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The Reaction of Lithium Vapor with Benzene and Halobenzenes

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The reaction of lithium vapor with benzene has been studied thoroughly over a wide range of temperatures and reaction conditions. While the primary products are polylithium compounds derived from fragmentation of benzenes and substituted benzenes, there are measurable quantities of multi lithium substituted benzenes produced. Experiments under extreme reaction conditions give evidence for the production of small quantities of lithium substituted species with cyclohexene and cyclohexane structures.

Introduction

It is difficult or impossible to metallate benzene with lithium using conventional solution techniques. In fused aromatic ring systems such as naphthalene and anthracene which have more "acidic" protons this reaction proceeds producing a high degree of lithium substitution when alkyllithium/TMEDA reagents are employed. With benzene, however, only one proton can be replaced by this method [1]. To obtain more highly substituted lithiobenzenes, halogenated benzene starting materials have been reacted with alkyllithium reagents. In such reactions lithium halide elimination can readily occur, and apparently it has not been possible for this reason to prepare more highly metallated benzenes than 1,3 or 1,4-dilithiobenzene [2].

Lithium vapor reactions which have been investigated in our laboratory [3, 4], have previously established a synthetic route to products inaccessible by other means. For this reason we thought it would be of interest to determine if the lithium vapor technique could be used to produce highly lithium substituted benzene species.

Experimental

Reactions of lithium vapor were studied with benzene, monochlorobenzene, 1,2-1,3 and 1,4-dichlorobenzene, 1,2,3-; 1,2,4- and 1,3,5-trichlorobenzenes, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene. The ultrapure lithium was supplied by Alfa Products.

The reactor designs shown in figures 1, 2 and 3 were used to investigate these reactions. All three reactors consisted of a stainless steel chamber (12 inches high and 5 inches in diameter) with a removable stainless steel cold finger and a smaller inconel chamber welded to the bottom for lithium vaporization. The inlet configurations of the reactors varied as shown in the figures. The inlet of reactor B could be heated with a 30 kw, 250 kHz Lepel RF generator.

During a reaction the reactor was evacuated through the valve, the cold finger was filled with liquid nitrogen and the lithium was heated to 800 °C using a resistance oven and a West model JP temperature controller. Ten grams of lithium were used and the average reaction duration was 25 minutes. The benzene and chlorinated benzenes were admitted to the reactors as gases except for those that were low vapor pressure solids (1,2,4,5-tetrachlorobenzene, pentachlorobenzne and hexachlorobenzene). These were studied in reactor C, only, by dropping powdered samples down the inlet tube where they sublimed from the inlet ring which was heated by condensing lithium vapor. The benzene species were admitted into reactors A and B at a rate of 1×10^{-3} mol/min. For reactor C the rate was 3×10^{-5} mol/min.

The products were analyzed after each reaction by transferring the sealed reactor to a glove bag filled with argon, opening the reactor, then removing the products from the cold finger. The products were hydrolyzed by passing helium saturated with D_2O vapor over

$$C_nLi_m + D_2O \longrightarrow C_nD_m + mLiOD$$

them on a vacuum line. The resulting deuterated hydrocarbons were separated and identified using gas chromatography and their identity was confirmed by mass spectrometry. The material remaining in the reactor after the cold finger products were removed were hydrolyzed by placing a clean cold finger on the reactor, then connecting the reactor to a vacuum line and carefully passing a D_2O, helium mixture over it.

Normally as a confirmation step in the characterization of polylithium compounds we have also derivatized the product with $ClSiMe_3$ [3, 4]. This

TABLE I. Relative Intensities.

