METALATIONS—XVI

POLYLITHIATION AT BENZYLIC POSITIONS

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Abstract—Metalation of mesitylene with butyllithium in hexane in the presence of tetramethylethylenediamine yields mono-, di- and trilithiated benzylic compounds (1-5), characterized as their silylated derivatives. Dilithiation occurred partly at the same but preferentially at different methyls. The symmetrical tris-1,3,5-(lithiomethylene)benzene was the main product. Similar metalation occurred with m-xylene. o-Xylene gave also dilithiated products, but at a slower rate, and p-xylene gave slowly and exclusively the gem-dilithio-derivative.

The results were explained by greater stabilization of polylithio derivatives with charges all on the starred carbons of the conjugated system, rather than those with charges uniformly dispersed on all carbons. CNDO/2 calculations of the energy of the anions account only partially for the order of stability of most of the studied compounds, but a good correlation between this experimental order and the energies of the lithium compounds was found.

The introduction of a catalyst, particularly tetramethylethylenediamine¹ (TMEDA), during metalation with butyllithium increases the activity of the metalating agent. Its action on alkylbenzenes was found similar to that of alkylsodium.² The important discovery³ of toluene polylithiation with butyllithium in the presence of TMEDA made possible the preparation of new types of organolithium compounds. It is here reported that di- and trimethylbenzenes produce with this metalating agent various di- and trilithio derivatives, the lithiation occurring almost exclusively at the benzylic positions.

Metalation of mesitylene with butyllithium in hexane in the presence of TMEDA produced a mixture of lithiated derivatives (1A, 2A, 4, 5A), which, when treated with trimethylchlorosilane, gave the silylated derivatives (1B, 2B, 3B, 4B and 5B). The polylithiation did not occur during the silylation, since the ratio of the products 1B-5B was dependent on the time of metalation and the amount of metalating agent. The PMR data of these compounds are given in Table 1.

The symmetrically trilithiated derivative (5A) was the main product after 24 hr of metalation at room temperature, when a 6:1 molar ratio of butyllithium to substrate was used and more than 60% of 5B was obtained on

silylation. The dimetalated compound (3A) was obtained in a 25% yield under these conditions. The *gem*-dilithiated derivatives (2A and 4A) were formed in a 4-15% yield each, depending on the duration of the reaction.

m-Xylene was also lithiated readily and no starting material was left after 14 hr of metalation at room temperature. The lithiated products were **6A**, **7A**, **8A** and **9A** as evidenced by the formation of the silylated products (**6B-9B**) in a 7:1:5:1 ratio. This ratio between the *gem*-and other lithiated products is not constant, since under different conditions the ratio of **6B**:**7B**:**8B**:**9B** was found to be 5:4:3:2.

Dimetalation (geminal and on different methyls) was also found in the case of o-xylene, where the reaction proceeds more slowly than with m-xylene. The lithiated and subsequently silylated products (10, 11, 12 and 13) were obtained in a 4:4:1:1 ratio (with 6% starting material) after 40 hr of reaction.

Slow metalation was also observed in the case of p-xylene. Moreover, only one Me was attacked, giving 14, 15 and a small amount (7%) of another product, probably by ring metalation.

The change in the ratio of metalating agent to TMEDA influenced the ratio of products, as already observed by

Proton chemical shift (δ) in ppm ^e								
Compound	а	b	c	d e	f	g	R	R'
1B	2.21(s)	6·46(m)	6-38(m)	1·93(s)		-0.02(s)	_
2B	2·2(s))	6·41(m)	6·3(m)	_	1·33(s)	_	0·0(s)
3B		2·2(s)	6-23(m) 6·18(m)) 1.9(s)		-0.02(s)	_
4B	_	2.2(s)	6-23(m)	1.9(s)	1·3(s)	-0.03(s)	0·0(s)
5B	_		6-01(s)		1.9(s)	_	-0.03(s)	
6B	2·28(s)	6·63(m)			2.0(s)	_	0.0(s)	
7B	2.26(s)	6·56(m)				1·36(s)	_	0.0(s)
8B	- 6-83(1	t)	6.2(d)	6-43(s)	2.0(s)		0·0(s)	_
9B	— 6·8(t)		6·46(d)	6-4(s)	2.0(s)	1·4(s)	0.0(s)	0·03(s)
10B	6-8(m)			2.2(s)	2.03(s)	_	0.0(s)	_
11B	6-56(m)			_	1-93(s)		0.0(s)	
12B		6.6	6(m)	2·13(s)		1.66(s)	-	0·0(s)
13B	6.78(1	m)		0-26(s)	2·18(s)	2.3(s)		0.0(s)
14B	6.73(0	d)	2·25(s)	6.56(d)	1.98(s)	_	0.02(s)	_
15B	6.78(d)	2·23(s)	6-60(d)		1·36(s)		0·0(s)

Table 1

^a At 60 MHz in CCL, relative to tetramethylsilane.



