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Reactions of Polyanions Derived from Alkylbenzenes

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Abstract: Alkyl- and dialkylbenzenes react with a 1:1 mixture of *n*-butyllithium and potassium *tert*-pentoxide (BuLi/KO-*t*-Pe) to give benzyl anion derivatives. These may either be metalated in a second α position to give dibenzyl dianions, which eliminate metal hydride to give styrenes, or in a "directed" second metalation at a methyl group adjacent to the anionic center. In this case the product styrene dianion loses an electron to give a styrene radical anion. In some cases high yields of styrene radical anion dimers are obtained. The relative importance of the two alternative reaction pathways can be predicted on the basis of the factors affecting the second metalation step. ESR experiments and MNDO calculations support these conclusions.

The use of extremely strong bases in essentially inert alkane solvents has made possible the synthesis of "anions" and "polyanions" (in reality organometallic species) that cannot exist in protic media. In particular, the use of alkyllithium/potassium tertiary alcoholate mixtures[2-5] has revealed some new chemistry of anions and polyanions that are normally too reactive to be observed directly as reaction intermediates.

This paper reports some of the consequences of this extreme basicity and describes two types of subsequent reactions of unstable polyanions: metal hydride elimination to give more stable conjugated anions[3,4] or electron loss to give radical anions.[5] Such one electron oxidations may occur spontaneously[5] or may be induced by reagents such as methyl iodide,[6] which normally react as electrophiles but can accept electrons from marginally stable dianions. We have carried out product studies, as well as ESR and theoretical (MNDO) investigations, on a series of alkylbenzene systems. We wish to determine those factors that control the behavior of unstable anions so that the course of reactions in extremely basic media can be predicted.

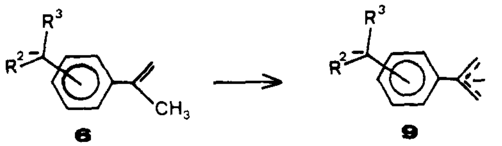
Results and Discussion

The products obtained by reacting a series of alkylbenzenes with a 4-fold excess of 1:1 *n*-butyllithium/KO-*t*-C_5H_{11}(BuLi/KO-*t*-Pe) for 24 h at room temperature followed by 24 h at reflux are shown in Table I. The observed products can be explained by the mechanism shown in Scheme I.

This mechanism accounts for three types of products on quenching with D_2O: deuterated starting material produced from **2** or **3**, eliminated or dideuterated products from **6** or **4**, and dideuterated "dimeric" products derived from **8**. The ratios of these products depend on the relative rates of the metalation steps **1** → **2** or **3**, **2** → **4**, **3** → **4**, and **3** → **5**.

The first metalation takes place in an α-position to give either **2** or **3**, depending on which benzylic position is the least substituted. Interestingly, BuLi/KO-*t*-Pe shows a much greater preference for benzylic metalation than *n*-butyllithium/1,2-bis(dimethylamino)ethane (BuLi/TMEDA), which attacks mainly at the ring positions of isopropylbenzene.[7] We found no evidence of ring-metalated products although BuLi/KO-*t*-Pe metalates benzene effectively.[8] Presumably metalation in a benzylic position deactivates the ring toward metalation with BuLi/KO-*t*-Pe, although activation of the ortho positions could be expected on the basis of other reactions[9-12] with BuLi/TMEDA or from MNDO calculations[12] (see below).

There are two alternative second metalations. The more conventional of these occurs in the second benzylic (α') position to give the substituted xylene-α,α'-diyl dianion, **4**. Dianions of this type are stable for $R^1 = R^2 = H$ and can be quenched directly.[3] If, however, either R^1 or R^2 and R^3 are methyl, the dianion undergoes metal hydride elimination[2-4] to give the styrene with an anion substituent **6**. If R^1 has α-hydrogen atoms, **6** is further metalated to give dianions of type **9**:



6 $R^1 = CH_3$ **9**

Products derived from **4**, **6**, or **9** are the only dimetalation products found for alkylbenzenes with at least one benzylic methyl group (shown in Scheme I). As methyl groups are the most active in the first metalation step, the second metalation occurs in the α' position. The alternatives would be ring metalation, which does not seem to occur with BuLi/KO-*t*-Pe, or a second metalation on the same carbon atom, as observed for toluene with BuLi/TMEDA.[13] This, α,α-dimetalation also seems to be slower than α,α'-dimetalation, as can be predicted from the reactions of xylenes with BuLi/KO-*t*-Bu.[14]

The more unusual second metalation is proposed to occur at a methyl group bound directly to the anionic center (**3** → **5**). This leads to a styrene dianion derivative (**5**) which cannot be detected by the usual quench reactions. This, α,β-dimetalation may appear to be unlikely but is supported by MNDO calculations (see below). Although no direct analogies are known, there are precedents for regiospecific second metalations in which the first metallic substituent appears to control the reaction. The ortho-metalation of *o*-lithiobiphenyl[9] and (1,2-diphenyl-1-hexenyl)lithium[10] or the second metalation of benzyllithium on the benzyl carbon[13] and the regiospecific metalations of 1-lithionaphthalene and 9-lithioanthracene[12] are known examples (see Scheme II).

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(1) (a) Universität Erlangen-Nürnberg; (b) University College London.

