Intramolecular Addition of Benzyl-lithium Derivatives to Norbornene Rings

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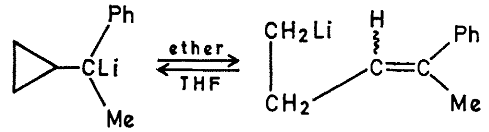
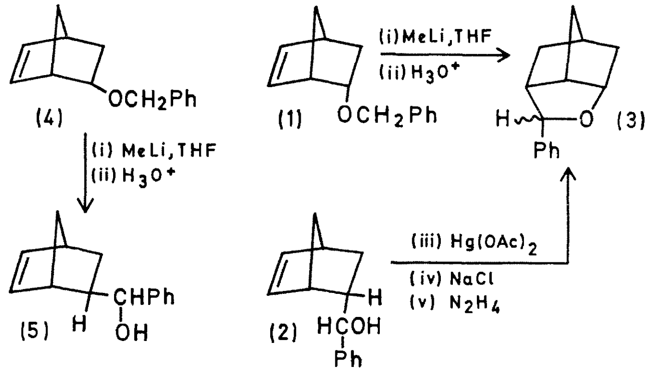
Summary Although α-aryl substituents stabilize organo-lithium reagents in tetrahydrofuran, such derivatives can attack a norbornene double-bond intramolecularly to produce a more reactive, tricyclic s-alkyl-lithium that appears to abstract a proton preferentially from the solvent.

REVERSIBLE, intramolecular additions of simple Grignard and organo-lithium reagents to alkenes are well known.[1–4] In general, the process produces the more stable cyclic species (*i.e.*, primary > secondary > tertiary), when the ring is five- or six-membered whereas strained cycloalkyl-carbinyl-lithiums serve only as intermediates in isomerization to the more stable acyclic derivative.[1,4] The relative stability of primary alkyl-lithiums is also indicated by the ready monoethylenation of secondary and tertiary alkyl-lithiums.[5] α-Aryl-substituted alkyl-lithiums are resonance-stabilized in tetrahydrofuran (THF)[6]; thus benzyl-lithium does not add to ethylene[5] (although it has surprising kinetic basicity towards triphenylmethane[7]), and a single α-phenyl substituent not only prevents the normally rapid opening of cyclopropylcarbinyl-lithium in tetrahydrofuran,[8] but can even induce cyclization.[9]

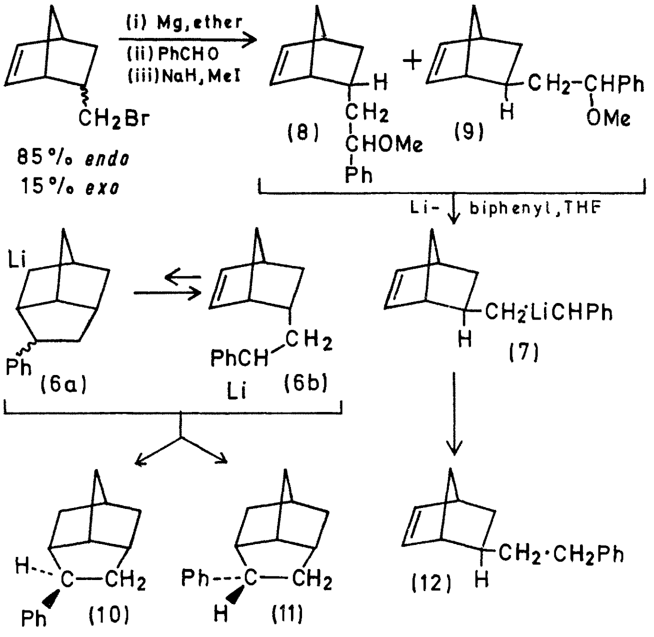


In view of the above stabilizing effect of α-phenyl groups, we were surprised to find several examples in which substituted benzyl-lithiums in THF add intramolecularly to a norbornene double bond, producing tricyclic s-alkyl-lithiums. Thus attempted Wittig rearrangement[10] of *endo*-norborn-2-en-5-yl benzyl ether (**1**) did not produce the expected carbinol[†] (**2**), whereas the *exo*-isomer (**4**) did.[11] Tricyclic ether (**3**) was the sole product[‡] from α-metallated (**1**). As indicated in Scheme 1, the lithium salt of (**2**) is *not* a precursor of (**3**), although (**2**) served as an independent, unambiguous source of (**3**), using Henbest's mercuration–demercuration sequence.[12]

We next examined the simpler benzyl-lithiums (**6**) and (**7**), containing no destabilizing α-oxygen substituents, which were generated together in straightforward fashion from the methyl ethers (**8**) and (**9**), using 2 : 1 lithium–biphenyl in tetrahydrofuran.[13] The ether cleavage produced an initially yellow–orange solution that faded to colourless before hydrolysis. After conventional work-up, tricyclic hydrocarbons (**10**) and (**11**) were isolated (48 and 25% yields), separation being accomplished by preparative g.l.c. (a 6 ft. 20% FFAP on Chromosorb W column at 170° was used). The structures of (**10**) and (**11**) were deduced from the lack of vinyl proton signals at *ca.* δ 6·0 in the n.m.r. and a complex benzylic proton resonance (1H) at *ca.* δ 3·0 in each compound; their stereochemistry has not yet been clearly established. The third product (*ca.* 15%) from reaction of the mixture of (8) and (9) was the β-phenethyl-norbornene (**12**) (exhibiting a 2 vinyl H multiplet at δ 6·0), which represents the expected fate of (7) since it is sterically unable to attack its alkene function internally.[§]



SCHEME 1



SCHEME 2

[†] Neither (**1**) nor (**4**) afforded any carbinol in which the migrating group had undergone norbornenyl to nortricyclyl rearrangement. Thus, if rearrangement of (**4**) proceeds *via* the radical-pair mechanism,[10] recombination occurs faster than reorientation of the partners, which is necessary to give a nortricyclyl carbinol.

[‡] G.l.c. analysis on Carbowax and FFAP columns indicated that only one stereoisomeric racemate was present.

[§] The isolation of (**14**) in yields corresponding to the amount of (**11**) originally accompanying (**10**) neatly rules out the possibility that saturated tricyclic brendanes (**12**) and (**13**) could have other structures in which some anomalous reduction of the double bond had occurred.

It appears that (**6a**) is the *major* species present in equilibrium with the tricyclic s-alkyl-lithiums (**6b**). The latter may, however, abstract a proton from THF (whereas $PhCH_2Li$ is relatively stable in this solvent), thus continually displacing the equilibrium away from (**6a**), and accounting for the bleaching of the reaction mixture before hydrolysis.

Insofar as scope is concerned, no cyclization occurred upon metallation of the corresponding *endo*-bicyclo[2,2,2]-octenyl benzyl ether and *endo*-5-benzyloxymethylnorborn-2-ene; both underwent normal Wittig rearrangement instead.

Satisfactory elemental analyses and consistent i.r. and n.m.r. spectra were obtained for all new compounds.

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