West.3 Here the effect was extreme. Although increase of the amount of catalyst accelerated the rate of metalation, as evidenced by the disappearance of the starting material, it also decreased the rate of gem-dimetalation. An extreme example was p-xylene where a 1:1 ratio of butyllithium to TMEDA converted the substrate totally to mono-lithiated compound without observable the amounts of the dilithiated derivative. On the other hand, a 4:1 ratio of metalating agent to catalyst, with the same ratio of metalating agent to substrate as before, gave, after a much longer reaction period, 25% of the mono and 25% of the dilithiated compound, with 50% of the substrate unreacted. This is not a general inhibition of dimetalation: in the presence of 1:1 BuLi/TMEDA, o-xylene underwent dimetalation to 11A (monometalation of each Me), but at a reagent-ratio of 4:1, the reaction time being the same, ring metalation took place. When the catalytic reaction is slow, ring metalation is probably competitive.

A similar effect was found when pentamethyldiethylenetriamine (PMDETA) was used as catalyst. The yield of the *gem* product (2B) was lowered from 38% to 7.5% when the amount of catalyst was doubled from a 1:2 to a 1:1 molecular ratio with butyllithium.

The effect of the amount of TMEDA may be attributed to several factors. Firstly, in the presence of an excess of catalyst the lithium in benzyllithium is possibly coordinated with two molecules of TMEDA, thus bringing into effect a stabilization by delocalization of the negative charge into the aromatic ring. Further metalation at the same benzylic carbon is hindered sterically by the solvating molecules. The affinity of the benzyllithium derivatives for TMEDA is apparently larger than that of butyllithium for this amine. Secondly, in these conditions of high cation solvation, the methylene group is planar and abstraction of a second proton would not enhance the stabilization significantly. Ring metalation is also slower because of the high influx of electrons.

On the other hand, coordination of lithium with only one molecule of TMEDA occurs in the presence of low amounts of the catalyst. The lithium cation is then partially bonded to the methylene and charge delocalization into the ring is lower than in the more solvated molecule. Steric inhibition to methylene metalation is also smaller. Ring metalation is faster than in the presence of large amounts of catalyst, since less charge is introduced into the ring. It is also probable that, with little catalyst, one molecule of TMEDA coordinates simultaneously with one benzylic- and one butyllithium, thus facilitating an intramolecular gem-dimetalation.

Dimetalation of *m*-xylene with amylsodium-TMEDA in hexane leading to 9 (R-Na) has recently been observed⁴ but no *gem*-dimetalation was found. The dilithiation of dihydroacenaphthylene was also observed recently.⁵

The facile polylithiation seems to contradict our notions on metalation as a nucleophilic proton abstraction, a deactivation being expected after the removal of the first proton. The introduction of the additional charges into separate non-bonding benzylic orbitals should not entirely eliminate charge repulsions created by further proton abstractions. West rationalized ring metalation of benzyllithium during proton removal by butyllithium by a direct lithium attack on the carbon to be metalated (electrophilic assistance).³ Such attack by lithium on the Me from which the proton is abstracted is difficult to envisage. Electrophilic assistance by lithium might occur by a cyclic mechanism, e.g. (16), where lithium coordinates with a ring carbon, or even with the ring in a π -complex, at the same time that a proton of the Me group is abstracted by the base. It seems that in polymethylbenzenes the reaction by this mechanism is favored over the 4-center one leading to ring metalation.

