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Scission of C-C σ-Bonds via Electron Transfer Processes

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Abstract: Certain hydrocarbons, preferrable strained ones, can be cleaved via electron transfer processes whereby lithium dust or lithium 4,4′-di-*tert*-butylbiphenylide (LiDBB) have been used as electron transfer reagents. For the scission of a C-C σ-bond the presence of a π-system in the neighborhood (α or β) is an absolute prerequisite.

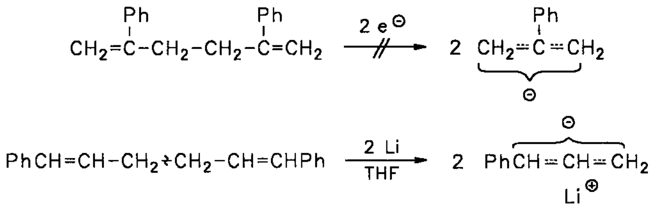
INTRODUCTION

Many unsaturated hydrocarbons react with electron transfer reagents, but only in a very few cases this leads to scission of a C-C σ-bond. Thus σ-bonds are cleaved occasionally during the reduction of cyclic conjugated hydrocarbons with lithium metal - a subject not discussed here (see Ref. 1). Examples are the reductive cleavage of benzocyclobutene (Ref. 2) and biphenylene (Refs. 3,4).

RESULTS AND DISCUSSION

Open-chain Hydrocarbons

For the scission of a C-C σ-bond the possibility to form a resonance stabilized carbanion is an absolute prerequisite. But even then - as shown with 2,5-diphenyl-1,5-hexadiene (Ref. 5) - the cleavage of open-chain hydrocarbons is seldom successful. On the other hand, small changes may help as we have found out starting with the isomeric bicinnamyl which can be cleaved using lithium dust in THF as the solvent. The phenyl groups at the ends of the chain obviously restrain polymerization:



$$\mathrm{CH_2{=}\overset{Ph}{\overset{|}{C}}{-}CH_2{-}CH_2{-}\overset{Ph}{\overset{|}{C}}{=}CH_2}\;\not\xrightarrow{2\,e^{\ominus}}\;2\ \underbrace{\mathrm{CH_2{=}\overset{Ph}{\overset{|}{C}}{=}CH_2}}_{\ominus}$$

$$\mathrm{PhCH{=}CH{-}CH_2{\wr}CH_2{-}CH{=}CHPh}\;\xrightarrow[\mathrm{THF}]{2\ \mathrm{Li}}\;2\ \underset{\mathrm{Li}^{\oplus}}{\overbrace{\mathrm{PhCH{=}CH{=}CH_2}}^{\ominus}}$$

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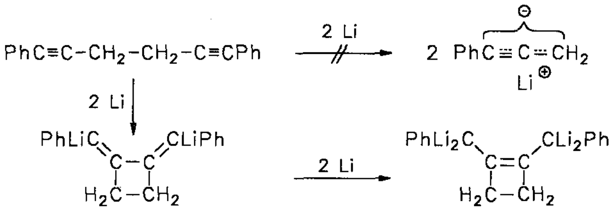
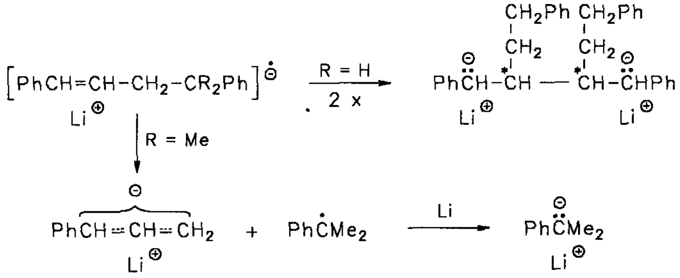
The corresponding compound with triple bonds instead of double bonds, however, again cannot be cleaved. Cyclization is observed instead and the primarily formed cyclobutane derivative adds another two lithium atoms yielding finally an interesting tetralithiumorganic compound (Ref. 6):

