Allyl-lithium Adducts from Buta-1,3-diene and s- or t-Butyl-lithium

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Summary The 1 : 1 adducts of buta-1,3-diene and s- or t-butyl-lithium in hydrocarbon solution have been shown by n.m.r., u.v., and i.r. spectroscopy to be σ-bonded carbon–lithium species of the allyl-lithium type.

THE overall stereochemistry of alkyl-lithium-initiated diene polymerizations has generally been regarded as the result of an "anionic" process.[1] Under the conditions usually employed for polymerizations (10^{-1}—10^{-4} M RLi; 10^{-1}—10^{1} M diene) and with the most common initiator, n-butyl-lithium, the propagation reaction is at least as fast as the initiation reaction, and it is virtually impossible to determine the structure of the initial adduct in the complex mixture of oligomers present. However, initiation with s- or t-butyl-lithium is several times faster than propagation and it is possible, using a 1 : 1 molar ratio of reactants in hydrocarbon solvents, to produce the mono-adducts as the major species present in solution. Hydrolysis of a 1 M solution of the s-butyl-lithium adducts after 30 min. at 35° in n-pentane results in a near quantitative yield of the C_8H_{16} compounds 5-methylhept-1-ene (11%), *cis*-5-methylhept-2-ene (25%), and *trans*-5-methylhept-2-ene (64%).†‡

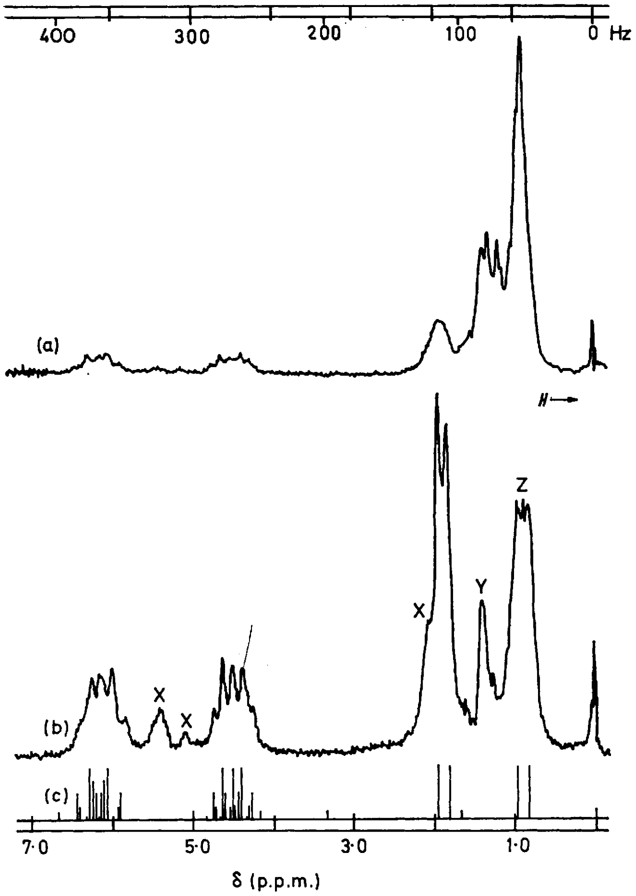
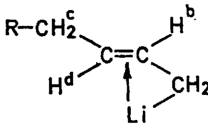
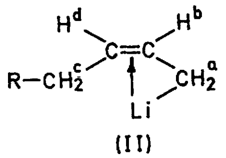


FIGURE. (a) s-BuLi + *butadiene in* [$^2H_{12}$]*cyclohexane.*
(b) [$^2H_9$]t-BuLi + *butadiene in* [$^2H_{12}$]*cyclohexane.*
(c) *First-order simulation for* [$^2H_9$]*t-butyl adduct.*

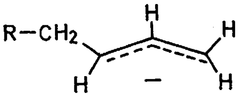
The complete n.m.r. spectrum (a) of the s-butyl-lithium and butadiene adducts in [$^2H_{12}$]cyclohexane is shown in the Figure.§ The more simple spectrum of the [$^2H_9$]t-butyl adduct is (b). The two spectra are virtually identical in the low-field region where two one-proton multiplets are found at τ 3·8 (H^b) and 5·5 (H^d). Of particular interest is the two proton resonance at τ 8·2 (H^c) which appears as a doublet in the t-butyl adduct spectrum and as an unresolved multiplet in the s-butyl case. In the [$^2H_9$]t-butyl spectrum the two lithiomethylene protons appear as a doublet at τ 9·1 (H^a). These two protons are obscured by the alkyl resonances in the s-butyl and non-deuteriated t-butyl spectra. The resonances marked x in the [$^2H_9$]t-butyl spectrum are due to polymer protons, resonance y is due to residual n-pentane, and z is due to <10% protonated t-butyl. Decoupling at each resonance frequency demonstrated the validity of the assignments of the various protons. We interpret these spectra in terms of two σ-bonded species (I) and (II) which do not interconvert on the n.m.r. time scale. The line spectrum (c) (see Figure) is a composite first-order spectrum for the [$^2H_9$]t-butyl adducts assuming a 3 : 1 ratio of (I) : (II) and the following parameters: J_{ab} 9, $J_{bd(cis)}$ 10, $J_{bd(trans)}$ 14, and J_{cd} 7 Hz. These assignments are in substantial agreement with those in but-2-enyl-lithium[3] and but-2-enylmagnesium bromide.[4] The spectra are not consistent with those expected for a 1,2-adduct or a delocalized species (III).[5]



(I)



(II)



(III)

Further evidence for the σ-bonded character of the adduct comes from u.v. and i.r. spectroscopy. The u.v. spectrum of the s-butyl adducts in cyclohexane consists of an intense band with maxima at 208, 214, 219, and 253 nm. (sh), almost identical to that reported for but-3-enyl-lithium,[6] a non-delocalized species.¶ The observed maxima are in contrast to the value of 310—320 nm. reported for π-delocalized allyl-lithium in T.H.F.[5a] The i.r. spectrum of (I) and (II) consists of a C=C stretch band at 1600 cm.$^{-1}$, again in sharp contrast to the value of 1525—1540 cm.$^{-1}$ reported for allyl-lithium.[5a] Although we consider these data to establish that allyl-lithiums are not to be regarded as delocalized anions in hydrocarbon media, the spectral data do indicate some type of interaction between the metal atom and the C=C double bond.[6] The addition of

† Verified by n.m.r. and i.r. methods after preparative g.l.c.

‡ I.r. studies of the residue after removal of the C_8-adducts indicate considerably higher amounts of 1,2-adducts (910 cm.$^{-1}$ absorption) in the C_{12} and C_{16} adducts.[2]

§ The spectrum of the s-butyl adduct broadens only slightly upon cooling the sample to −50°, and sharpens upon heating to 100°. Further experiments are under way to determine whether this is a viscosity effect.

¶ The maximum at 253 nm. has been attributed to an interaction between the C=C bond and one lithium atom in the hexamer.[6] Such an interaction would account for the rather low n.m.r. frequency observed for the lithiomethylene protons in our work and elsewhere.[3,4]

T.H.F. increases this interaction, taking the compound towards, if not to a delocalized form.

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