The Methylenecycloheptatrienyl Dianion

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Summary Successive metallation–metal hydride elimination reactions using equimolar mixtures of n-butyl lithium and potassium t-pentoxide have been used to synthesize resonance-stabilized anions, including the methylenecycloheptatrienyl dianion, (III), which is indicated by simple molecular orbital arguments to be a stable species.

EQUIMOLAR mixtures of hexane solutions of n-butyl-lithium and potassium t-alkoxides appear[1,2] to react as butyl-potassium, a very active reagent for allylic metallation. It is also known[2,3] that potassium hydride elimination from metallated species occurs readily at 70 °C. Lithium hydride elimination has been observed at room temperature,[4] or in refluxing ether[5] when strain relief or aromatization provide extra driving force. Since these metal hydride eliminations are catalysed by alkoxides,[6] equimolar mixtures of n-butyl-lithium and potassium t-pentoxide in hexane (BuLi–KTP) provide a simple route to many conjugated olefins.

We have combined these two reactions to afford a one-step synthesis of many resonance-stabilised anions and dianions.[7] For example, the benzyl anion can be obtained in quantitative yield ($>$ 95% as shown by the yield of α-deuteriotoluene from D_2O quenching) by reaction of 1-methylcyclohex-1-ene or methylenecyclohexane with a three-fold excess of BuLi–KTP at room temperature overnight, followed by 2 h at reflux. Although kinetic factors, such as substitution type,[1] affect rates of monometallation, dimetallation is promoted by formation of stable trimethylenemethane-type dianions.[8] Thus, at room temperature in an excess of BuLi–KTP for two days, cyclohexene is 5% monometallated, cycloheptene is 100% monometallated, and 1-methylcyclohex-1-ene is completely dimetallated.

1-Methylcyclohept-1-ene (I) was treated with a six-fold excess of BuLi–KTP for 12 h at room temperature to accomplish initial metallation. The mixture was then refluxed for 8 h and poured slowly into vigorously stirred excess D_2O. Only two products, mono- and di-deuteriated starting material, (V) (40%), and 1-deuteriomethyl-7-deuteriocyclohepta-1,3,5-triene (VI) (60%) were formed;[9]† neither methylcycloheptadienes nor isomeric methylcycloheptatrienes were detected in the products. Despite the fact that cycloheptatriene[10] and 1-methylcycloheptatriene[7] undergo rapid addition with either BuLi–KTP or BuLi–TMEDA (*NNN'N'*-tetramethylethylenediamine),[11] no C_{12} alkenes were found. These observations suggest that the

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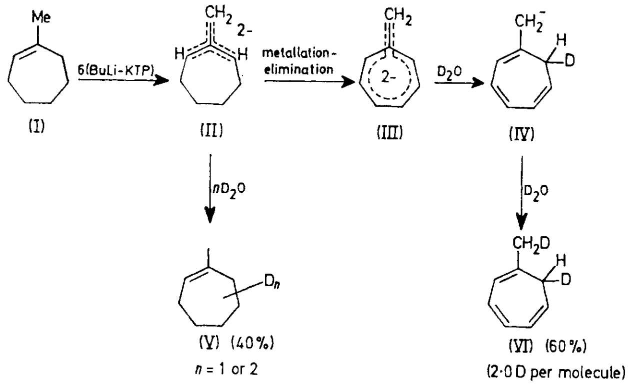
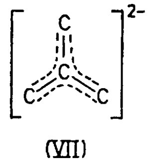
† Yields based on g.l.c. analysis of $>$90% recovery of C_8 hydrocarbons. (VI) was identified by n.m.r. and mass spectrometry, both of which show only the di-deuteriated species. With quenching in H_2O, 1-methylcycloheptatriene is obtained.

dianionic species present in the reaction mixture does not behave as a simple cycloheptatriene. It must also be extremely stable, as the metallation–elimination reaction of the diene intermediate is fast enough to preclude the observation of anything but (V) and (VI) in the products.

The cycloheptatrienyl anion is an anti-aromatic species[12] which has been the subject of a great deal of experimental interest.[13] Heptafulvene is an 8-electron, pseudo-aromatic cross-conjugated molecule which is crystalline at 80 °C, but polymerizes rapidly at room temperature.[14] We now suggest that the dianionic species present in the reaction mixture is the methylenecycloheptatrienyl dianion (III), derived by the formal addition of two electrons to heptafulvene.[15]‡ Roberts *et al.*,[16] using a Hückel M.O. (HMO) treatment, found that cyclobutadiene, also an anti-aromatic species, was greatly stabilised by substitution with a methylene cation, anion, or radical. Consideration of the π MO's of (III) as a combination of those of the stable dianion (VII) and butadiene predicts considerable stabilization relative to these two species ($1{\cdot}16\beta$ by HMO) by virtue of the interaction of the dianion E″HOMO with the butadiene LUMO, despite the fact that the HOMO of (III) is a low-lying antibonding orbital.





(VII)

Reaction of (III) with one molecule of D_2O leads to the known methylenecycloheptatrienyl anion, (IV),[17] which gives (VI) exclusively on reaction with a further D_2O molecule. These results are expected from the HMO charge densities, assuming kinetically controlled protonation of (III) and of (IV). Although it is possible to propose norcaradienyl dianions which would also lead to (VI) *via* (IV), such ions should be considerably less stable than (III).

We thank the S.R.C.–N.A.T.O. for the award of a Postdoctoral Fellowship (T.C.), Dr. P. Hofmann for HMO calculations and discussion, Professor M. Schlosser for critical comments, and the N.S.F. for financial support.

(*Received*, 28*th June* 1976; *Com.* 728.)

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‡ Although it is convenient to describe species like (II) and (III) as 'dianions,' considerable interaction (bonding) with the metal counterions probably is present; see M. Schlosser, 'Struktur und Reactiuität Polare Organometalle,' Springer-Verlag, Heidelberg, 1973.

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