

POLYMETALATION OF AROMATIC COMPOUNDS

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SUMMARY

It was found that polynuclear aromatics such as anthracene, biphenyl, fluorene and indene are easily polyolithiated by *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in hydrocarbon solvent. This was established by quenching the reaction mixtures with deuterium oxide. The deuterated compounds were isolated and examined by mass spectrometry. The mass spectral data revealed that as many as ten lithium atoms are placed on some of the polynuclear aromatic compounds. The polyolithiated aromatic compounds were also derivatized with chlorotrimethylsilane. The mass spectra of the trimethylsilylated derivatives confirmed the results obtained from the deuteration experiments.

n-Butyllithium alkylated aromatic compounds simultaneously with the lithiation reactions, *e.g.* mono-, di and tri-alkylated biphenyls and anthracenes were isolated from their respective reaction mixtures.

INTRODUCTION

Chelating diamines have been found to enhance the reactivity of organolithium compounds in metalation reactions^{1,2}. It has been noted that benzene⁴ and toluene⁵ undergo facile metalation under mild conditions using *n*-butyllithium-tetramethylethylenediamine. High yields of phenyl- and benzyllithium, respectively, were obtained. These were identified as their corresponding acid derivatives. Similar results have been reported by Eastham and Screttas using tertiary amines⁶. Dimetalation of ferrocene⁴ using the *n*-butyllithium-tetramethylethylenediamine complex has also been reported. It should be emphasized that in the previous work only dimetalation was reported.

Recently, polymetalation of aromatic compounds using *n*-butyllithium with or without *N,N,N',N'*-tetramethylethylenediamine was reported³. It was also reported that ferrocene, a compound showing typical aromatic substitution reactions, underwent metalation with *n*-butyllithium and produced a reaction product containing species with varying degrees of polyolithiation.

RESULTS AND DISCUSSION

In the present work, it has been found that anthracene, biphenyl, fluorene and

TABLE 1

MASS SPECTRA OF DEUTERATED ANTHRACENE

<i>m/e</i>	Ions	Product distribution (%)	Relative abundance
179			9.5
180	C ₁₄ H ₈ D ₂	11.33	38.0
181	C ₁₄ H ₇ D ₃	20.14	71.4
182	C ₁₄ H ₆ D ₄	27.75	100.00
183	C ₁₄ H ₅ D ₅	17.02	66.6
184	C ₁₄ H ₄ D ₆	14.73	52.3
185	C ₁₄ H ₃ D ₇	6.55	23.8
186	C ₁₄ H ₂ D ₈	1.92	9.5
187	C ₁₄ HD ₉	0.10	4.7
188	C ₁₄ D ₁₀	0.02	2.3

TABLE 2

MASS SPECTRUM OF SILYLATED ANTHRACENE

<i>m/e</i>	Ions	Relative abundance
322	C ₁₄ H ₈ (SiMe ₃) ₂	80.0
394	C ₁₄ H ₇ (SiMe ₃) ₃	100.0
466	C ₁₄ H ₆ (SiMe ₃) ₄	60.0
538	C ₁₄ H ₅ (SiMe ₃) ₅	50.0
610	C ₁₄ H ₄ (SiMe ₃) ₆	20.0
682	C ₁₄ H ₃ (SiMe ₃) ₇	20.0
754	C ₁₄ H ₂ (SiMe ₃) ₈	10.0
826	C ₁₄ H(SiMe ₃) ₉	10.0
898	C ₁₄ (SiMe ₃) ₁₀	10.0

TABLE 3

MASS SPECTRUM OF DEUTERATED FLUORENE

<i>m/e</i>	Ions	Product distribution (%)	Relative abundance
168	C ₁₃ H ₈ D ₂	10.0	31.2
169	C ₁₃ H ₇ D ₃	22.90	75.0
170	C ₁₃ H ₆ D ₄	29.60	100.0
171	C ₁₃ H ₅ D ₅	18.50	68.7
172	C ₁₃ H ₄ D ₆	13.50	50.0
173	C ₁₃ H ₃ D ₇	2.00	12.5
174	C ₁₃ H ₂ D ₈	0.50	3.10
175	C ₁₃ HD ₉	0.20	3.10
176	C ₁₃ D ₁₀	0.05	1.50

indene undergo facile metalation reactions with *n*-butyllithium-tetramethylethylenediamine at 70°, in hexane solvent. A mixture of polyolithiated species in the form of a brown precipitate is normally produced from these reactions.