The fast formation and apparent greater stability of diand trilithiomesitylenes and of dilithio-m-xylene relative to the metallic derivatives of the other xylenes is surprising at first sight. In the first two compounds all the charges are delocalized on one set only of alternate (starred) carbons, whereas in 1,2-bis(lithiomethylene)benzene (11A), the charges can be visualized as delocalized over all carbons of the compound. Bis-1,4(lithiomethylene)benzene is notably absent among the metalation products of p-xylene. It seems that compounds with alternately charged C atoms,⁶ are more stable than those with a uniform charge distribution like those derived from metalation of both Me's in *m*-xylene. A similar phenomenon was observed in sesquiacetylenes⁷⁻¹⁰ and other dimetalated compounds." This effect is not restricted to charges that arise from π -electrons, since 1,3-dilithiophenyl also is formed faster than its isomers,¹² and may be a result of general preference for charge alternation.

It may be noted that there is an equal or even greater stability of the di- and trilithio derivatives, with the charge delocalized in the same π -system, relative to the monolithio compounds. The second ionization constants of dibasic acids, where the second charge is located near the first, as in sulfuric,¹³ phosphoric¹³ or carbonic¹⁴ acids, are much lower than the first ionization constant and the differences between pk₁ and pk₂ for the three acids are 4.5; 5.3 and 6.5 respectively.

Table 2. Metalation of mestitylene and xylenes"

Substrate	Metalating agent (equiv.")	Hours of men (temp.)	t. Products ^c (%)
1 Mesitylene	BuLi(6); TMEDA(3)	12(15-20°)	S ^a (33); 1A(25; 2B(14·5); 3A(17); 4B(6·8); VA(3·7)
2 Mesitylene	BuLi(6); TMEDA(3)	48(15-20°)	1A(16); 2A(7·5); 3A(36); 4A(6·7); VA(34)
3 Mesitylene	BuLi(6); TMEDA(3)	60(15-20°)	1A(11); 2A(14·2); 3A(23·6); 4A(10·3); VA(40·5)
4 Mesitylene	BuLi(6); TMEDA(3)	12(20-25°)	S(4); 1A(30·5); 2A(9); 3A(27·7); 4A(7·2); VA(21)
5 Mesitylene	BuLi(6); TMEDA(3)	24(20-25°)	1A(8·2); 2A(3·3); 3A(25); 4A(3); VA(61·5)
6 Mesitylene	BuLi(6); TMEDA(3)	48(20-25°)	1A(2); 2A(5); 3(21·5); 4A(5); (VA) (66·5)
7 Mesitylene	BuLi(6); TMEDA(6)	48(20-25°)	1A(4); 2A(-); 3A(25); 4A(1·5); V(69)
8 Mesitylene	BuLi(4); TMEDA(2)	24(15-20°)	S(4); 1A(27); 2A(9·3); 4A(32·9); 4A(6·8); VA(19)
9 Mesitylene	BuLi(4); TMEDA(4)	24(15-20°)	1A(8); 2A(0.8); 3A(32.7); 4A(2.7); VA(55.6)
10 m-Xylene	BuLi(4); TMEDA(2)	23(15-20°)	S(5); 6A(36); 7A(24); 8A(19·3); 9A(15)
11 m-Xylene	BuLi(4); TMEDA(2)	14(20-25°)	6A(48); 7A(6·8); 8A(37·6); 9A(7·3)
12 m - Xylene	BuLi(4); TMEDA(2)	24(15-20°)	6A(53·6); 7A(6·5); 8A(20); 9A(5)
13 m-Xylene	BuLi(4); TMEDA(1)	96(15-20°)	S(8); 6A(32); 7A(34); 8A(6·6); 9A(15)
14 m-Xylene	BuLi(4); TMEDA(4)	24(15-20°)	6A(35·9); 7A(27); 8A(57·2); 9A(3·0)
15 o-Xylene	BuLi(8); TMEDA(4)	40(15-20°)	S(6); 10A(40); 11A(36·2); 12A(10·8); 13A(7·1)
16 o-Xylene	BuLi(4); TMEDA(2)	24(15-20°)	S(37·2); 10A(41·4); 11A(13); 12A(4·3); 13A(3·8)
17 o-Xylene	BuLi(4); TMEDA(2)	50(15-20°)	S(12·2); 10A(52·6); 11A(19·8); 12A(5·8); 13A(9)
18 o - Xylene	BuLi(4); TMEDA(2)	24(20-25°)	S(7); 10A(60·8); 11A(27·2); 12A(4·8)
19 o-Xylene	BuLi(4); TMEDA(1)	96(15-20°)	S(52); 10A(17·8); 11A(0); 12A(9·6); 13A(18·1)
20 o-Xylene	BuLi(4); TMEDA(4)	24(15-20°)	10A(49); 11A(51);
21 p-Xylene	BuLi(4); TMEDA(2)	26(15-20°)	S(16); 14A(64); 15A(16)
22 p-Xylene	BuLi(8); TMEDA(4)	48(15-20°)	S(35); 14A(25); 15A(33·3)
23 p-Xylene	BuLi(4); TMEDA(1)	96(15-20°)	S(50); 15A(25); 15A(25)
24 p-Xylene	BuLi(4); TMEDA(2)	24(15-20°)	S(21); 14A(64); 15A(11)
25 p-Xylene	BuLi(4); TMEDA(4)	24(15-20°)	14A(100)
26 Mesitylene	BuLi(6); PMDETA*(3)	24(15-20°)	S(6·6); 1B(55·6); 2B(38); 3B(0)
27 Mesitylene	BuLi(6); PMEDTA(6)	24(15-20°)	1B (90·6); 2B (7·5); 3B (1·7)
28 p-Xylene	BuLi(4); PMDETA(2)	24(15–20°)	14B(100)
29 p-Xylene	BuLi(4); PMDETA(4)	24(15-20°)	14B(91); 15B(9)
30 Mesitylene	BuLi	16(20–25°)	1A(30); 3A(70)
31' Mesitylene	BuLi	24(20-25°)	1A(10); 3A(60); 5A(30)

