta* hydrogens fall into narrow sets. The values in each set are determined by the number of phenyl rings involved in the delocalization with three exceptions. These differing values are downfield shifts for the *ortho* position when the C(1) carbon has a group larger than hydrogen. Thus it appears that in the absence of steric effects, charge considerations determine the proton chemical shifts. However, for the sensitive *ortho* position the chemical shifts of the anions of the structure $Ar_2\bar{C}R$ where $R = CH_3$ for III and IX are some 0.33 ppm downfield from the average of the anions of the form $Ar_2\bar{C}H$.

This is not the expected anisotropic effect since the methyl group should increase the deviation from planarity in the anion thereby causing an upfield shift. The observed downfield shift is likely due to a steric interaction at the *ortho* hydrogens. The peculiarly large downfield chemical shift for the *ortho* hydrogens of triphenylmethyl anion, R = phenyl, probably is the result of a similar effect. The same kind of change for a methyl and a phenyl, groups of greatly differing electronic demands but of similar size, signals a steric effect. Support for this rationale is afforded by the carbon-13 NMR chemical shifts. These appear to be determined solely by charge and the values for the *ortho* position are not anomalous.

In a related vein, the data can be used to obtain an estimate of the large acid weakening effect of methyl substitution in going from diphenylmethane to 1,1-diphenylethane. From the work of Streitwieser it is known that the value of the pK_a lies above 35 units [8]. In competition experiments of *p*-xylene and 1,1-diphenylethane with t-butyllithium in THF only the 1,1-diphenylethyl anion is present. Thus 1,1-diphenylethane is at least 2 pK_a units more acidic than *p*-xylene.

Similar considerations apply to the total conversion of anion V to anion III. With reasonable estimates for the effects of *p*-methyl substitution on anions the

value of the pK_a of 1,1-diphenylethane lies between 35 and 39 and is likely to be ~37. Thus introduction of the methyl group results in an increase of the pK_a value of ~4 units or ~5.5 kcal/mol. Such an increase cannot be attributed to the inductive effect of a methyl group but is adequately explained by the steric requirements of the methyl group. The quantitative precedence and foundation for this assertion has been amply demonstrated by the pioneering work on steric effects by Prof. H.C. Brown.

Finally it is interesting to note that the homomorph concept is useful here. Brown proposed the term for molecules with similar molecular dimensions and noted that such molecules would possess similar steric strains [2]. The structure of N-methyldiphenylamine is similar to that of the anion of 1,1-diphenylethane and does in fact exhibit a parallel effect. This effect is demonstrated by

comparison of the basicities of select substituted methyl aromatic amines.

Introduction of a *para*-methyl substituent in aniline [9] and diphenylamine [10] has virtually identical effects on the base strength, namely 0.45 pK_a units. However, whereas replacement of a nitrogen hydrogen by methyl brings about an increase in base strength of 0.23 units in aniline [9] the same structural change in diphenylamine brings about an increase in base strength of 1.0 pK_a units [10]. Clearly this is not a polar effect and moreover it is in the opposite direction to that expected for B strain [2]. Importantly, it is the expected effect if the methyl group in N-methyldiphenylamine decreases lone pair delocalization in a manner analogous to the steric effects of the methyl group in the diarylethyl anions described in this work.

Experimental

General comments

All solvents were rigorously dried prior to use. Tetrahydrofuran was refluxed over sodium-benzophenone ketyl. Prior to collection of THF, ~1% TMS (tetramethylsilane) was added and allowed to reflux for 10 min. Hexane was purified over concentrated H_2SO_4, with rapid stirring for several days, then washed with 5% $NaHCO_3$ and stored over $CaCl_2$. Prior to use a 20 ml portion was treated with ~1 ml of the alkyllithium solution in a septum-capped flask under argon.