A. Metalation of anthracene. The brown precipitate from anthracene metalation

TABLE 4
MASS SPECTRUM OF SILYLATED FLUORENE

m/e	Ions	Relative abundance
310	$C_{13}H_8(Me_3Si)_2$	75.01
382	$C_{13}H_7(Me_3Si)_3$	100
454	$C_{13}H_6(Me_3Si)_4$	87.50
526	$C_{13}H_5(Me_3Si)_5$	31.25
598	$C_{13}H_4(Me_3Si)_6$	12.50
670	$C_{13}H_3(Me_3Si)_7$	6.25

was quenched with deuterium oxide (D_2O) and the product, after isolation by sublimation, was examined by mass spectrometry. The mass spectral analysis in Table 1 shows the appearance of mass numbers, m/e , of 178 to 188. This corresponds to anthracene containing from one to ten deuterium atoms. This indicates that products ranging from partially to fully lithiated anthracene have been prepared. The relative abundance as well as yields are included in the above table. The yields are based on corrected values for the naturally occurring isotope of carbon.

In a separate experiment, the polyolithiated anthracene was allowed to react with a large excess of chlorotrimethylsilane. A dark brown oil was isolated. This oil was examined by mass spectrometry. The results of the mass numbers found are tabulated in Table 2. The data show the appearance of m/e values at 250 up to 898. This corresponds to the various polysilylated anthracene derivative up to and including the deca(trimethylsilyl) derivative. It is clear from the mass spectra of the deuterated and silylated anthracenes that complete lithiation of some of the anthracene nuclei was realized with the *n*-butyllithium-tetramethylethylenediamine mixture. The fully lithiated anthracene ($C_{14}Li_{10}$) gave $C_{14}D_{10}$ on deuterolysis and $C_{14}(SiMe_3)_{10}$ on silylation.

B. Metalation of fluorene. The same metalation reaction was applied to fluorene. The results are similar to those obtained with anthracene. The product analysis by mass spectrometry after treatment with deuterium oxide is shown in Table 3. These results suggest that some of the fluorene is polyolithiated to the extent of nine lithium atoms on the aromatic rings. The products obtained, based on the mass spectral data, show that $C_{13}H_6D_4$ is the predominant species.

The deuteration results were partially confirmed by silylation of the polyolithiated fluorene with chlorotrimethylsilane. These data are included in Table 4. The absence of the higher trimethyl silylated fluorenes from the mass spectral data may be due to low volatility preventing their detection.

C. Metalation of biphenyl. The brown solid obtained was found to contain one to six lithium atoms per molecule of biphenyl as determined by hydrolysis with deuterium oxide. The mass spectral data in the deuterated biphenyl, Table 5, included m/e values of 155 to 160. Similarly, the trimethylsilylation results (Table 6) confirmed the deuteration results.

D. Metalation of indene. The metalation product of indene after deuterolysis was isolated by distillation. Mass spectral examination of the products showed the presence of mass numbers of 117 to 122 (Table 7), clearly indicating that indene under-

TABLE 5

MASS SPECTRUM OF DEUTERATED BIPHENYL

<i>m/e</i>	Ions	Product distribution (%)	Relative abundance
154	C ₁₂ H ₁₀	12.98	25.5
155	C ₁₂ H ₉ D	20.12	42.8
156	C ₁₂ H ₈ D ₂	47.6	100.00
157	C ₁₂ H ₇ D ₃	20.99	53.1
158	C ₁₂ H ₆ D ₄	8.98	21.1
159	C ₁₂ H ₅ D ₅	2.03	3.80
160	C ₁₂ H ₄ D ₆	0.32	0.60

TABLE 6

MASS SPECTRUM OF SILYLATED BIPHENYL

<i>m/e</i>	Ions	Relative abundance
226	C ₆ H ₉ SiMe ₃	100.0
298	C ₆ H ₈ (SiMe ₃) ₂	100.0
370	C ₆ H ₇ (SiMe ₃) ₃	30.0
442	C ₆ H ₆ (SiMe ₃) ₄	10.0

TABLE 7

MASS SPECTRUM OF DEUTERATED INDENE

<i>m/e</i>	Ions	Relative abundance	Product distribution (%)
116	C ₉ H ₈	20.0	3.48
117	C ₉ H ₇ D	54.0	15.11
118	C ₉ H ₆ D ₂	66.0	17.44
119	C ₉ H ₅ D ₃	100.0	27.32
120	C ₉ H ₄ D ₄	86.60	23.25
121	C ₉ H ₃ D ₅	40.0	13.30
122	C ₉ H ₂ D ₆	18.0	3.48

TABLE 8

MASS SPECTRUM OF SILYLATED INDENE

<i>m/e</i>	Ions	Relative abundance
188	C ₉ H ₇ SiMe ₃	26.30
260	C ₉ H ₆ (SiMe ₃) ₂	11.10
332	C ₉ H ₅ (SiMe ₃) ₃	100.0
404	C ₉ H ₄ (SiMe ₃) ₄	20.0
476	C ₉ H ₃ (SiMe ₃) ₅	3.0

went lithiation reactions to the extent of at least six lithium atoms. These results were further confirmed by the appearance of mass spectral numbers of 188 to 476, in the trimethylsilyl derivatives prepared from the polyolithiated indene, (Table 8).