"With 1.6F butyllithium (BuLi) in hexane at room temperature. Tetramethylethylenediamine (TMEDA) was used as catalyst; "Relative to the substrate; "After silylation; "S: starting substrate; "PMDETA: pentamethyldiethylenet-riamine; 'neat TMEDA.

It was therefore of interest to compare the ease of anion formation¹⁵ with computed anion energies. Calculations were performed both by the "omega-beta" method¹⁶ and by CNDO/2.¹⁷ In the latter case, the molecular geometry is required as input; in preliminary work, we used omegabeta lengths¹⁸ and angles,¹⁹ but it was later found that standard geometries lead to lower energies. The results are recorded in Table 3.

Apart from the fore-mentioned species, Table 3 also includes the starting hydrocarbons, the anions 17, 18, 20, 21 and several lithium derivatives.

The energy of the gas reactions

 $\Delta H_2 \rightarrow AH^- + H^+$ or $AH^- \rightarrow A^{2-} + H^+$

is the difference ΔE in energy between the anion and the acid.

$$\Delta \mathbf{E} = \mathbf{E}_{\mathbf{A}\mathbf{H}^-} - \mathbf{E}_{\mathbf{A}\mathbf{H}_2} \quad \text{or} \quad \Delta \mathbf{E} = \mathbf{E}_{\mathbf{A}}^{2-} - \mathbf{E}_{\mathbf{A}\mathbf{H}_2}$$

Semiempirical calculations of gas phase acidities²⁰ were found to follow the experimental sequence.²¹ On the other hand, the sequence of solution acidities of aromatic

	Energy		ΔE or $\Delta E'$	
Compound	$\omega\beta$ (β units)	CNDO/2 (eV)	eV	(β)
Toluene	-12.59266	-1,539.674		
o-Xylene	-17.18370	-1,778-239		
m-Xylene	-17-18383	-1,778-194		
p-Xylene	-17.18389	-1,778.182		
Mesitylene	-21.77524	-2,016.7		
1C	-17.91085	-1,992-938	23.76	3.864
3C	-13.594	-1,964-41	28.53	3 ·9 57
5C	-9.934	-1,931-417	32· 99	4.020
6C	-13.3259	-1,754-389	23-81	3-858
8C	-9·37375	-1,725.73	28.66	3-941
10C	-13.3304	-1,754-389	23.79	3-853
11C	-9·34159	-1,724.569	29·88	3.989
14C	-13-3291	-1,754-3706	23.81	3.854
17C	-8.74092	-1,515-817	23.857	
18C	-9.2995	-1.723	29.71	4.030
19C		-1,483.72	29·90	
20C		-1,513.618	26.056	
21C		-1,481-205	34.612	
1A ^a		-2,010.03	6.67	
3A ^{4.6}		-2,004.12	5.91	
3A ^{a.c}		-2,000.25		
3A ^{a.d}		-2,003.68		
5A'		-1, 991 ·86		
5A ^{a.d}		-1,997.75		
5A ^{a.b}		-1,998.72	5.40	
7A ^{a.b}		-1,770.90		
8A ^{a.b}		-1,765-53		
15A ^{a.b}		-1,770.77		
17A°		-1,532.906	6.768	
17A*		-1,530.04	9·70	
18A ^{a.b}		-1,764.27		
19A ^a		-1,522.176	6.764	
20A		-1,528.940	10.734	
21A ^{<i>a</i>,<i>b</i>}		-1,532.25	0.65	
21A*		-1,524-32	5.72	
21A ^{a.a}		-1,523.26		

