Dilithiation of Propene and Allylbenzene and the Structure of the Dimetallated Product

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Summary Propene and allylbenzene have been metallated to give dilithio derivatives and the structure of the dilithio derivative of the latter has been suggested.

The enhanced reactivity of butyl-lithium in hexane in the presence of tetramethylethylenediamine[1] (TMEDA) facilitates lithiation of olefins,[2] and dimetallation to give derivatives of trimethylenemethane dianion[3] or to give a butadiene dianion.[4,5] We have now found that BuLi reacts with propene in hexane, in the presence of TMEDA, rapidly to give allyl-lithium, then slowly to give the dilithiated compound (I). The reaction of (I) with BuBr gave undec-5-ene (II) without appreciable amounts of other dialkylated products. This proves that (I) is attacked by BuBr in the first step at the methylene and not the methine end group to give a vinylic intermediate (III), which reacts further to yield (II). Attack at the methine group of (I) would have yielded hept-2-enyl-lithium (IV), which is known to give mainly branched chain products.[6]

Allylbenzene is metallated with BuLi instantaneously to give phenylallyl-lithium[7] (V), and then slowly to a dilithiated product, as indicated by the change in the n.m.r. spectrum

$CH_2=CHCHLi_2$

(I)

$Me[CH_2]_4CH=CH[CH_2]_3Me$

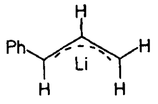
(II)

$Me[CH_2]_4CH=CHLi$

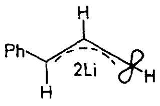
(III)

$Me[CH_2]_3CH=CHCH_2Li$

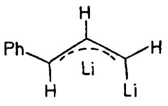
(IV)



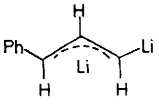
(V)



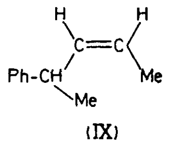
(VI)



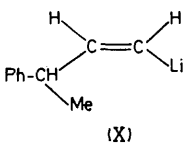
(VII)



(VIII)



(IX)



(X)

of (V). The benzylic proton signal at δ 4·0 disappears (shifted upfield and masked by TMEDA or side bands), the *para* proton signal is shifted from 6·1 to 5·8, but the *ortho* and *meta* proton signals change only slightly (from 6·54 to 6·51 and 6·66 to 6·6 respectively). The central methine proton signal, which was masked in the spectrum of (V) by the phenyl proton signals, is shifted to lower field as expected on dimetallation,[8] and appears at δ 8·18 as a quartet (*J ca.* 16 and 12 Hz) with the two central lines not separated clearly. Dimetallation of allylbenzene, deuteriated at the benzylic position, showed that the second proton was not abstracted from the benzylic, but from the terminal carbon atom. The proton on the central carbon atom of the side-chain of this dimetallated compound appeared as a doublet in the n.m.r. spectrum (*J* 16 Hz). This excluded structure (VI) for the dianion. Of structures (VII) and (VIII), we favour (VII) since a 16 Hz coupling constant would be closer to that expected for a *cis* rather than a *trans* structure in a vinylic lithium compound.[9] An additional reason for this assignment is the formation of the *cis* dimethylated product (IX) when the dilithium compound is treated with MeBr. The alkylation is believed to occur first at the benzylic carbon atom with the formation of the *cis* vinylic lithium intermediate (X).

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