It is interesting to note that the fluorene, anthracene, biphenyl and indene rings became more susceptible and reactive toward further lithiation upon the introduction of the first lithium atom. Samples from the fluorene reaction mixture were taken during the course of the metallation reaction and quenched with deuterium oxide. Mass spectral analysis of the deuterated aromatic compound showed the formation

TABLE 9

METALATION OF FLUORENE AT 80°

<i>m/e</i>	Metalation (%) after			No. of deuterium
	0.5 h	2 h	24 h	
166	11.33	5.09	2.94	0
167	31.80	13.65	4.54	1
168	36.22	28.41	11.51	2
169	13.19	28.60	20.63	3
170	4.83	15.28	25.24	4
171	1.36	5.48	18.00	5
172	0.58	2.25	13.94	6
173	0.15	0.48	2.71	7

of mono-, di- and tri-deuterated fluorene in the first 30 min of the reaction (Table 9) with the di-deuterated product predominating. However, as the reaction proceeded to longer time, the amounts of di- and tri-deuterated products decreased and substantial quantities of the tetra- and penta-deuterated products began to appear. After prolonged reaction times of 6 to 12 h or more, an equilibrium composition of tetra-, penta- and hexa-deuterated product was apparently established. The same sort of behavior was observed for each of the aromatic compounds studied. These data suggested that mono-metalation reaction is a kinetically controlled process while the polymetalation is favored by a thermodynamic process.

A substantial amount of alkyl derivatives of anthracene and biphenyl were observed during the metalation reactions. These products were identified in the residual oils left behind the sublimed deuterio anthracene and biphenyl. The alkylated products showed peaks in the mass spectrum at 212 and 268 for mono and dibutyl-biphenyl and for mono and dibutylanthracene. These results are in accord with published data on alkylation of aromatic compounds by organolithium reagents^{7,8}.

EXPERIMENTAL

Reagents

N,N,N',N'-Tetramethylethylenediamine was distilled over calcium hydride. *n*-Butyllithium, 15%, in hexane was purchased from Foote Mineral Co., and the Lithium Corp. of America. Anthracene, fluorene, biphenyl, and indene were purified by sublimation and distillation.

Apparatus

The apparatus used to determine the *m/e* values was Mellon Institute's MS 9.

Metalation of aromatic compounds

General procedure. A 28 oz. beverage bottle, which had been previously washed, rinsed and dried in an oven at 140° for 24 h, was placed in a dry box under an argon atmosphere. To this bottle was added 0.10 mole of the aromatic compound to be metalated, 600 ml (1.0 mol) of n-butyllithium in hexane solution followed by 0.50 mol of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The bottle was capped with a crown metal cap perforated for access with a syringe needle through a neoprene rubber liner. The bottle was then placed in a 70° constant temperature bath with tumbling action for 24–28 h. After removal from the water bath and cooling to room temperature, reactants to form the appropriate derivatives were introduced through the rubber liner in the bottle cap using syringe techniques.

Derivatization of metalated products

1. *Heavy water.* The metalated products were cooled to –40° and deuterium oxide was added incrementally (1 ml at a time) using a plastic syringe with occasional shaking and venting of off gases. After complete hydrolysis, the products were purified by sublimation or distillation. The oily residue after sublimation was found to contain the alkylated products.

2. *Chlorotrimethylsilylation.* The metalated products were cooled to –10° and a ten-fold excess of chlorotrimethylsilane was added. The reaction mixture was cautiously allowed to warm to room temperature and then placed in a 50° constant bath and tumbled for 12 h. A white solid was precipitated out by adding diethyl ether to the reaction mixture. It was then separated by filtration and the unreacted chlorotrimethylsilane was removed from the filtrate by azeotropic distillation with diethyl ether. The residue was washed four times with 300 ml portions of distilled water to remove the residual tetramethylethylenediamine. The oily residue obtained was examined by mass spectrometry at 7, 10, 20 and 70 eV.

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