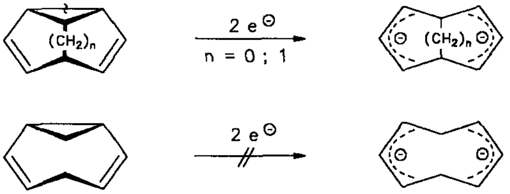


Schlenk dimerization is another reaction which often takes place. Small changes - replacement of hydrogen by methyl - again brings success. This speaks for cleavage already of the radical anion intermediate because the cumyl radical is more stable than the corresponding benzyl radical. On the other hand, the corresponding dianion would preferably cleave with R = H to yield the more stable benzyl anion:

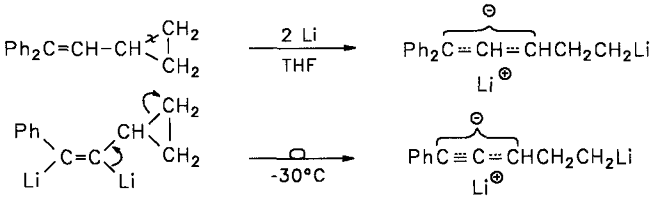


Cyclopropane Derivatives

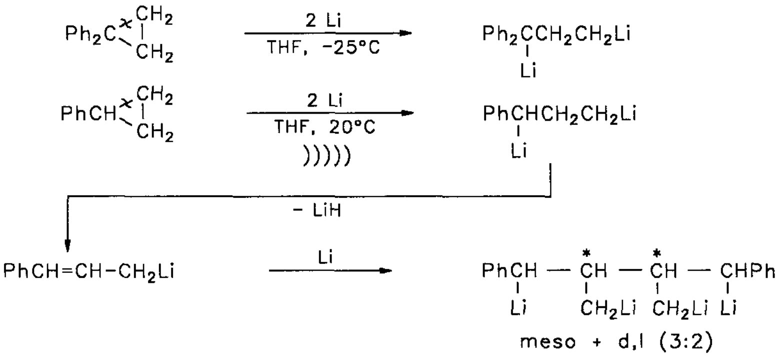
As to be expected strained hydrocarbon derivatives can be more easily cleaved via electron transfer processes. Examples are semibullvalene (n = O) investigated by Goldstein (Refs. 7, 8) and barbaralane (n = 1) investigated by Müllen (Ref. 9). On the other hand, the reaction did not work with the related *bicyclic* homotropylidene (Ref. 5):



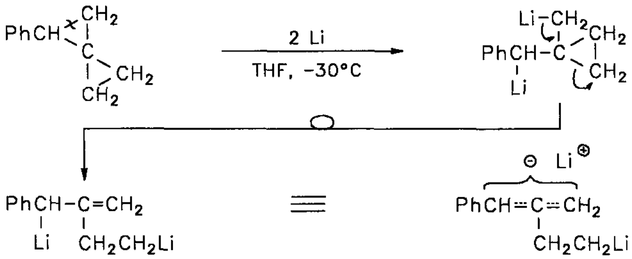
Again exclusively resonance stabilized carbanions are formed. That this not necessarily has to be so was already shown in 1970 with the very first example of these cleavage reactions (Ref. 10). Obviously *one* activating substituent at the cyclopropane ring is sufficient for the reaction to take place yielding a dilithiumorganic compound with only *one* π- as well as one σ-bonded lithium respectively. The first step proved to be an addition of two lithium atoms to the π-system followed by a carbanionic ring-chain rearrangement. Starting with the corresponding acetylene this vicinal dilithioalkene intermediate could be isolated - most interestingly as a pure *cis*-dilithioalkene which, however, is stable only below -30°C (Ref. 11):



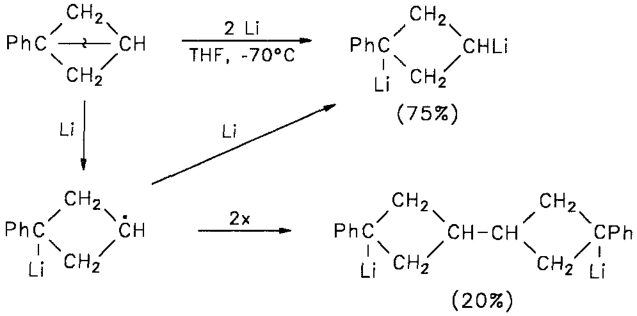
*Phenyl*substituted cyclopropanes can be similarly cleaved using lithium dust in THF although starting with the *mono*phenyl derivative room temperature and in addition ultrasonic activation is necessary. Under these conditions the primarily formed 1,3-dilithiumorganic compound loses lithium hydride, and the resulting cinnamyllithium shows Schlenk dimerization with the formation of an interesting *tetra*lithiumorganic compound in two diastereomers - *meso* and *d,l* (Ref. 12):