Mass Number	Reactor A (25 °C)	Reactor B	
		Arm Temperature	
		900 °C	1000 °C
78	43	35	18
79	100	100	7
80	45	68	5
81	22	41	5
82	23	37	6
83	22	33	8
84	17	30	8
85	10	19	9
86	5	10	17
87	–	3	28
88	1	2	23
89	–	2	23
90	–	–	79
91	6	3	100
92	1	1	71
93	1	1	50
94	1	1	18
95	1	2	7
96	5	7	9

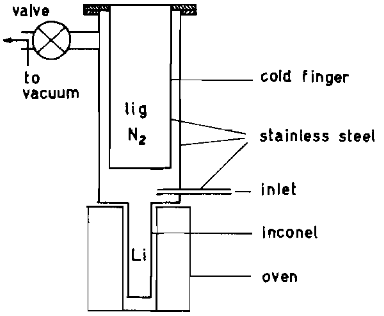

Figure 1. Basic reactor.

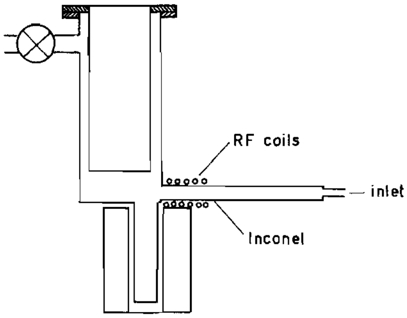

Figure 2. Heated arm reactor.

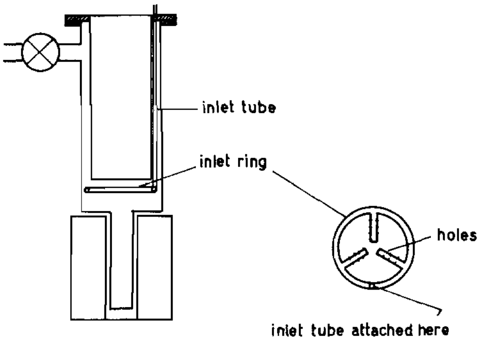

Figure 3. Improved basic reactor.

was done in this study. The expected mixtures of trimethylsilyl compounds were formed and observed mass spectrometrically. For example, in some reaction sequences $C_6(SiMe_3)_nH_{6-n}$ where n = 1–4 were observed in the high resolution mass spectra. However, as will be apparent, the observation of mixtures of trimethylsilyl substituted fragments and six carbon ring compounds were of little value due to their complexity.

Gas chromatograph data was collected on a Varian gas chromatograph, model 2700, using an 8 foot long, ¼ inch diameter Porapak isocyanate on Porasil C column. Low resolution mass spectra data was obtained on a Hitachi RMU 60 mass spectrometer. A CEC-21-110B mass spectrometer was used for high resolution mass spectra.

Results and Discussion

The total yield of cold finger products from the reaction of benzene carried out in reactor A was about 20%. About 35% of the benzene escaped unreacted, while the rest formed a mixture of C_2Li_2 and C_3Li_4 by interacting with the molten lithium on the reactor floor. The major part of the cold finger products consisted of two and three carbon fragments that were completely lithium substituted. These materials included C_2Li_2, C_2Li_4, C_2Li_6, C_3Li_4, C_3Li_6, and C_3Li_8. These products, although they are the major reaction products, are of secondary interest to the products in which the C_6 ring is intact. Their distribution does vary with the starting material and a more detailed discussion will follow.

There were a small amount of C_6 products present also; usually under 1% of the total products. The major C_6 product was C_6H_5Li (C_6H_5D) (Table I). The large numbers and small amounts of C_6 products made their absolute isolation and characterization impractical, so that only mass spectral characterization of the mixture was carried out. The possible species giving significant peaks for each mass number in Table I are shown in Table II. In an attempt to narrow the range of C_6 species, high resolution mass spectral analysis was employed, but even with high resolution data there are ambiguities in the assignment of some masses.

TABLE II. Observed and Calculated C_6 Exact Masses[a].