^aLithium bridges the benzylic and one of the ortho carbons; ^bAll lithium atoms are located on the same side relative to the ring and bridging different ortho carbons; ^cLithium atoms are located above benzylic carbon; ^dLithium atoms on opposite sides of the ring; ^cLithium linked to a tetrahedral carbon. hydrocarbons or substituted toluenes (abstraction of the benzylic proton) was not reproduced adequately by such treatments.^{22,23}

The ΔE values in Table 3 show no difference in acidity between the isomeric xylenes for formation of monoanions. However, the energy difference between the monoand dianions support the higher acidity of the *m*-xylene monoanion relative to its isomers in agreement with its faster metalation. The ΔE for the consecutive proton abstraction from mesitylene is similar to those of *m*-xylene.

The calculations also show the greater acidity of the Me relative to the ring protons (compare 17 and 19). The isomeric anions obtained by abstraction of the *ortho* or *meta* protons in toluene have similar energies to that of 20C).

Two results of the calculations for the dianions are not in agreement with experiment. The abstraction of the second proton from the benzylic position of benzyl anion is more endothermic than at the ring position (compare 21 and 19). Introduction of the charge in the *ortho* or *meta* instead of in the *para* position of the ring did not change the energy of the dianion significantly. Similarly, consecutive abstraction of two protons from different Me's in the xylenes is much more endothermic for the second than for the first, a result which is incompatible with the finding that during metalation these reactions are competitive. In order to examine whether the acidity sequence is affected by inclusion of the counterion, calculations were also performed for the lithium compounds. The energy difference $\Delta E'$

$$\Delta E' = E_{AHL_1} - E_{AH_2}$$
 and $\Delta E' = E_{ALL_2} - E_{AHL_3}$

for

$$AH_2 + CH_3(CH_2)_3Li \rightarrow AHLi + CH_3(CH_2)_2CH_3$$

and

$$AHLi + CH_3(CH_2)_3Li \rightarrow ALi_2 + CH_3(CH_2)_2CH_3$$

takes into account not only the acidity of the particular C-H bond but also the interaction of lithium with the anion, and may differ from anion to anion. Although no equilibrations were performed in our work, we assumed that the rate of lithiation is related to the equilibrium. A similar sequence for the rates and equilibria of monometalation of xylenes was found²⁴ making our assumption reasonable.

For each lithium compound, several molecular geometries were examined by CNDO/2. The arrangement of benzyllithium where the metal bridges the benzylic with an ortho position (using measured distances²⁵) was found more stable than that in which lithium occupies a tetrahedral benzylic position (replacing-with an appropriate modification of bond length-a hydrogen in toluene), or is located perpendicularly above a coplanar benzylic methylene. An analogous result was obtained for (1A). Transformation of the mono (1A) to the di-lithioderivative (3A) of mesitylene was computed as less endothermic than the formation of 1A itself from mesitylene. Still less endothermic was the transformation of 3A into the symmetric trilithio derivative (5A). In all these compounds, the bridged-form was more stable than other structures; the most stable forms of 3A and 5A all had Li atoms on the same side of the ring.

