

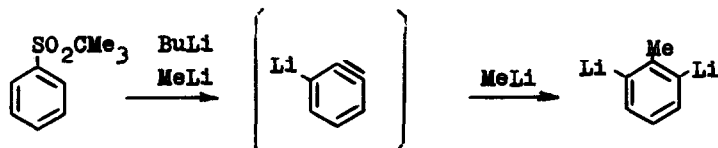
INDO CALCULATIONS OF LITHIODEHYDROBENZENES

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In 1966 one of us and Fedorov suggested that the substitution of a t-butylsulfonyl group for an alkyl group by the action of alkyllithium on t-butyl phenyl sulfone proceeds through the intermediate formation of 3-lithium-1,2-dehydrobenzene (3-Li-DHB).<sup>1</sup> Further experimental studies<sup>2-4</sup> provided data in agreement with this hypothesis. For example, MeLi which can only metalate t-butyl phenyl sulfone ortho to the sulfonyl group, forms 2,6-dilithiotoluene - the adduct of MeLi and 3-Li-DHB - by combined action with n-BuLi.<sup>3</sup>



The similar parallel addition of a weak nucleophile is observed at low temperatures and in more polar solvents, when ortho-lithiophenyl t-butyl sulfone performs the role of nucleophile.<sup>4</sup>

The experimental data obtained now indicate that the 1,2-bond of 3-Li-DHB, the participation of which in the reaction is rather probable, is apparently different from that of dehydrobenzene (DHB) itself. One should note the high selectivity of nucleophilic addition, which is always at position 2. In contrast to DHB all our attempts to isolate Diels-Alder adducts with Li-DHB were unsuccessful. To explain these peculiarities quantum-chemical calculations on Li-DHB were necessary.

DHB (I), its 3- and 4-Li-derivatives (II and IV) and anions (III,V), formed by Li-DHB ionization, were calculated using the INDO method<sup>5</sup> with the geometrical parameters obtained by Haselbach<sup>6</sup> for DHB ( $\text{C}_{2v}$ ):  $r_{\text{C}_1\text{C}_2}=1.256 \text{ \AA}$ ,  $r_{\text{C}_2\text{C}_3}=1.344 \text{ \AA}$ ,  $r_{\text{C}_3\text{C}_4}=1.399 \text{ \AA}$ ,  $\widehat{\text{C}_1\text{C}_2\text{C}_3}=130^\circ$ ,  $\widehat{\text{C}_2\text{C}_3\text{C}_4}=106^\circ$ ,  $\widehat{\text{C}_3\text{C}_4\text{C}_5}=124^\circ$  and  $r_{\text{CH}}=1.084 \text{ \AA}$ . We assumed that the ring geometry was not changed as a result of the substitution of a hydrogen for a lithium atom ( $r_{\text{CLi}}=2.1 \text{ \AA}$ ) and the ionization of Li-DHB on anion formation (III,V).

The singlet and triplet states of DHB and its derivatives were calculated.

The results are given in Table 1 and the full charges on the carbon atoms  $Q_1$  - in molecular diagrams (scheme 1).