Benzene Species		Cyclohexadiene (Parent minus one H or D Species)		Cyclohexadiene Species		Cyclohexene Species		Cyclohexane Species		Observed Masses
C_6H_6	78.04692									78.04671
C_6H_5D	79.05322	C_6H_7	79.05474							79.05176
$C_6H_4D_2$	80.059484	C_6H_6D	80.061022	C_6H_8	80.06256					80.05730
$C_6H_3D_3$	81.06577	$C_6H_5D_2$	81.067304	C_6H_7D	81.06884					81.07484, 81.06589
$C_6H_2D_4$	82.07205	$C_6H_4D_3$	82.073586	$C_6H_6D_2$	82.075124	C_6H_{10}	82.07820			82.07300, 82.07903
C_6HD_5	83.07833	$C_6H_3D_4$	83.079868	$C_6H_5D_3$	83.08142	C_6H_9D	83.08448			83.07970, 83.08405, 83.08621
C_6D_6	84.08461	$C_6H_2D_5$	84.08615	$C_6H_4D_4$	84.08769	$C_6H_8D_2$	84.090764	C_6H_{12}	84.09384	84.08748, 84.09233
		C_6HD_6	85.09243	$C_6H_3D_5$	85.09397	$C_6H_7D_3$	85.097046	$C_6H_{11}D$	85.1002	85.09389, 85.10106
		C_6D_7	86.098714	$C_6H_2D_6$	86.100252	$C_6H_6D_4$	86.10335	$C_6H_{10}D_2$	86.10640	86.10206
				C_6HD_7	87.10652	$C_6H_5D_5$	87.10961	$C_6H_9D_3$	87.112686	87.10882
				C_6D_8	88.112816	$C_6H_4D_6$	88.115892	$C_6H_8D_4$	88.11897	88.11272
						$C_6H_3D_7$	89.122174	$C_6H_7D_5$	89.12525	89.12308, 89.11460
						$C_6H_2D_8$	90.12846	$C_6H_6D_6$	90.13153	90.11770, 90.13102
						C_6HD_9	91.134738	$C_6H_5D_7$	91.13781	91.13663, 91.12075
						C_6D_{10}	92.141020	$C_6H_4D_8$	92.144096	92.13099, 92.14350
								$C_6H_3D_9$	93.15037	93.14872
								$C_6H_2D_{10}$	94.15664	94.15600
								C_6HD_{11}	95.16292	95.16202
								C_6D_{12}	96.169224	96.16924

[a] The observed masses are representative peaks from several spectra, all peaks are not necessarily found in each spectrum. The mass spectrometer is accurate only to ±0.003 mass numbers at the mass region investigated. Therefore, if two peaks from different spectra differed by less than 0.003 mass units, only one was shown in the table, since they were assumed to be the same. In a given spectrum, there were occasionally listed two peaks differing by less than 0.003 mass units. They may or may not have been due to different species, and because of this uncertainty, only one of the pair have been listed.

TABLE III. Comparison of C_4 Products from Reactors A and C.

Halogenated Benzene	Major C_6 Product			
	Reactor A		Reactor C	
	Species	Yield	Species	Yield
C_6H_5Cl	C_6H_5Li	1%	C_6H_5Li	10%
1,2-; 1,3-; 1,4-$C_6H_4Cl_2$	C_6H_5Li	1%	$C_6H_4Li_2$	10%
1,2,4-; 1,2,5 $C_6H_3Cl_3$	C_6H_5Li	1%	$C_6H_4Li_3$	10%
1,3,5-$C_6H_3Cl_3$	C_6H_5Li	1%	none	
1,2,4,5-$C_6H_2Cl_4$	–		none	
C_6HCl_5	–		none	
C_6Cl_6	–		none	

The yields of C_6 products were disappointing, but since so much benzene did not react we felt insufficient activation energy may have been a problem. This led to the use of the heated inlet reactor (B) in an attempt to thermally excite the benzene. In most of the reactions studied in reactor B the results were nearly identical with the reactor A results. However, when the inlet temperature was raised to 1000 °C, there was a remarkable shift in the distribution of the C_6 products toward more saturated cyclohexane, cyclohexadiene, and cyclohexene species (see Table I).