Formation of benzyllithium (18A) was calculated to be energetically more favorable than that of p-tolyllithium (20A). Similarly, formation of benzylic dilithio derivative (21A) is favored over that of the isomeric (19A), where one Li is on the ring. Calculations showed that (21A), where the two lithiums are on the same side of the ring and bridge two different ortho positions, is more stable than structures with metal atoms on the two sides or in tetrahedral positions of the benzylic carbon (there are only small differences of energy for several conformations of the last species). The relative stability of dilithio compounds, formed by abstraction of protons from the same or from two Me's, is also of interest, because of the low energy computed for 21A. Calculations showed that gem-derivatives (7A and 15A) are more stable than the isomeric 8A and 18A. This seems to contradict the results of most metalations, but corresponds to the result of metalation of *p*-xylene. Moreover, the observation that more gem-dilithio products are formed in the presence of only small amounts of catalyst seems to indicate that the relative stabilities of the isomers is changed from 7A > 8Ato 7A < 8A by solvation. Solvated lithium compounds have charge delocalization to a larger extent than the unsolvated derivatives and their relative stabilities should be closer to that of the dianions.

The differences in calculated energies for the various compounds should not be taken too literally. In these charged, electron-rich compounds, electron correlation should play an important role and this is not taken into consideration in CNDO. Linear correlations are therefore not to be expected.^{22,23} Another source of error is that Coulomb repulsion integrals are calculated for spherical orbitals, which exaggerates electron repulsion from the negative charge. It seems to us, however, that relatively large differences in calculated energies are significant. They do correspond also to our experimental results.

The agreement between the energies of the lithium derivatives and the ease of metalation strengthens the conviction that lithium-anion interaction can effect drastic changes in the order of stabilities of various anions, particularly when charge-charge repulsion is involved. Additional proof for the formation of the

Additional proof for the formation of the polylithioderivatives (and against the stepwise metalationsilylation after the addition of trimethylchlorosilane) was found in the NMR spectra of the aromatic protons in the metalation products. The results are recorded in Table 4. An upfield shift of the *ortho* and *para* protons was found in the dilithiated relative to the monolithiated compounds. The chemical shift depends only weakly on the excess of TMEDA once one mole of the coordinating amine is

Table 4. Chemical shifts^a (ppm) of the aromatic protons in the lithium derivatives

Compound	Ortho	Meta	Para [®]
1A	5.76(s)	_	5-41(s)
3A	5-21(s)	_	4.71(s)
5A		_	4.51(s)
6A	5-87(Sb)	6·27(q)	5.30(d)
8A	5-10(Sb)	5·97(q)	4.77(d)
10A	5.63(m)		4-93(m)
11A	5-24(m)	·	4-93(m)
14A	6-13(d)		6-25(d)
17A	6·09(d)	6-30(t)	5-50(t)

"Relative to TMS. Determined relative to mesitylene in hexane-TMEDA.

*Para at least to one of the methylenes.

s, singlet; Sb, broad singlet; d, doublet; t, trip-

let; q, quartet; m, multiplet.

introduced. The chemical shift of the aromatic protons of the benzylic lithium compounds in the presence of TMEDA in hexane is almost identical to that of the same compounds in THF, suggesting a similar charge delocalization.²⁵⁻³² Similar chemical shifts were found also in neat TMEDA. In this solution mono- di- and trilithio derivatives of mesitylene were formed, showing that the reaction proceeds in solution. The products and butyllithium are not stable in this solution.

EXPERIMENTAL

Metalation. All metalations were carried out by a standard procedure an example of which is given for mesitylene. To 33 ml of BuLi 1.6 F in hexane (0.05 eq) kept in an ice bath were added dropwise 3.4 ml (0.025 mole) of TMEDA. A white ppt was developed (or a clear soln when the ratio of BuLi to TMEDA was 1:1). To the mixture of BuLi and TMEDA 1 g of mesitylene was added. The ice bath was removed and the mixture was left at room temp for the indicated period. Soon after adding the substrate, the mixture became heterogeneous and remained so throughout the metalation time. The mixture was then cooled in an ice bath and a five molar excess (6.5 ml) of trimethylchlorosilane was rapidly added to the soln. The mixture was left overnight (shorter quenching time was also used, but this had no influence on the results), then it was filtered. The filtrate was washed with 5% NaHCO₃ aq, HCl aq, and again with NaHCO₃ aq. The solvent was evaporated and the products in the residue were separated by GLPC on a 2 m×1/4 column of 10% SE-30 on Chromosorb W, mesh size 60/80 at 140-180°. The yields given in the Table are obtained by referring to a standard which in this experiment was mesitylene.