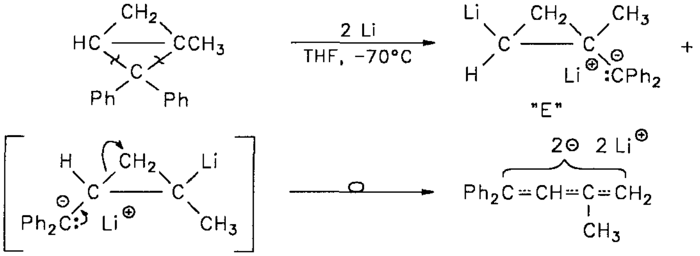
Starting with phenyl-spiropentane a *regioselective* cleavage takes place followed by a ring-chain rearrangement. Again one of the lithium atoms of the end product is σ-bonded (Ref. 12):



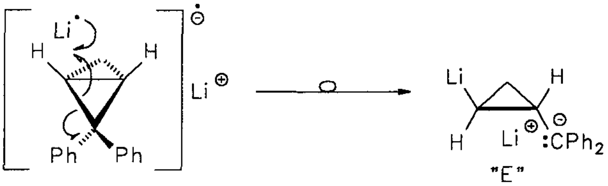
Interestingly, unsubstituted spiropentane despite its high ring-strain of 65 kcal/mol could not be forced to react with lithium dust neither upon heating nor under the influence of ultrasonic irradiation. Obviously the lowest unoccupied σ* orbital still lies too high to accept an electron from the lithium metal. The same is true for unsubstituted bicyclobutane showing even 69 kcal/mol ring-strain. However, in contrast to bicyclobutane itself phenylsubstituted bicyclobutanes again can be cleaved with lithium metal even at -70°C in THF as the solvent. Starting with 1-phenylbicyclobutane up to 20% of a dimeric dilithiumorganic compound could be detected. It is therefore reasonable to assume that the scission of the highly strained O-bond already takes place within the primarily formed radical anion step (Ref. 12):



Most interestingly starting with a *2,2*-diphenyl derivative it is not the weakest σ-bond which is cleaved but those conjugated with the phenyl rings. However, it is not only *regio*selectivity which one observes but also *stereo*selectivity. While one half of the primarily formed products shows ring-chain rearrangement as expected the E-compound is kinetically stable due to hindered rotation of the benzhydryl anion part by the adjacent methyl group (Ref. 12):

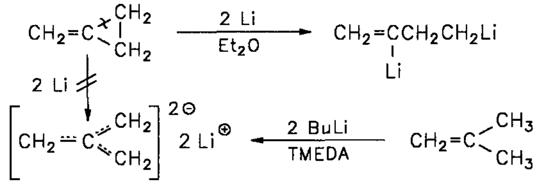


The formation of the pure E-derivative with inversion at the cyclopropane carbon atom is difficult to understand because opening of the primarily formed radical anion should yield an E/Z-mixture while the corresponding dianion should open with retention to the pure Z-compound. Only in accordance with the experimental results is the attack of the second lithium atom at the cyclopropane ring of the radical anion intermediate thus initiating the ring opening. These exciting results, of course, have to be confirmed by further experiments.



