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Polylithiumorganic Compounds - 19.[1]

Regioselective Carbon-Carbon σ-Bond Scission followed by a 1,6-Proton Shift upon the Reductive Metalation of Benzylidenecyclopropane Derivatives with Lithium Metal

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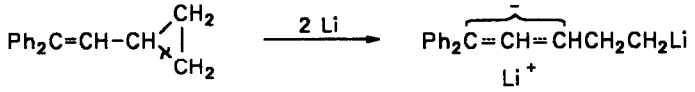
Abstract: Depending on the substituent, α-substituted benzylidenecyclopropanes (**32**) react more or less readily with lithium dust (2% sodium) in diethyl ether whereby a regioselective scission of only the cyclopropane σ-bond *cis* to the phenyl ring takes place. Upon raising the temperature the primarily formed 1,3-dilithiumorganic compound due to an agostic interaction rearranges by a 1,6-proton shift into a doubly bridged 1,4-dilithio compound. With α-methylbenzylidenecyclopropane (**32c**) this rearrangement was shown to occur *inter*molecularly via a trilithiumorganic compound **56**. The suggested mechanism of these reductive metalation reactions via a bisected radical anion **87** where the lithium is mainly bound to the cyclopropyl carbon atom and oriented *syn* to the phenyl ring, was supported by MNDO (geometries) and ab initio (energies) calculations.

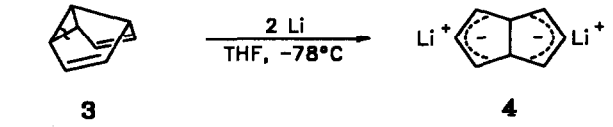
Introduction

In special cases cyclopropane σ-bonds can be reductively cleaved by lithium metal to yield dilithiumorganic compounds.[3] The first example was the reaction of 2-cyclopropyl-1,1-diphenylethylene (**1**) with lithium in diethyl ether or THF as the solvent.[4]



1 **2**

Other cyclopropane derivatives can be cleaved as well especially if both carbanionic centers formed are resonance stabilized by π delocalization of the two negative charges. Thus on treating semibullvalene (**3**) with lithium in THF or dimethyl ether at -78°C two diastereoisomeric dimers of "dilithium semibullvalenide" (**4**) have been obtained,[5,6] and the same is true for barbaralane (**5a**) and 2,6-diphenylbarbaralane (**5b**) yielding the corresponding bis-allyl anions **6**:[7]



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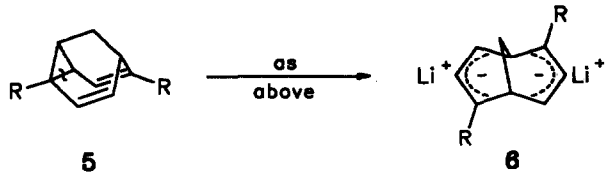
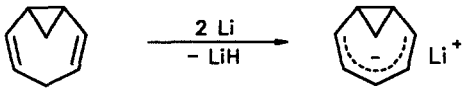


5 6

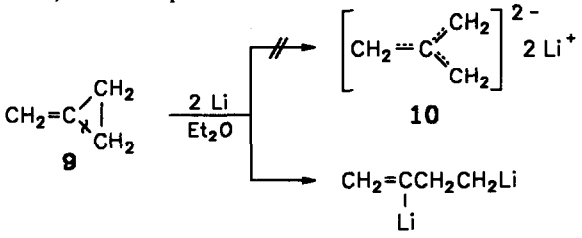
a: R = H b: R = Ph

On the other hand, the related 3,4-homotropilidene (**7**) could not be caused to react in the same manner, a monoanion **8** is formed instead:[8]



7 8

We recently have found that also methylenecyclopropane (**9**) reacts smoothly with lithium powder, both neat at its boiling point (10°C, 1 h) and in diethyl ether at room temperature (0.5 h).[9] However, scission of the weakest cyclopropane bond to form the extremely stable, Y-delocalized trimethylenemethane dianion (**10**)[10-12] does not occur. Instead the non-resonance stabilized 2,4-dilithio-1-butene (**11**), combining both vinyl and homoallyl character, is the sole product:[9]