Benzene did not give high yields of the desired highly lithium substituted C_6 products regardless of the conditions chosen. Earlier lithium vapor work had indicated, however, that polylithium compounds could be formed from normally unreactive hydrocarbons by using the halogenated form [3]. For this reason a series of reactions using chlorinated benzenes were studied in reactor A.

The types of products and overall yields from these reactions differed only slightly from the earlier reactions using unsubstituted benzene. An interesting observation, however, was that although not all the starting material formed lithium compounds, it did react with the lithium. This was shown by the formation of less highly chlorinated benzene species than the starting material. For instance, no unreacted $C_6H_4Cl_2$ was found from its reaction, only C_6H_5Cl and C_6H_6. There was apparently dehalogenation by Li followed by hydrogenation, possibly by LiH in the molten lithium (it is known, for example, that ethylene will interact with molten lithium to give ethane [5]. This has been proposed to result from hydrogenation by LiH in the lithium. The LiH is formed by the decomposition of some of the ethylene to lithium carbide).

At this point we felt that the best chance for success lay in minimizing the interaction of the benzene with the hot lithium on the reactor bottom. For this reason, reactor C, with its inlet spraying the

TABLE IV. Relative Distribution of Fragment Products from the Benzene Reactions (%).

	C_6H_5I	C_6H_5Br	C_6H_5Cl	C_6H_5F	C_6H_5F	$C_6H_4Cl_2$[a]			$C_6H_3Cl_3$[a]			C_6H_6	C_6Cl_6	C_6F_6
				slow	fast	o	m	p	1,3,5	1,2,4	1,2,3			
C_2D_6	18	19	15	30	14	6	7	6	11	9	22	10	25	12
C_2D_4	66	5	5	4	2	2	2	2	7	1	6	1	3	t
C_2D_2	10	4	6	5	24	29	20	25	31	28	53	20	21	10
C_3D_8	18	20	20	19	10	5	9	7	8	9	5	12	18	28
C_3D_6	30	33	29	34	14	5	8	6	15	3	3	11	9	13
C_3D_4	18	19	25	8	36	54	56	54	28	50	9	46	24	37
C_4D_{10}	t[b]	t	t	t	t	t	t	t	t	t	t	t	t	t

[a] Distribution is dependent on the rate of admission to reaction.

[b] t = trace.

reactant directly on to the cold finger, was constructed. A series of reactions using chlorinated benzenes were studied in this reactor.

In this reaction system, the cold finger product yields nearly doubled, while the amount of product formed on the reactor floor decreased. In some instances the C_6 products accounted for over 20% of the cold finger products and contained only one major species (see Table III). The evidence obtained for the formation of trilithium substituted benzenes is significant because only two lithium atoms have been reported to be substituted for benzene protons by conventional methods [2].

Attempts to obtain substitution of more than three lithium on benzene using 1,2,3-trichlorobenzene, tetra, penta and hexachlorobenzene, led only to fragmentation. The extensive fragmentation of the benzene and substituted benzene observed in this study are almost certainly a direct consequence of the formation and exothermic decomposition of extremely reactive benzyne intermediates early in the reaction sequence. One would expect that the different reaction sequences of benzyne formation and decomposition which occur when benzene and variously substituted halobenzenes are selected as reactants would lead to individually distinct polylithium fragments. It can be seen in Table IV that this is so. The variation in the D_2O hydrolysis products is interesting. However, for compounds such as C_2Li_4, C_2Li_6, and C_3Li_8 we have previously published more selective syntheses resulting in higher yields [3, 4].

We cannot yet control the reaction sufficiently such that lithium atom attack on many adjacent sites occurs without substantial fragmentation. This investigation has shown, however, that some polylithium compounds of the types $C_6H_{6-n}Li_n$, n = 1 to 6, and $C_6H_{12-n}Li_n$, n = 1 to 12, as well as cyclohexenes multisubstituted with lithium are probably stable and are suitable targets for further synthetic work by entirely different synthetic methods or by some modified lithium vapor approach to be developed in the future.

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