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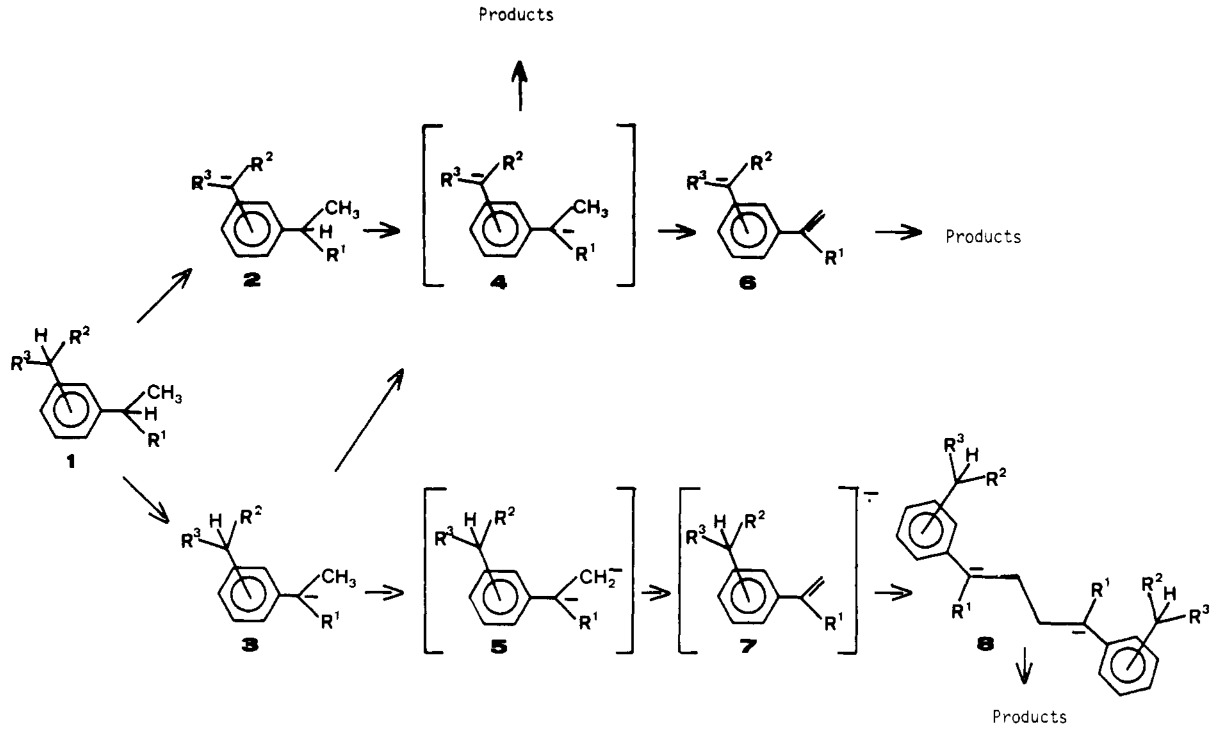
Scheme I



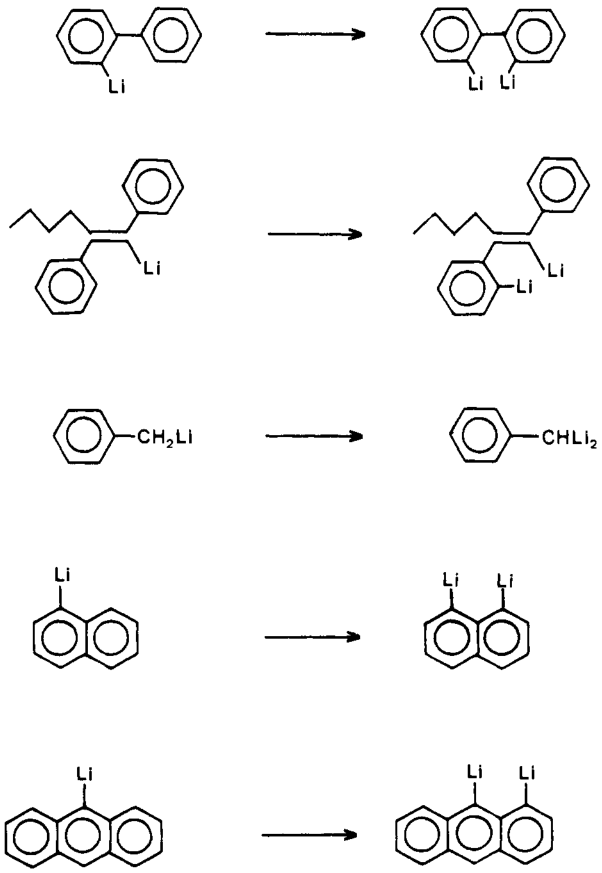
MNDO calculations on the monolithium compound indicate that LUMO coefficients for the hydrogen atoms are a reliable method for predicting the site of the second metalation and also that dimetalated intermediates obtained from such reactions may have doubly bridged structures.[9,15] Our MNDO calculations (see below) suggest that a β-hydrogen in 3-Li$^+$ is activated by C-Li-H bridging.