Of the hydrocarbons studied, *p*-xylene was commercially available; 1,1-diphenylethane was prepared by hydrogenation of the commercially available 1,1-diphenylethylene; 1,1-di-*p*-tolylethane (II) was prepared by hydrogenation of 1,1-di-*p*-tolylethylene which had been prepared by reaction of *p*-tolylmagnesium bromide and 4-methylacetophenone and subsequent dehydration. n-Butyllithium in hexane and t-butyllithium in pentane were purchased from Aldrich.

All glassware was oven-dried overnight and purged with purified argon while hot before use. Transfers were made by syringe and double-tipped needles under argon pressure [12]. A description of the reaction apparatus follows.

Several 50 ml flasks were prepared with inner 24/40 joints. A special adapter was prepared with double outer 24/40 joints and in-line and access ground-glass stopcocks (Fig. 3).

The formations and manipulations of the anions were performed while the reaction apparatus was attached to an Ace Glass No-Air vacuum-inert gas delivery system. ^{1}H NMR spectra were run on a Varian A60 spectrometer while ^{13}C NMR spectra were performed on a Bruker WH 90. Purification of the methylated hydrocarbons was performed on a Hewlett—Packard 5750 gas chromatograph using a 6' × $\frac{1}{8}$" 10% UCW 98 with 80—100 mesh size at a flow rate of 60 ml per min.

General procedure for anion formation

The reaction apparatus equipped with a glass magnetic stirrer was oven-dried overnight, assembled hot, the access port fitted with a septum cap and then attached to the high vacuum-inert gas delivery system. While hot, the apparatus was purged with argon and evacuated several times.

After cooling to room temperature, approximately 1 equivalent of the alkyllithum solution was added by syringe. The solvent was removed by vacuum distillation until a white salt remained. The hydrocarbon was added using a tared syringe and the flask was cooled with dry ice. Separate experiments indicate that the reaction temperature was —60 to —70°C.

Freshly distilled THF (~1% TMS) was added at a rate 2 ml/5 min with stirring. Color due to anion formation was generally immediate. The reaction was allowed to proceed for 15 min after which time the flask was allowed to warm slowly to room temperature.

THF was removed by vacuum-distillation until a colored salt remained. The salt was washed with two 4 ml portions of dry hexane. The insoluble salt remained in the flask while unreacted hydrocarbon was withdrawn with the hexane. The hexane residue was removed by vacuum distillation. Of the hydrocarbon remaining in the flask generally 90—100% was present as anionic material. Freshly distilled THF (1% TMS) was introduced to dissolve the colored salt. Samples were then transferred to septum-capped flame-purged NMR tubes
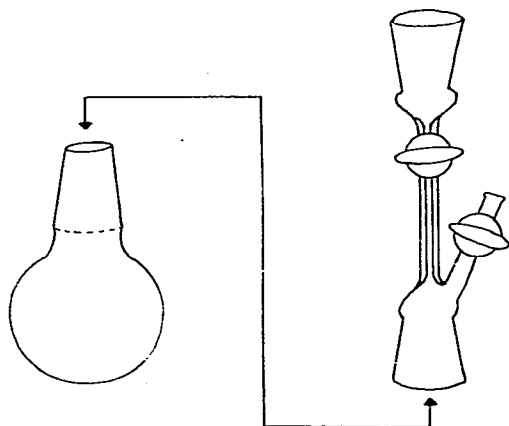

Fig. 3. Inert atmosphere apparatus for preparation and sampling of anions.

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using double-ended needles and the spectra were obtained. For ^{13}C NMR 10% benzene-d_6 (dried over CaH$_2$ several days) was added as a lock prior to sampling.

Methylation procedure

An oven-dried 50 ml Erlenmeyer flask equipped with a glass magnetic stirrer was fitted with a septum cap and purged with argon. When cool, ~7 equivalents of MeI (dried over CaH$_2$ several days) were introduced followed by 10 ml of THF (dry). The anion to be methylated was transferred to the flask using a double-ended needle and quenched in the rapidly stirred THF/MeI solution. Reaction was instantaneous as noted by loss of color. After the transfer was complete an equal volume of distilled water was added and the organic layer extracted with methylene chloride. The organic layer was dried (CaCl$_2$) and the methylene chloride was removed by rotary-vacuum evaporation.