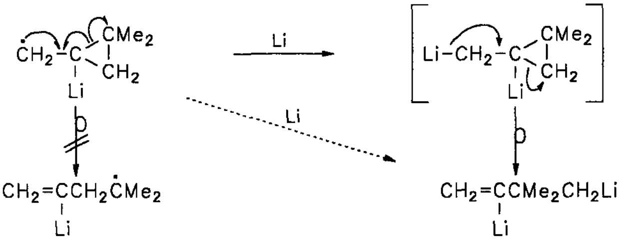
Methylenecyclopropane and Derivatives

Cyclopropane derivatives containing π-systems *not* in conjugation with the three-membered ring can also be cleaved via electron transfer processes. Thus methylenecyclopropane readily reacts with lithium metal in diethyl ether at room temperature to yield 2,4-dilithio-1-butene, which obviously is *not* a resonance stabilized compound, both lithium atoms being σ-bonded (Ref. 13). It is remarkable that it is the stronger cyclopropane σ-bond which is cleaved. The most stable y-delocalized cross-conjugated trimethylenemethane dianion which is known to be readily available even by a double deprotonation of isobutene (Refs. 14-16) is not formed:

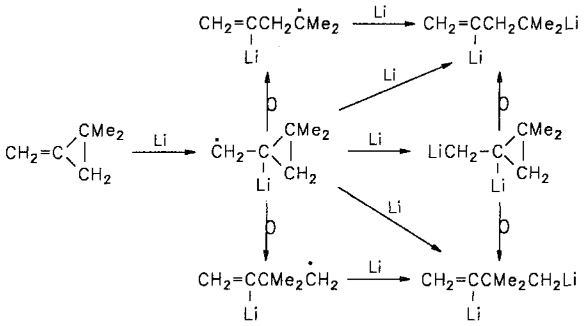


We therefore argued that the electron transfer again does not take place into the corresponding σ* orbital but into the π* orbital of the neighboring double bond followed by an exocyclic ring-chain rearrangement. The postulated vicinal dilithiumorganic intermediate, however, this time could *not* be trapped, so that ring-opening already of the primarily formed radical anion also had to be discussed.

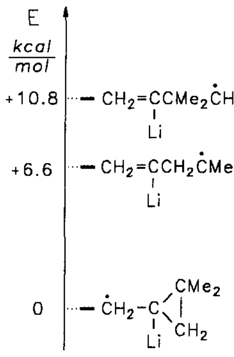
On the other hand, the reaction of 2,2-dimethylmethylenecyclopropane with lithium powder under the same conditions yielding the *primary* lithiumorganic compound indicates that the initially formed radical anion reacts with a second lithium atom *before* ring-opening occurs because otherwise the more stable *tertiary* radical anion should be passed as an intermediate. However, the direct attack of the second lithium atom at the cyclopropane ring of the radical anion as discussed before in connection with bicyclobutane derivatives is also in accordance with the experimental results:



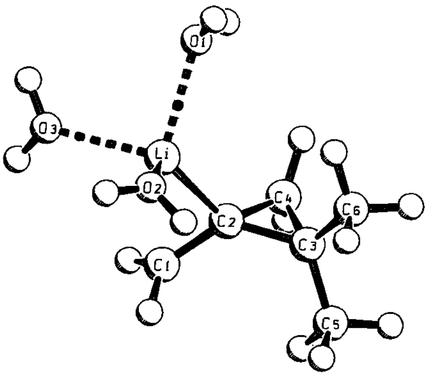
In Scheme 1 all the possible intermediates and reaction products have been written down which in addition were treated calculationally (Ref. 17). Lithium metal will react first by a single electron transfer reaction and this has to be the rate determining step. According to MNDO calculations the lithium atom in the primarily formed radical anion is coordinated mainly to C2 of the cyclopropane ring leaving the single electron at C1. Fig. 1 shows the MNDO geometry of this radical anion using three molecules of water to mimic the solvation (Ref. 17). As to be expected the primary open-chain radical anion is less stable than the tertiary one, but surprisingly the most stable of all is the cyclic one (Scheme 2) (Ref. 17).