The step $3 \rightarrow 5$ is also analogous to the dimetalation of dibenzyl with BuLi/TMEDA to give the stilbene dianion dilithium salt.[16] However, the extra stabilization by the second phenyl group clearly favors the stilbene reaction. A reaction reported recently by Bates et al.[8] also indicates that the second metalation step can be controlled by the first metallic substituent. Reaction of 1,2-di-*p*-tolylethane (**10**) with BuLi/TMEDA gave only two products, **11** and **12**. The unsymmetrical dianions **13** and **14** were not produced. The mechanism can be formulated as in Scheme III. As in Scheme I, the first metalation can give either **15** or **16**, but the primary anion, **15**, is more favorable. The most likely second metalation of **15**, at the other methyl group, gives **11**, the main product. Although two benzylic methyl groups are available in anion **16**, further metalation occurs at the second methylene group, vicinal to the first anionic center. This reaction indicates that there is a strong *activation* of the vicinal methylene group in the monolithiated derivative of **16**. The inductive destabilization that would normally be expected is overcome by the favorable electrostatic arrangements in ion triplets.[15]

The dianion **5** is not observable by quenching but undergoes a fast spontaneous one-electron oxidation (see below) to give the styrene radical anion **7**, which dimerizes to give dianion **8**. The reaction of styrenes with potassium has been shown to lead to dianions of this type;[17] presumably styrene radical anion intermediates are once again involved.

An alternative mechanism for the generation of **7**, metal hydride elimination and subsequent one-electron reduction (Scheme IV), can be ruled out for two reasons: benzylic monoanions, such as **3**, do not eliminate under our conditions;[3] the neutral styrene product, **17**, is not stable in BuLi/KO-*t*-Pe[9] and undergoes butyllithium addition. Such butyllithium addition products were not found.

Scheme II. Directed Second Lithiations[a]



[a] The products are represented conventionally; doubly bridged structures are more favorable.

The mechanism shown in Scheme I accounts for the products given in Table I providing the relative rates of the competing metalation steps are taken into account. Substituted toluenes

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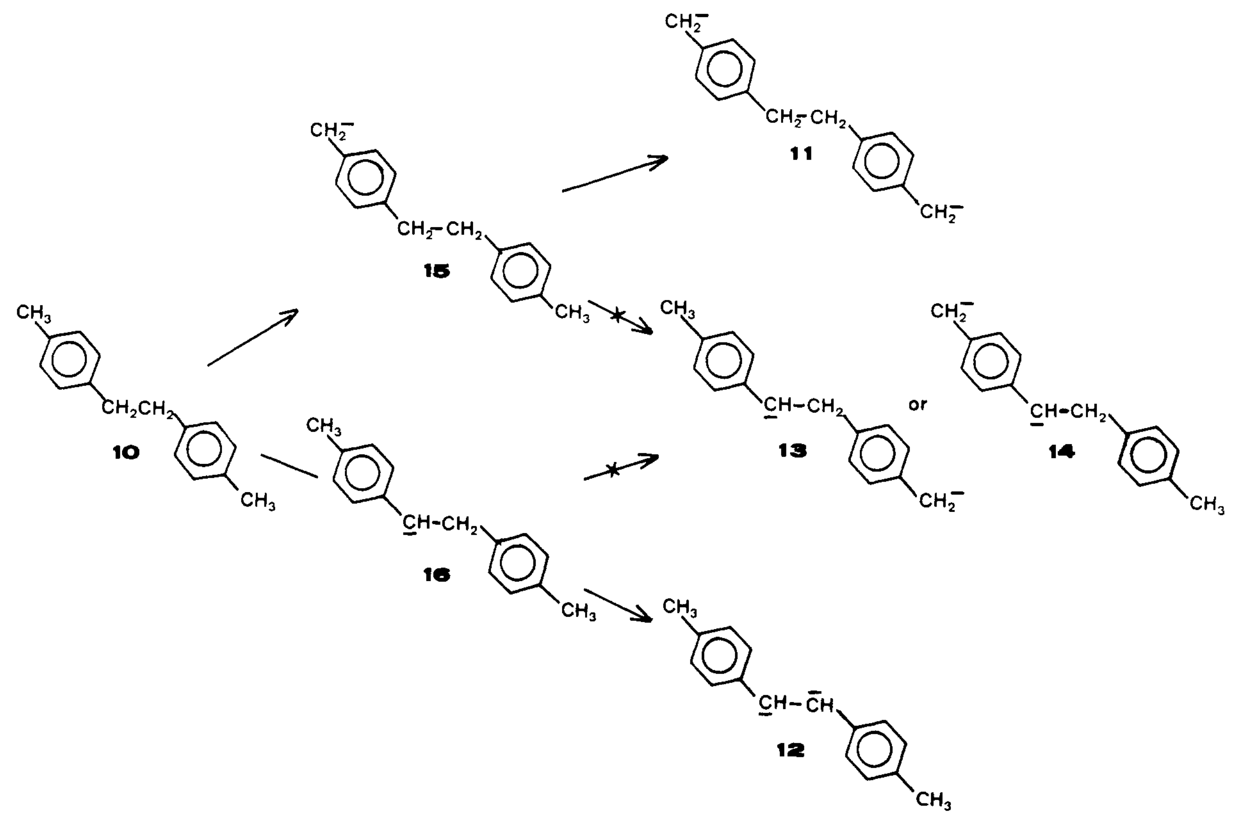
Scheme III