The analyses and absorption spectra of the products are recorded in Table 5.

	Anal.							
	Calcd. (%)		Four	nd (%)				
	С	Н	С	Н	IR: cm ⁻³	UV: $\lambda_{\max}^{EtOH} nm(\epsilon)$		
1b	75·0	10.4	74.84	10-15	700, 840, 1155, 1170, 1250, 1605	271 (260)		
2b	68·1	10.4	67.74	10.88	690, 700, 835, 1040, 1180, 1260, 1600	266 (440)		
3b	68 ∙1	10.6	67.86	10 ·96	705, 840, 1155, 1170, 1250, 1600	274 (360)		
5b	64.28	10.7	64.49	10.06	690, 705, 825, 960, 1165, 1250, 1590	276 (320)		
6b	74.18	10-1	74-43	10.42	700, 750, 780, 840, 1080, 1165, 1250, 1605	279 (460)		
7b	67-2	10.40	67-15	10-33	685, 700, 770, 825, 1035, 1255, 1600	282 (580)		
8b	67.2	10-40	67.09	10.48	700, 830, 930, 1070, 1170, 1250, 1600	283 (720)		
10b	74.1	10-1	73-31	10-13	690, 740, 850, 1040, 1150, 1250, 1600			
11b	67-2	10.40	67.39	10.36				
14b	74-1	10-1	71-25	10-18	690, 760, 835, 1155, 1250, 1510	282 (660)		
15	67-2	10-4	67-44	10.74	680, 770, 860, 1030, 1100, 1200, 1250, 1510	285 (760)		

Table 5.

The NMR data were obtained on a Varian T60. The NMR spectra of the Li derivatives were taken directly on products of metalation performed in NMR tubes in various conditions similar to those indicated in Table 1. After short reaction times the anions were still in soln and their spectra could be taken in the metalation media, but as the amount of di and tri anions increased a ppt was developed. The ppt was redissolved by addition of excess of TMEDA and the composition of the products of the reaction in the NMR tubes was checked by quenching with trimethylchlorosilane. The addition of excess of TMEDA produced an upfield change of the chemical shift of no more than 2-4 c/s. The chemical shifts in Table 4 were recorded in the presence of excess of TMEDA. Addition of more TMEDA did not change the position of the signals. The spectra of the Li derivatives were self consistent since the formation of di and trilithio derivatives were accompanied by the disappearance of the lower metalated compounds and by an upfield chemical shift. The change in the composition of the metalation products, derived from the NMR spectra corresponded to that obtained from the silvlation products. The assignment of the various protons is supported by the integration results of their signals.

Metalation in TMEDA. The solvent from a hexane soln of BuLi was evaporated in vacuum at room temp and the residue dissolved in TMEDA. The hydrocarbon was added to this soln at room temp and the metalation followed by NMR spectroscopy and reaction with trimethylchlorosilane. The two methods gave similar results. The reaction proceeded throughout in solution and no ppt was formed. The ratio of mono-, di and trimetalated compounds changed with time showing a continuous increase of the polymetalated products. Only 30% of 6A was obtained owing to the relatively fast decomposition of BuLi in neat TMEDA.

Calculations. CNDO/2 calculations were performed by a modified version of the program written by Clark and Ragle.³³ Standard bond length were used; C-H 1.094 Å; C-C in ring, 1.39 Å; C-CH₂ 1.39 Å; C-CH₃, 1.54 Å. Details of the " $\omega\beta$ " procedure have been given elsewhere.³⁴

REFERENCES

- ¹G. G. Eberhardt and W. A. Butte, J. Org. Chem. 29, 2928 (1964).
- ²C. D. Broaddus, *Ibid.* 35, 10 (1970).
- ³R. West and P. C. Jones, J. Am. Chem. Soc. 90, 2656 (1968).
- ⁴G. B. Trimitsis, A. Tuncay and R. D. Beyer, *Ibid.* 94, 2152 (1972);
- G. B. Trimitsis, H. Tuncay, R. D. Beyer and K. J. Ketterman, J. Org. Chem. 38, 1491 (1973).
- ⁵L. D. Kershner, J. M. Gaidis and H. H. Freedman, J. Am. Chem. Soc. 94, 986 (1970).
- W. J. Hehre and J. A. Pople, *Ibid.* 92, 2191 (1970).
- ⁷J. Klein and S. Brenner, *Ibid.* **91**, 3094 (1969); *J. Organomet. Chem.* **18**, 291 (1969); *Tetrahedron* **26**, 2345 (1970); *Ibid.* **26**, 5807 (1970); J. Klein and E. Gurfinkel, *J. Org. Chem.* **34**, 3952 (1969).
- ⁸R. West, P. A. Carney and I. C. Mineo, J. Am. Chem. Soc. 87, 3788 (1965); R. West and G. A. Gornowicz, *Ibid.* 93, 1720 (1971).