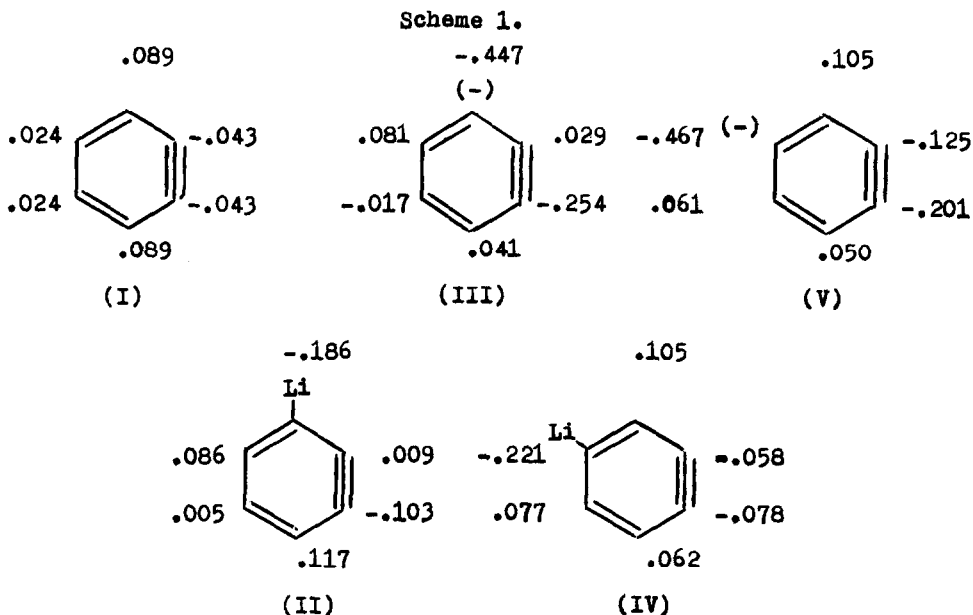


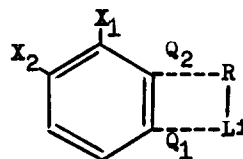
Table 1

	I	II	III	IV	V
$E_S$ (a.u.)	-43.6838	-43.2928	-42.6930	-43.3223	-42.7119
$E_T$ (a.u.)	-43.5679	-43.2113	-42.6493	-43.2105	-42.6378
$\Delta E_{S-T}$ (a.u.)	0.1159	0.0815	0.0437	0.1118	0.0741
$\int M_S(D)$	0.291	5.601	3.753	6.126	3.716
$\Delta Q = Q_1 - Q_2$	0.0	0.112	0.283	0.020	0.076

As one can see from the data, the calculated value of the singlet-triplet splitting,  $\Delta E_{S-T}$ , is 0.1159 a.u. (72.7 kcal/mole) for I and smaller (a factor of 1.4-2.6) for its lithium derivatives and anions. The ground states of systems I-V are therefore singlets and the possibility of their reacting via triplet states can be neglected for the cases considered here.

In the light of the charge distributions in I-V we can consider the behavior of these compounds towards polar addition to the dehydro bond, and compare the tendency to reactions of this type for the noncharged compounds

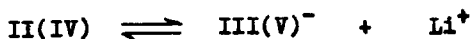
I, II and IV. Assuming a potential barrier of similar shape the activation energy for the formation of activated complexes of type VI will be determined by the polarization of the charges on the dehydro bond  $\Delta Q = Q_1 - Q_2$ , i.e. as seen from Table 1, the following sequence in the tendency to polar addition can be proposed: II > IV > I. Clearly the selectivity of addition also depends on  $\Delta Q$  and follows the same sequence. The



VI

experimental data for I and II are in agreement with this conclusion. In fact, both in the case of II and its 5-substituted derivatives, the products of the reaction with alkyllithium are single isomers - 2,6-dilithio-1-alkylbenzenes.

Let us consider the dependence of rate of competitive addition of various nucleophiles upon solvent polarity. We have supposed that the latter determines the degree of ionization of the lithium compound:



In fact, as seen from Table 1,  $\Delta Q^{\text{III}} > \Delta Q^{\text{II}}$ , and this results in the greater reactivity of III, in comparison with II, towards polar addition, and its lower selectivity with respect to various nucleophiles.<sup>8</sup> In fact, in the more polar THF the lithium derivative of a sulfone can play the role of a nucleophile similar to alkyllithium.

It is seen from a comparison of the charge distributions in II(III) and IV(V) that special effects result from the presence of a lithium atom in the 3-position. The presence of Li in the 4-position influences the charge distribution of the dehydro bond and  $\Delta E_{S-T}$  to a lesser extent, and therefore the properties of IV(V) are expected to be similar to those of I, but not to II (III). The same conclusion can be derived from calculations on DHB-derivatives with an electron-acceptor substituent, the  $\text{NO}_2$ -group.<sup>7</sup>

It should be emphasized that in the case of polar addition we assumed that the reaction proceeds through the intermediate complex VI. However, from the charge distribution data (scheme 1) we cannot rule out the initial addition of lithium cation to II, or to III, followed by attack by nucleophile. In this case the reaction rate is determined by the negative charge on the dehydro bond and, as seen from scheme 1, the sequence of activity towards polar addition (II > IV > I) is the same as in the case of a cyclic transition complex such as VI.

For nonpolar additions, in particular for Diels-Alder reactions, the reverse situation will apparently be observed, i.e.  $I > IV > II$ . This is caused by the increased irregularity of the charge distribution and by the decreased electrophilic properties of the  $C_1-C_2$  bond in this series. It is well understood that in the presence of strong nucleophiles in the reaction sphere, the competition between polar and non-polar addition will be shifted in favour of the former, in agreement with our experimental data.

Thus, our results are completely in accord with the Li-DHB intermediate reaction mechanism, but not rule out other possible mechanisms for this reaction.

#### R E F E R E N C E S

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8. Supposing that III has in fact got  $C_{2v}$  symmetry ( $C_1=C_3$ , etc.), this would lead to an increase in  $\Delta Q$ , and so the qualitative picture would be unaltered.