Scheme 1



Scheme 2



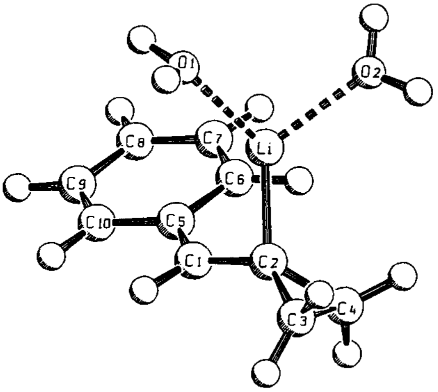
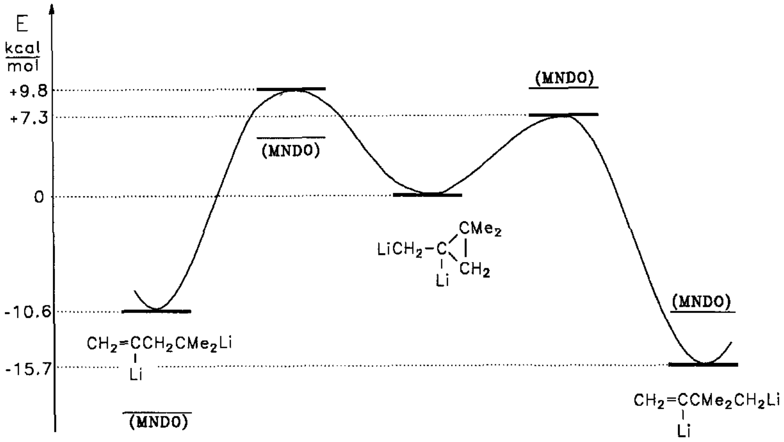


Fig. 1. MNDO geometry of the radical anion of 2,2-dimethylmethylene cyclopropane/lithium

Fig. 2. MNDO geometry of the radical anion of benzylidenecyclopropane/lithium

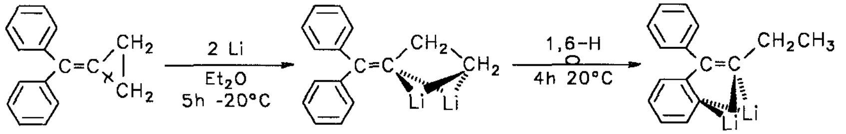
The various *di*lithiumorganic compounds were also treated calculationally (Ref. 17). The energies calculated by the MNDO method, however, were not in accordance with the experimental results leading to the tertiary anion as the most stable compound which was not formed at all. The energies of the MNDO geometries were therefore recalculated by ab initio with a minimal basis set (STO-3g) yielding the more plausible values shown in Scheme 3. The obviously wrong MNDO energies are included. The energies of the radical anions shown before (Scheme 2) had also been obtained by ab initio calculations, while for the corresponding *structures* (Figs. 1,2) always MNDO was used.



Scheme 3

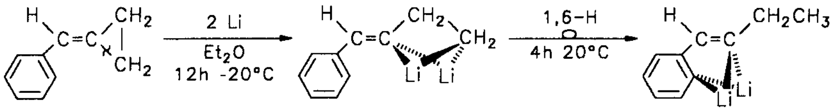
While (*dialkyl*methylene)cyclopropane derivatives do not at all react with lithium dust even when using forcing conditions, (*diphenyl*methylene)cyclopropane is cleaved already at -20°C (Ref. 17). Most interestingly, at room temperature the primarily formed presumably double-bridged 1,3-dilithio compound slowly undergoes rearrangement with 1,6-proton shift yielding a 1,4-double-bridge which is rather stable in diethyl ether. The final compound, however, as shown with the next higher homologue - starting with the corresponding methylenecyclobutane and lithium 6 (Ref. 18) - obviously is a dimer showing in the NMR spectrum a homonuclear scalar ^{6}Li, ^{6}Li spin-spin coupling detected for the first time by Günther, via the ^{6}Li, ^{6}Li INADEQUATE experiment (Refs. 19, 20).

The driving force for the rearrangement assisted by *agostic interactions* (Ref. 21) seems to be the greater stability of a 1,4-double-bridge compared with a 1,3-double-bridge which according to calculations by Schleyer accounts for about 10 kcal/mol in the gas phase (Ref. 22). In addition lithium bound to an sp^2 center is more stable than bound to an sp^3 center which brings another 14 kcal/mol (Refs. 18, 23).