- ⁹K. C. Eberly and H. E. Adams, J. Organomet. Chem. 3, 165 (1965).
- ¹⁰J. Y. Becker, A. Y. Meyer and J. Klein, *Theort. Chim. Acta* 29, 313, (1973).
- ¹¹E. M. Kaiser and C. R. Hauser, J. Am. Chem. Soc. 93, 4237 (1971).
- ¹²A. A. Morton, E. L. Little and W. O. Strong, *Ibid.* 65, 1339 (1943).
- ¹³Phillipps and Williams, *Inorganic Chemistry*, Oxford University Press (1965).
- ¹⁴E. J. King, Acid-Base Equilibria. Pergamon Press, Oxford (1965).
- ¹⁵For a discussion of acidity see D. J. Cram, Fundamentals of Carbanion Chemistry. Academic Press, New York (1965).
- ¹⁶G. V. Boyd, Tetrahedron 22, 3409 (1966); see also A. Streitwieser, Molecular Orbital Theory for Organic Chemists. Wiley, New York (1961).
- ¹⁷J. A. Pople, D. A. Santry and G. A. Segal, *J. Chem. Phys.* 438, 129 (1965); J. A. Pople and G. H. Segal, *Ibid.* 43S, 136 (1965); 44, 3289 (1966).
- ¹⁸G. V. Boyd and N. Singer, Tetrahedron 22, 3383 (1966).
- ¹⁹J. Almog, A. Y. Meyer and H. Shanan-Atidi, J. Chem. Soc. Perkin II, 451 (1972).
- ²⁰T. P. Lewis, Tetrahedron 25, 4117 (1969).
- ²¹J. I. Brauman and L. K. Blair, J. Am. Chem. Soc. **90**, 6561 (1968); **92**, 5986 (1970).
- ²²R. G. Jesaitis and A. Streitwieser, Jr., *Theor. Chim. Acta* 17, 165 (1970).
- ²³A. Streitwieser, Jr., P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens and P. M. E. Reuben, Proc. Israel Acad. Sci. and Hum. 160 (1970).
- 24G. Gau, Bull. Soc. Chim. 1942 (1972).
- ²⁵S. P. Patterman, I. L. Karle and G. D. Stucky, J. Am. Chem. Soc. 92, 1150 (1970); J. J. Brooks, W. Rhine and G. D. Stucky, *Ibid.* 94, 7339 (1972).
- ²⁶V. R. Sandel and H. H. Freedman, Ibid. 85, 2328 (1963).
- ²⁷L. D. McKeever and R. Waack, J. Organomet. Chem. 28, 145 (1971).
- ²⁸H. Yuki and Y. Okamoto, J. Pol. Sci. 9A, 1247 (1971).
- ²⁹K. Takahashi et al., Bull. Chem. Soc. Jap. 41, 231 (1968); J. Phys. Chem. 75, 1062 (1971); Org. Mag. Res. 3, 349, 539 (1971); Bull. Chem. Soc. Jap. 44, 2559 (1971).
- ³⁰S. Bywater and D. J. Worsfold, *J. Organomet. Chem.* **33**, 237 (1971).
- ³¹J. B. Grutzner, J. M. Lawlor and L. M. Jackman, J. Am. Chem. Soc. 94, 2306 (1972).
- ³²G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *Ibid.* 82, 5846 (1960); T. Schaeffer and W. G. Schneider, *Can. J. Chem.* 41, 966 (1963).
- ³³P. A. Clark and T. L. Ragle, CNDO TWO-SCF-LCMO-QCPE
- Catalog, Vol. VIII, Program 100. Indiana University (1972). ³⁴A. Y. Meyer and H. Yinnon, Tetrahedron 29, 3915 (1972).