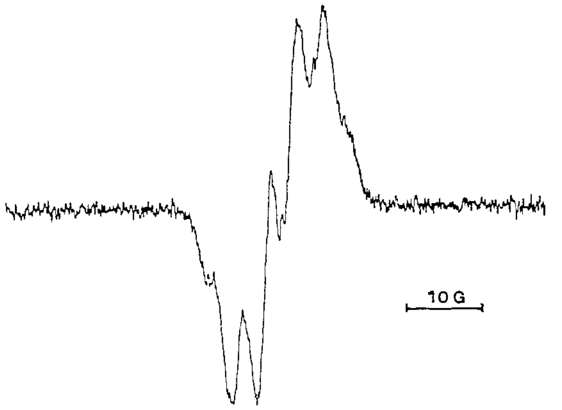
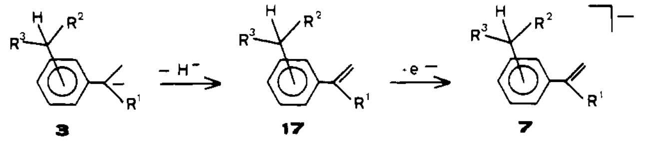


Figure 1. ESR spectrum obtained from the heterogeneous mixture given by the reaction of *p*-diisopropylbenzene with BuLi/KO*t*Pe in hexane. The spectrum was recorded at −50 °C.

metalate first at the methyl group; only α,α'-dimetalation products are observed. *m*-Dialkylbenzenes undergo α,α'-dimetalation faster than the para isomers, so that α,β-dimetalation is more important for paradisubstituted benzenes than for their meta counterparts. *m*-Diisopropylbenzene is the only compound investigated that gives both α,α'- and α,β-dimetalation products.

Scheme IV



ESR Experiment. The BuLi/KO-*t*-Pe reaction mixtures were investigated by ESR spectroscopy in order to characterize the intermediate radical anions. The heterogenous nature of the reaction mixtures in hexane made them unsuitable for well-resolved ESR spectra. Homogeneous solutions were obtained by the addition of dry THF, but the radical anions proved not to be stable under these conditions, as would be expected of styrene radical anions, which are short-lived in solution.[18] Figure 1 shows an ESR spectrum obtained from the metalation of *p*-diisopropylbenzene with BuLi/KO-*t*-Pe. The spectrum is strong, indicating a high concentration of radical anions. A strong transient blue-violet color can also be seen on quenching with water, and all reactions that gave significant yields of "dimeric" products deposited a metal mirror on the walls of the flask. All reaction mixtures in which styrene radical anions are proposed as intermediates gave similar spectra to that shown in Figure 1, although in no case was a well-resolved spectrum obtainable.

We therefore chose to investigate the dibenzyl/stilbene system as a model for the alkylbenzene/styrene reactions.[19] The stilbene radical anion is stable in solution[20,21] and, as discussed above, dibenzyl undergoes an analogous dimetalation to that proposed in Scheme I. Reaction of dibenzyl with 2 equiv of BuLi/KO-*t*-Pe for 3 h at room temperature followed by addition of dry THF gives a homogeneous solution from which the ESR spectrum shown in Figure 2a can be measured. This spectrum remains stable, even after 4 h at 45 °C.

Simulation (Figure 2b) gave the hyperfine coupling constants shown in Table II. These can be compared with those obtained previously[20,21] for the stilbene radical anion. The same spectrum was obtained when crystals of the stilbene dianion dilithium salt[16] were dissolved in dry THF. The redox behavior of the dianion salts observed here is probably not a typical disproportionation equilibrium between stilbene, its radical anion, and its dianion[22]

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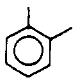
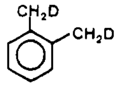
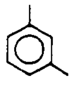
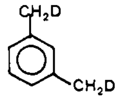
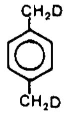
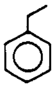
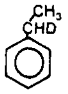
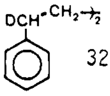
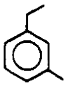
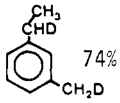
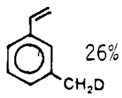
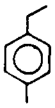
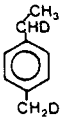
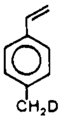
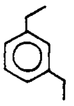
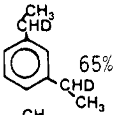
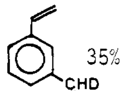
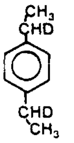
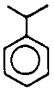
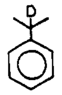
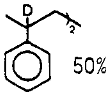
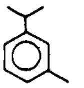
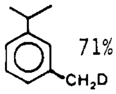
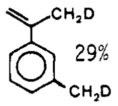
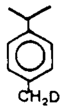
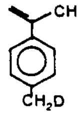
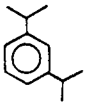
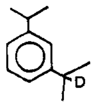
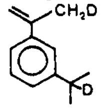
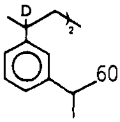
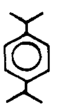
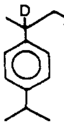
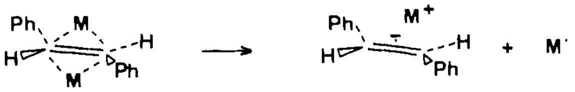
Table I. Products Obtained from the Reaction of Alkylbenzenes with a 4-Fold Excess of BuLi/KO-*t*-Pe for 24 h at Room Temperature and 24 h at Reflux Followed by Quenching with D_2O^e

starting material	monoanion product	α,α′-dimetalation product	α,β-dimetalation product
 a)		 100%	
 a)		 100%	
 a)		 70%	
	 68%		 b) 32%
		 74%  26%	
		 55%  45%	
		 65%  35%	
		 40%  60%	
	 50%		 b) 50%
	 71%	 c) 29%	
	 92%	 c) 8%	
	 25%	 15%	 d) 60%
	 20%		 d) 80%