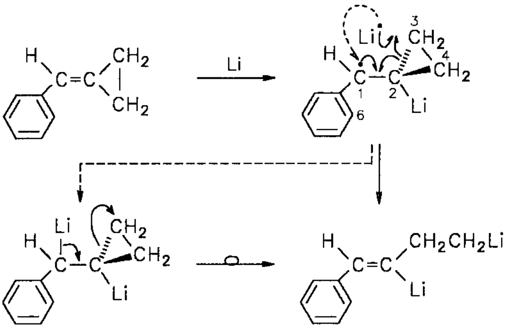
As expected benzylidenecyclopropane, the *mono*phenyl substituted methylenecyclopropane reacted more slowly with lithium dust than (*di*phenylmethylene)cyclopropane. In diethyl ether as the solvent 12 hours at -20°C were necessary instead of 5 hours before. Most interestingly, the reaction took place completely regioselectively, only the cyclopropane σ-bond *cis* to the phenyl ring was cleaved. Hydrolysis of the dark red solution after filtration from the excess lithium gave pure *trans*-1-phenyl-1-butene in 70% yield. Not even a trace of the *cis* isomer could be detected (Ref. 17).

Due to the agostic interaction of the lithium atom *cis* to the phenyl ring, at room temperature again a 1,6-proton shift takes place which has been shown upon working up with dimethyl sulfate instead of water:

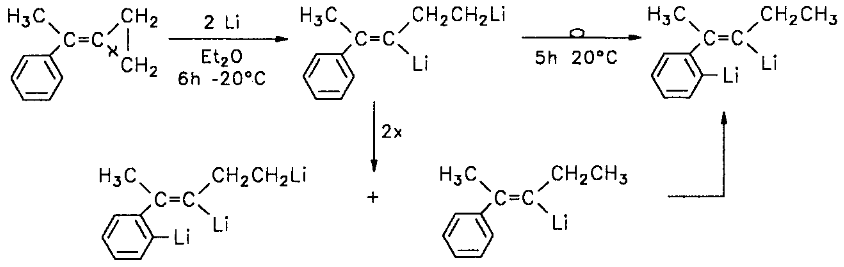


What is finally the reason for this stereoselectivity? According to MNDO calculations the corresponding radical anion solvated with two molecules of water shows a nearly bisected conformation with the lithium atom at C2 oriented syn to the phenyl ring (Fig. 2). Besides coordination with C2 there is a remarkable interaction of the lithium atom with the phenyl ring especially with the proton at C6. This way both the cyclopropane methylene groups are forced anti to the phenyl ring, so it makes no difference wether C2-C3 or C2-C4 is cleaved, in each case the pure *trans* derivative is formed (Ref. 17).

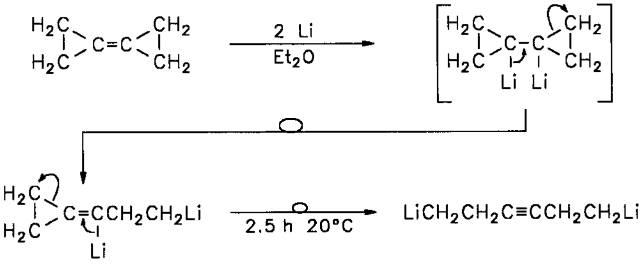
Wether the second lithium atom immediately attacks C3 or first C1 followed by an anionic cyclopropylcarbinyl-allylcarbinyl rearrangement is not known.



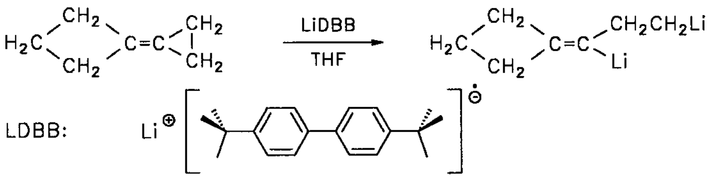
It is remarkable that *α-methyl*benzylidenecyclopropane is more reactive towards lithium metal than benzylidenecyclopropane the lithium again being forced stereoselectively into the *cis* position to the phenyl ring. This time it could be unequivocally shown that the 1,6-proton shift - as expected - is not an *intra*molecular process but takes place by an *inter*molecular disproportionation/comproportionation mechanism via a *tri*lithiumorganic compound. Only after 5 hours at room temperature the formation of the final dilithio compound is nearly complete, leaving still 2% of the disproportionation compounds, respectively (Ref. 17):