The oily residue was dissolved in DCCl$_3$ and ^{1}H and ^{13}C NMR spectra were obtained. Yields of recovered materials were determined by adding weighed amounts of methylene chloride to the material recovered. Integrations of the ^{1}H NMR spectra were used to calculate the molar yields.

Generation of p-xylyllithium (VII)

The reaction apparatus was prepared as previously described. Then 2.0 ml of 1.35 M t-butyllithium in pentane were added. After solvent removal by vacuum distillation, 0.286 g (0.0027 moles) p-xylene were added. After cooling 2.0 ml of dry THF (1% TMS) were added at a rate of 1 ml/min. The yellow color of the anion was immediately apparent. The anion solution was allowed to stir for 15 minutes after which time the flask was allowed to warm slowly to room temperature.

Using double-ended needles, samples were taken for ^{1}H and ^{13}C NMR. With a slight excess of t-butyllithium, 100% of the p-xylene could easily be converted to anion. The yield of p-ethyltoluene after methyl iodide quenching was greater than 80%.

Generation of 1,1-diphenylethyllithium (IX)

The reaction vessel was prepared as previously described. Then, 2.0 ml of 1.35 M t-butyllithium in pentane were added. After solvent removal 0.15 g (0.00082 mol) of 1,1-diphenylethane were added. After cooling, 2 ml of dry THF (1% TMS) were added at a rate of 1 ml/min. The red color due to anion was immediately apparent.

Solvent was removed leaving a colored salt. Then 4 ml of dry hexane was introduced by syringe and the hexane was stirred vigorously for ~2 min. The colored salt was allowed to settle to the bottom and the hexane decanted by syringe. The remaining hexane was removed under *vacuo*. Finally, 2 ml of THF (1% TMS) were added and samples removed by double-needle for ^{1}H and ^{13}C NMR.

Solutions in which 90% of hydrocarbon present was in the anionic form were easily prepared. From the methylation, 2,2-diphenylpropane was isolated in 54% overall yield from starting material and ~99% yield from the anion solution.

Generation of 1,1-bis(p-lithiomethylphenyl)ethane (V)

The reaction apparatus was prepared as previously described. Then, 2.0 ml of ~1.35 *M* t-butyllithium in pentane were added. After the solvent was removed 0.28 g (0.0013 mol) of 1,1,-di-*p*-tolylethane were added and the flask cooled. Then, 2.0 ml of THF (1% TMS) were added at a rate of 1 ml/min.

The solvent was removed and 4 ml of hexane was introduced. The hexane solution was stirred rapidly for 2 min after which the insoluble anion salt was allowed to settle. The hexane was decanted by syringe followed by vacuum distillation. The final solution was made by adding 2 ml THF (1% TMS).

Samples were removed for ^{1}H and ^{13}C NMR by double-ended needles. Of the hydrocarbon present in the final solution 90% was in the form of the mono-aryl anion. Methylation led to the isolation of 1,1-bis(*p*-ethylphenyl)ethane in ~99% yield from the final anion solution.

Generation of 1,1-di-p-tolylethyllithium (III)

The reaction apparatus was prepared as usual and was allowed to cool. 2.0 ml of 1.35 *M* t-butyllithium in pentane were added to the flask and the solvent removed by vacuum distillation. Then, 0.500 g (0.0054 mol) of toluene were added and the flask cooled in dry ice for 15 min. Then, 2.0 ml THF (1% TMS) were added at a rate of 1 ml/min and the typical anion color formed immediately. Reaction was allowed to proceed with stirring for 15 min before warming to room temperature. Solvents were removed by vacuum-distillation until an orange salt remained and 0.50 g (0.0024 mol) 1,1-di-*p*-tolylethane were added.

Then 2.0 ml THF (1% TMS) were added rapidly and ^{1}H NMR showed that reaction was complete after 2.0 h at room temperature. The methylation led to the isolation of 2,2-di-*p*-tolylpropane in 80% yield overall and 92% from the final anion solution

Acknowledgements

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