[a] See ref 14. [b] Identification see ref 17. [c] Preparation and identification see ref 36. [d] See Experimental Section. [e] Products were identified by GLC and/or NMR comparison with commercially available samples unless otherwise noted. In all cases a total yield of at least 97% was obtained; the percentages given are relative to this total yield.

as there is initially no neutral stilbene in the system. Furthermore, the metal mirror observed in the preparative reactions can best be explained in terms of a redox reaction from dianion salt to radical anion salt plus a neutral atom:



This reaction can either be regarded as an oxidation of the dianion or as a homolytic dissociation of a carbon–metal bond.[19] The constancy of the ESR signal at different temperatures for long periods suggests that there is an equilibrium between dianion salt and radical anion as found for the tropenide trianion and the corresponding radical dianion.[23] If the radical anions, unlike the stable stilbene radical anion, are removed from the system by a fast dimerization, this equilibrium leads to high yields of dimeric

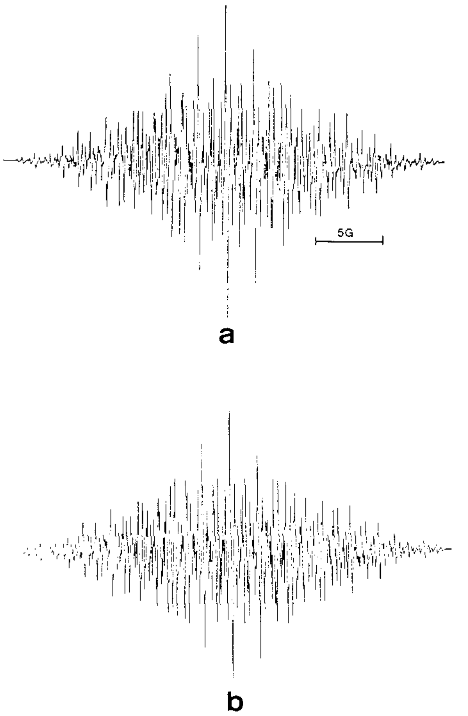


Figure 2. (a) ESR spectrum obtained from the reaction of bibenzyl with BuLi/KO*t*Pe followed by addition of THF to give a homogeneous solution. The spectrum was recorded at room temperature. (b) Simulation of the above spectrum using the coupling constants shown in Table II and a line width of 0.09 G.

Table II. Stilbene Radical Anion Hyperfine Coupling Constants

proton[a]	hyperfine coupling constants, G		
	this work[b]	ref 20	ref 21
H_1	4.52	4.32	4.51
H_2	1.94	1.90	1.94
H_3	3.02	2.96	3.03
H_4	0.34	0.30	0.30
H_5	0.87	0.81	0.83
H_6	3.88	3.89	4.00

[a] Numbering as shown above. The assignments are based on ref 21. [b] In THF/hexane mixtures at −20 °C.

products as found above. Not all dianion salts undergo this type of carbon–metal bond homolysis. The TMEDA complex of the tribenzylidenemethane dilithium salt[24] gives no ESR spectrum even when photolyzed or treated with oxidants such as O_2, $AlCl_3$, or radical sources such as *t*-BuOO-*t*-Bu. Unstable dianions that are produced by metalations with very strong bases are spontaneously oxidized to the corresponding radical anions. This behavior is not limited to BuLi/KO-*t*-Pe systems but is also observed in, for instance, some similar BuLi/TMEDA reactions. The main reason that these reactions are more often found with BuLi/KO-*t*-Pe is that the base is strong enough to form the dianions that are precusors of the radical anions. In order to investigate these and other aspects of the above reactions we have performed MNDO semiempirical molecular orbital calculations[25] on some lithium salts of the intermediate anions, dianions, and radical anions.

MNDO Calculations. We have investigated both the kinetic and thermodynamic aspects of the second metalation step and the thermodynamics of the one-electron oxidation of the dianion salt. We have used *p*-diiosopropylbenzene as a model, as it undergoes

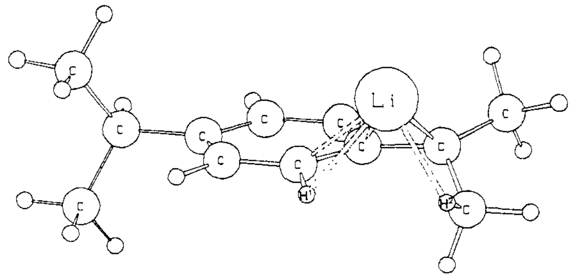
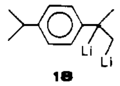
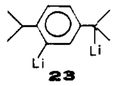
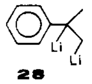
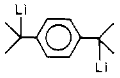
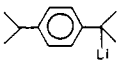
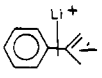
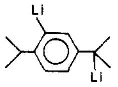
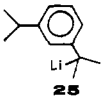
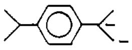
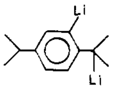
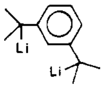
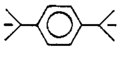
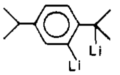
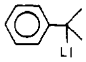
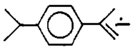


Figure 3. MNDO-optimized structure of **24**.