While for the reductive cleavage of a cyclopropane σ-bond usually two lithium atoms are necessary, with the same amount of lithium *two* σ-bonds of the so-called butterfly olefin bicyclopropylidene are cleaved. In diethyl ether as the solvent - not in THF - the primarily formed (1,3-dilithiopropylidene)cyclopropane can be isolated before it rearranges to 1,6-dilithio-3-hexyne within 2.5 hours at room temperature (Ref. 24):

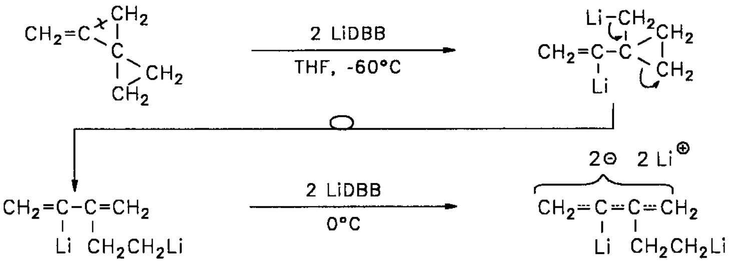


On the other hand, the next higher homolog of the butterfly olefin cannot be cleaved with lithium dust. But it works with Freeman's lithium 4,4′-di-*tert*-butylbiphenylide (LiDBB) which allows electron transfer in homogeneous solution (Ref. 25). It is remarkable that the cyclobutane ring this time does not open up even at room temperature and in THF as the solvent (Ref. 17):

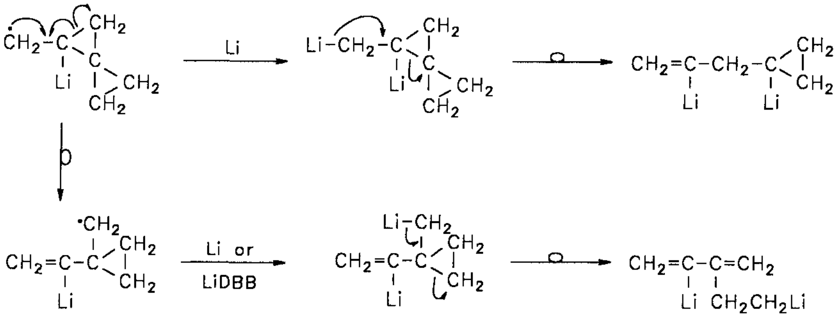


Methylenespiropentane and Higher Homologues

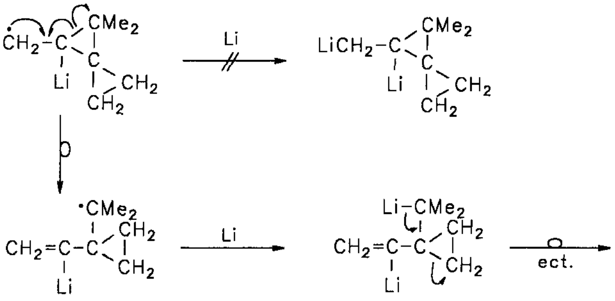
Without any doubt the most fascinating system we have studied is methylenespiropentane, which is an isomer of the butterfly olefin. It turned out that the scission is regioselective here *only* on using lithium di-*tert*-butylbiphenylide as electron transfer reagent. The reaction then takes place even at -60°C in THF as the solvent yielding within 16 hours 81% of a dilithio compound, a butadiene derivative which at 0°C adds two further lithium atoms to yield an interesting *tetra*-lithiumorganic compound with different kinds of σ- and π-bonded lithiums (Ref. 26):



Most interestingly on using lithium dust instead of LiDBB as electron transfer reagent the reaction does *not* proceed regioselectively. The reason is not known until now. But lithium metal with its higher reduction potential might compete with the opening of the radical anion yielding the corresponding dianion which will open up to the more stable dilithiumorganic compound bearing a cyclopropyllithium functionality with the lithium-carbon bond having higher s-character than in the cyclopropylcarbinyl system, the latter, however, is the main product here too:



An argument in favour of the discussed mechanism is the reaction of the corresponding *dimethyl* substituted methylenespiropentane which even with lithium dust as electron transfer reagent is running completely regioselectively due to the higher stability of the opened radical anion with a tertiary cyclopropylcarbinyl radical functionality:



ACKNOWLEDGEMENTS

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