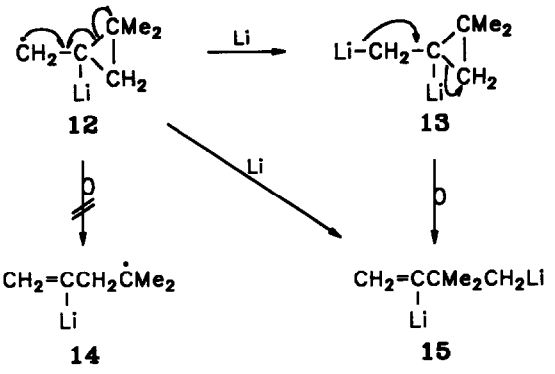


9 10 11

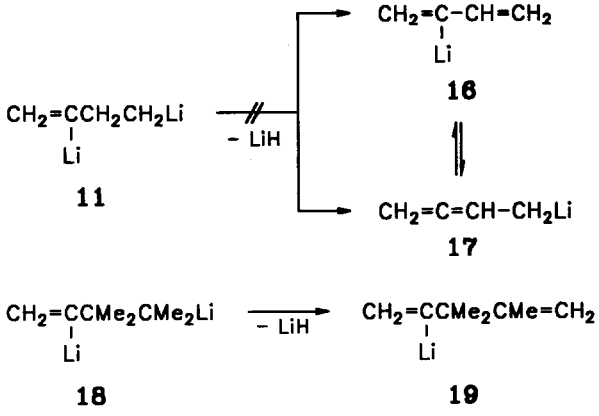
We therefore argued that the electron transfer does not take place to the corresponding σ^* orbital but to the π^* orbital of the neighboring double bond followed by a ring-chain rearrangement.[4,9] The postulated vicinal dilithiumorganic intermediate e.g. **13**, however, could not be trapped, so that ring-opening already of the primarily formed radical anion **12** also had to be discussed.

On the other hand, the reaction of 2,2-dimethylmethylenecyclopropane with lithium powder under the same conditions, yielding **15** indicates that, before ring-opening occurs to give **14**, the initially formed radical anion **12** reacts with a second lithium atom whereby a direct attack of the second lithium at the cyclopropane ring of the radical anion **12** is also in accord with the experimental results.

Compared with unsubstituted 1,3-dilithiopropane which looses lithium hydride with a half reaction time of one hour at room temperature[13] 2,4-dilithio-1-butene (**11**) is remarkably stable: not even a trace of



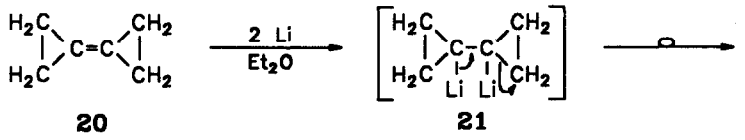
the expected monolithio tautomers **16** ⇌ **17** could be detected.[9] Interestingly, the tetramethyl substituted derivative **18** does eliminate lithium hydride, although in the other direction to yield **19**.[9]



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 "butterfly olefin" 1,1'-bicyclopropylidene (**20**) are cleaved. In diethyl ether as the solvent - not in THF - the primarily formed (1,3-dilithiopropylidene)cyclopropane (**22**) can be isolated before it rearranges to 1,6-dilithio-3-hexyne (**23**) within 2.5 hours at room temperature.[14]

For the reaction of the corresponding dicyclopropylacetylene (**24**) with lithium the addition of catalytic amounts of 4,4'-di-*tert*-butylbiphenyl is necessary and the reaction - even in THF as the solvent - stops after the cleavage of only one cyclopropane ring.[15] Molar amounts of lithium-4,4'-di-*tert*-butylbiphenyl (LDBB)[16] had to be used for the reductive metalation of the next higher homolog of 1,1'-bicyclopropylidene (**20**), cyclopropylidenecyclobutane (**26**), whereby the cyclobutane ring does not open up.