Table III. MNDO Calculated Heats of Formation (kcal/mol)

 **18**	C_2	-16.0	 **23**	C_1	-21.1	 **28**	C_s	-4.7
 **19**	C_2	-14.3	 **24**	C_1	-11.9	 **29**	C_1	21.1
 **20**	C_1	-19.7	 **25**	C_1	-6.4	 **30**	C_1	105.2
 **21**	C_1	-26.5	 **26**	C_1	-12.3	 **31**	D_{2h}	68.7
 **22**	C_1	-32.5	 **27**	C_1	1.3	 **32**	C_1	8.3

α,β-dimetallation exclusively. The model nature of these calculations should be emphasized. We have not considered the effects of oligomerization or complexation with the alkoxide and have used lithium throughout although the nature of the counterion in BuLi/KO-*t*-Pe systems is uncertain. Nevertheless, we hope to gain some insight into the factors governing reactivity in such systems.

Kinetic Factors in Dimetalation Reactions. The MNDO calculated structure of α-lithio-*p*-diisopropylbenzene is shown in Figure 3. The lithium atom occupies a bridging position similar to that in benzyllithium.[26] We have previously found[12] that Li–C–H bridging leads to a large LUMO coefficient for the hydrogen s orbital and that this hydrogen is found experimentally to be the most active toward a second metalation. This is also the case for α-lithio-*p*-diisopropylbenzene, although the *o*-hydrogen marked H^1 in Figure 3 has a larger (0.092) LUMO coefficient than the methyl hydrogen, H^2 (0.042). This situation is similar to that found in benzyllithium,[12] for which MNDO calculations predict an activation of the benzylic position itself and of one ortho position, but for which only a benzylic second metalation is observed.[13] The reasons for the absence of *o*-metalation in benzyllithium systems may be steric as this position is also thermodynamically most favorable (see below). An APS population analysis[27] (an indication of bond order) also indicates that the ortho

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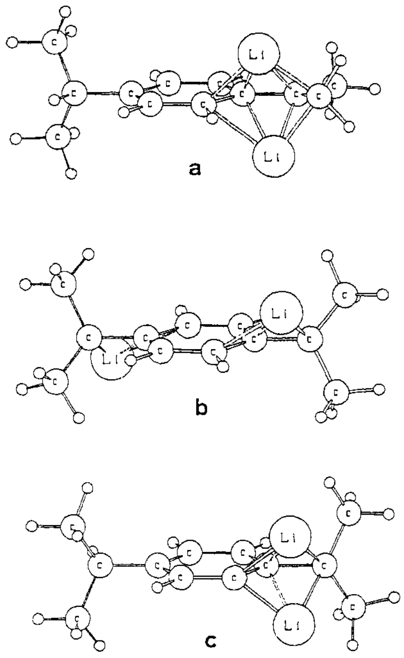

Figure 4. MNDO-optimized structures of (a) **18**, (b) **19**, (c) **22**.

C–H bond is the weakest, although one β-CH bond is also activated (see Figure 3). We conclude that MNDO calculations on monomeric α-lithio-*p*-diisopropylbenzene show a kinetic activation of one β-hydrogen toward metalation, as expected from our experimental results, but also indicate that metalation in a ring ortho position should be more favorable. The reasons for this discrepancy may be due either to steric effects or, more likely, to the fact that the monolithium compound is aggregated in the experimental systems.[28]

Thermodynamic Stabilities of Dilithium Compounds. Table III shows the MNDO calculated heats of formation of the dilithio-*p*-diisopropylbenzenes obtainable by metalation of α-lithio-*p*-diisopropylbenzene and of some related molecules. The calculations refer to unsolvated monomers but should nonethelss reflect the experimental stabilities. The ring metalated isomers **20–23** are more stable than both the α,β- and the α,α'-dilithiated species **18** and **19**. This result is in accord with the observed products of the reaction of isopropylbenzene with BuLi/TMEDA[7] but does not agree with our results using BuLi/KO-*t*-Pe. Once again we are forced to conclude that BuLi/KO-*t*-Pe is relatively less active toward ring positions than BuLi/TMEDA (i.e., that the ratio of benzylic to ring metalation is far higher than with BuLi/TMEDA). Surprisingly, the α,β-dilithiated speces **18** is 3.2 kcal/mol more stable than the α,α'-dilithio isomer **19**. This result is particularly surprising when the corresponding dianions **30** and **31** are considered. The α-methylstyrene dianion **30**, which corresponds to α,β-dilithio-*p*-diisopropylbenzene (**18**), is calculated to be 36.5 kcal/mol less stable than the α,α'-dianion **31**. The formation of the dilithium salt is therefore calculated to change the relative stabilities of the two dianions by almost 40 kcal/mol.

The formation of a doubly bridged structure, as shown in Figure 4a, is responsible for this extra stabilization of the α,β-isomer. The α,α'-dilithio species **19** has no possibility for such extra stabilization and therefore adopts a geometry for both lithium atoms analogous to that of benzyllithium[26] (Figure 4b). The extraordinary stability of doubly bridged dilithium structures may be due to Möbius aromaticity[29] and favorable electrostatic interactions.[30] The significance of such double bridging in the chemistry of dilithiated hydrocarbons is apparent both from theoretical[9,12,31] and experimental[15,16,31,32] studies. The most stable dilithiated *p*-diisopropylbenzene found in this study, the *o*-lithio isomer **22**, also has a doubly bridged structure, as shown in Figure 4c.

The relative ease of the second α-metalation for *m*-diisopropylbenzene relative to the paraisomer is shown by the difference in heats of formation between the monolithio compounds **24** and **25** and the α,α'-dilithiated species **19** and **26**. ΔH_f for the para systems **24** and **19** is −2.9 kcal/mol, compared with −4.0 kcal/mol for the meta isomers **25** and **26**. As the other reactants are common to both species, this indicates that α,α'-dimetalation is thermodynamically more favorable for the meta compound, as expected from simple Hückel theory for the dianions.[14]

The thermodynamics of the one-electron oxidation have been considered in isopropylbenzene derivatives **28**, **29**, **30**, and **32**. The dianion **30** is calculated to be unstable by 97 kcal/mol with respect to loss of an electron to give radical anion **32**. The dissociation of a lithium atom from the dilithium salt **28** to give the radical anion/lithium cation ion pair **29** is, however, calculated to be endothermic by 64.2 kcal/mol (ΔH_f(Li.) = 38.4 kcal/mol). Neither of the calculated values is likely to be very accurate: MNDO overestimates C–Li bond strengths and, although it gives reasonable results for the electron affinities of monoanions,[33] it is unlikely to be able to treat dianions satisfactorily. Even when these deficiencies are taken into account however, it is likely that the dianion **30** is unbound but that the unsolvated lithium compound is bound, so that the electron-transfer step probably depends on the solvation and the nature of the ion pairs.[34]

The question of the nature of the cation in BuLi/KO-*t*-Pe reactions may be of paramount importance for the above conclusions. If the counterions are potassium, a lower tendency to bridge would be expected than calculated for the lithium compounds. This may be the reason for the lack of ortho-metallation in the above reactions.[35] In general, potassium would be expected to approach the anion case more closely than lithium because of its larger ionic radius, which leads to decreased electrostatic interactions. The overall effects should, however, be similar to those found for lithium.

Conclusions

The products of reactions of alkyl and dialkyl benzenes with BuLi/KO-*t*-Pe are consistent with the mechanism shown in Scheme I and the following conclusions:

(1) Metalation at nonequivalent benzylic centers is fastest for primary (methyl) groups and becomes slower with increasing substitution.

(2) BuLi/KO-*t*-Pe is a strong enough base to produce unstable anions (organometallic intermediates), which then undergo metal hydride elimination or one-electron oxidation.

(3) *p*-Xylenediyl dianions are less stable than their meta counterparts and therefore undergo elimination more readily. Increasing methyl substitution also destabilizes the dianions and favors elimination or oxidation reactions.

MNDO calculations indicate both a kinetic and a thermodynamic activation of a β-hydrogen in α-lithioalkylbenzenes, but ortho ring metalation should be more favorable on both counts. BuLi/KO-*t*-Pe, however, shows a string preference for non-ring metalations, in contrast to BuLi/TMEDA.

Experimental Section

Instruments. IR: Beckman Acculab 1 or 3. NMR: JEOL PMX-60 or JNM PS-100; all chemical shifts in ppm downfield from Me_4Si. MS: Varian MAT CH 4 or 311 A. HPLC: preparative high-performance liquid chromatograph Du Pont 830. Preparative GLC: Perkin-Elmer F 21. ESR: Varian E-4 or E-109.

Solvents were dried and stored over molecular sieves. Reagents, unless otherwise specified, were commercially available.

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Table IV. Ratio of Dimeric to Monomeric Product from *p*-Diisopropylbenzene after *X* h at Room Temperature and *Y* h at Reflux

X, h	*Y*, h	dimer:monomer
12	3	35:65
24	3	50:50
24	24	80:20

The number of deuterium atoms and positions of substitution were confirmed by mass spectrometry and NMR. Dry nitrogen atmosphere was used for all reactions. The *n*-butyllithium and potassium *tert*-alkoxide solutions were approximately 1.6 M. For the preparation of potassium *tert*-pentoxide solution and 1:1 Bu/LiKO*t*Pe, see ref 4.

Metalation-Elimination Reactions. The starting material (Table I) was added slowly by syringe to a stirred 4-fold excess of BuLi/KO-*t*-Pe. The mixture was stirred for 24 h at room temperature. During this time the intense color of the metalated olefins and, in the case of radical anions, a metallic mirror developed. The reaction was then slowly heated and refluxed for 24 h. After cooling to room temperature, the reaction mixture was quenched by pouring slowly under nitrogen into a large excess of cooled D_2O. Care was taken not to allow any color to develop. The organic layer was separated, washed twice with water, and dried over calcium chloride. After the hexane was distilled, the products were separated by preparative GLC with a $^3/_8$ in × 20 ft 30% SE-30 on Chromasorb-W-column or HPLC with Zorbax ODS and light petroleum as solvent.

The ratio of dimeric to monomeric products depends on both the reaction time at room temperature and the time at reflux. Examples are shown in Table IV.

ESR Sample Preparation. The heterogenous reaction mixture (0.1 mL) was transferred by syringe to a nitrogen-flushed ESR-tube. After cooling to −78 °C, 0.1–0.2 mL of THF was added and the whole mixed by a slow current of nitrogen passing through the mixture for a short time. The tube was then sealed.

2,5-Bis-(*p*-isopropylphenyl)hexane and 2,5-bis(*m*-isopropylphenyl)-hexane were obtained as a mixture of SS, RR, and *meso* enantiomers.

2,5-Bis(*p*-isopropylphenyl)hexane: mp 53–55 °C, ^{1}H NMR(CCl_4) δ 1.15 (d, ^3J = 6 Hz, 6 H, $2CH_3$), 1.25 (d, ^3J = 6 Hz, 12 H, $4CH_3$), 1.35–1.45 (m, ^3J = 4 Hz, 4 H, $2CH_2$), 2.2–3.1 (2 m overlapping, 4 H, 4CH), 7.0 (s, 8 H, ar); IR (liquid fil) 3050, 3030, 3010, 2985, 2970, 2940 (CH) cm^{-1}; MS (96 eV), *m/e* 322 (100%), 307 (5%), 279 (25%); ^{13}C NMR ($CDCl_3$) δ 22.3, 22.5 (2 q, CH_3), 24.1 (q, CH_3), 33.6 (d, CH), 36.2, 26.6 (2 t, CH_2), 39.6 (d, CH), 126.1, 126.7 (2 d, C-ortho, C-ortho′), 144.8, 144.9 (2 s, C-ipso), 145.9 (s, C-ipso′).

Anal. Calcd for $C_{24}H_{34}$ (322.5): C, 89.4; H 10.6. Found: C, 89.4; H 10.3.

2,5-Bis(*m*-isopropylphenyl)hexane: Mp 48–50 °C, Bp 0.1 torr 150–160 °C (short path distillation), ^{1}H NMR (CCl_4) δ 1.15 (d, ^3J = 6 Hz, 6H, $2CH_3$), 1.25 (d, ^3J = 6 Hz, 12H, $4CH_3$), 1.35–1.55 (m, ^3J = 4 Hz, 4H, $2CH_2$), 2.3–3.2 (2 m overlapping, 4H, 4CH), 6.8–7.35 (m, 8H, ar); IR (liquid film) 3010, 2970, 2955, 2930 (CH) cm^{-1}; MS (96 eV) m/e = 322 (40%), 320 (15%), 147 (100%).

Anal. Calcd for $C_{24}H_{34}$ (322.5): C, 89.4; H 10.6. Found: C, 89.0; H, 10.8.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the SERC, and the Fonds der Chemischen Industrie. ESR experiments were performed during a visit to UCL financed by the British Council. We thank G. W. Spitznagel for computational assistance and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

Registry No. 18, 88158-19-4; **19**, 88158-20-7; **20**, 88158-21-8; **21**, 88158-22-9; **24**, 88158-23-0; **25**, 88158-24-1; **26**, 88158-25-2; **27**, 27271-53-0; **28**, 52340-00-8; **29**, 63949-25-7; **30**, 88158-26-3; **31**, 88158-27-4; **32**, 88158-28-5; (R^*,R^*)-2,5-bis(*p*-isopropylphenyl)hexane, 88158-29-6; *meso*-2,5-bis(*p*-isopropylphenyl)hexane, 88158-30-9; (R^*,R^*)-2,5-bis(*m*-isopropylphenyl)hexane, 88158-31-0; *meso*-2,5-bis(*m*-isopropylphenyl)hexane, 88158-32-1; stilbene radical anion, 34467-73-7; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; ethylbenzene, 100-41-4; *m*-ethylmethylbenzene, 620-14-4; *p*-ethylmethylbenzene, 622-96-8; *m*-diethylbenzene, 141-93-5; *p*-diethylbenzene, 105-05-5; isopropylbenzene, 98-82-8; *m*-isopropyltoluene, 535-77-3; *p*-isopropyltoluene, 99-87-6; *m*-diisopropylbenzene, 99-62-7; *p*-diisopropylbenzene, 100-18-5; BuLi, 109-72-8; KOtPe, 53535-81-2.

Supplementary Material Available: Summaries of MNDO calculations (*z*-matrices) for **18**–**32** (15 pages). Ordering information is given on any current masthead page.

Conformational Analysis. 45.[1] Syn-Axial Methyl/Phenyl and Gauche Methyl/Methyl Interactions[†]

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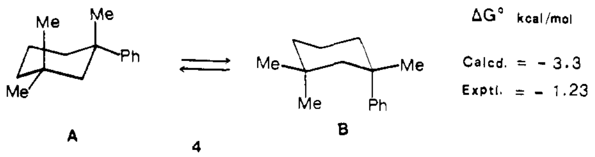
Abstract: Examination of the conformational equilibria of 1-phenyl-3,3,*t*-5-trimethylcyclohexane and 1-phenyl-1,3,3-trimethylcyclohexane by low-temperature ^{13}C NMR spectroscopy indicates the 1,3-diaxial interaction of phenyl and methyl to amount to 3.4 ± 0.1 kcal/mol. The gauche interaction of the methyl substituents in *trans*-1,2-dimethylcyclohexane is measured as 0.74 kcal/mol through determination, by the same technique, of the conformational equilibrium of *r*-1-phenyl-*t*-3,*c*-4-dimethylcyclohexane.

The Phenyl/Methyl Syn-Axial Interaction

In the determination of predominant conformations of complex molecules with six-membered rings, 1,3-diaxial (or syn-axial) interactions play an important role. Among 18 such interactions recently tabulated[2] is the phenyl/methyl interaction, assigned a value of 2.9 kcal/mol. This value is derived from a determination of the excess of a methyl/methyl/H interaction over a phenyl/methyl/H interaction (cf. Scheme I) by NMR spectroscopy of α-fluoro-3-phenyl-3,5,5-trimethylcyclohexanones,[3] which yields a difference of 0.9 kcal/mol. Taking the value of the methyl/

Scheme I



[†] Dedicated to Professor Günther O. Schenck in honor of his 70th birthday.