Exocyclic mono-alkyl substituted methylenecyclopropane derivatives like pentylidenecyclopropane react extremely slow with lithium even when using forcing conditions under the influence of ultrasonic irradiation.[14] On the other hand, dialkylmethylenecyclopropanes as well as cyclopropylidenecyclopentane and -cyclohexane do not react at all, neither LDBB nor sonication in boiling THF was successful.[14]



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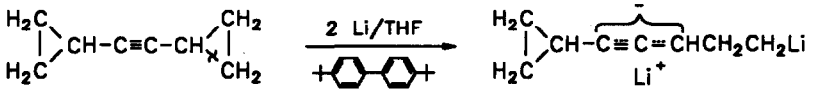

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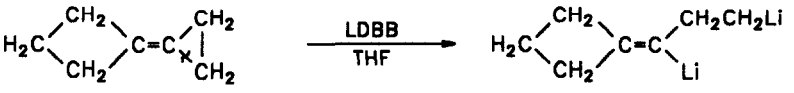
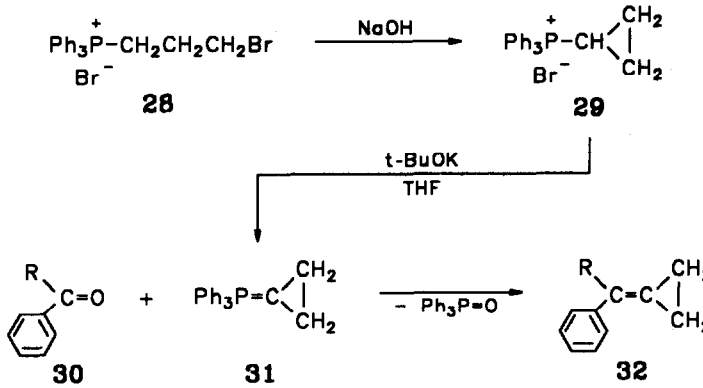


26 27

Now, we have found that exocyclic phenyl substituents activate methylenecyclopropanes for the reaction with lithium dust, so that the retarding effect of alkyl substituents in the same position can be compensated. Most interestingly, the scission of the carbon-carbon σ-bond then takes place regioselectively and is followed by rearrangement with 1,6-proton shift.

Results and Discussion

Starting Materials: In addition to benzylidenecyclopropane (**32a**) itself the α-substituted phenyl- (**32b**), methyl- (**32c**), cyclopropyl- (**32d**), and *tert*-butylbenzylidenecyclopropane (**32e**) were used as starting material. The synthesis of these compounds was achieved by a Wittig reaction first reported by K.Utimoto et



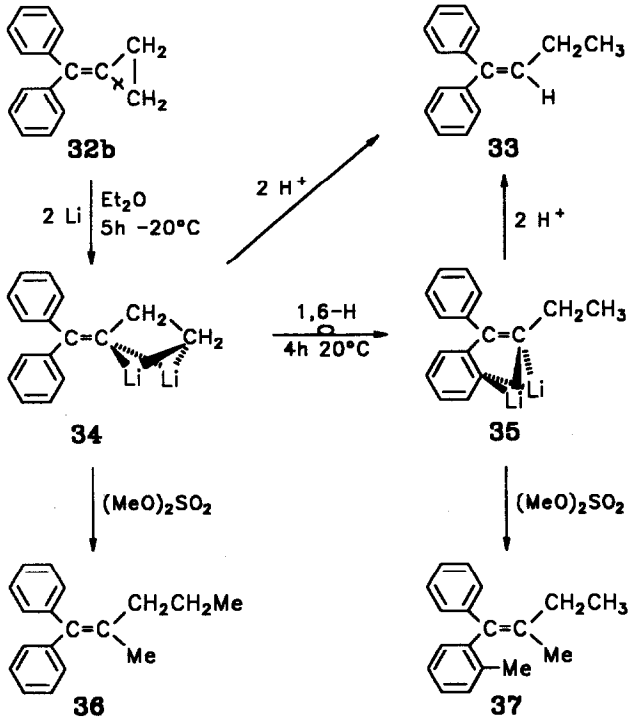
a: R = H **c**: R = CH_3 **e**: R = t-Bu
b: R = Ph **d**: R = cyclopropyl

al.[17,18] Cyclopropyltriphenylphosphonium bromide (**29**) was in our hands best available according to H.J.Bestmann et al.[19,20] For the preparation of cyclopropylidenetriphenylphosphorane (**31**) potassium *tert*-butoxide in THF was used as the base.

Reactions with Lithium Dust

***(Diphenylmethylene)cyclopropane* (32b)**

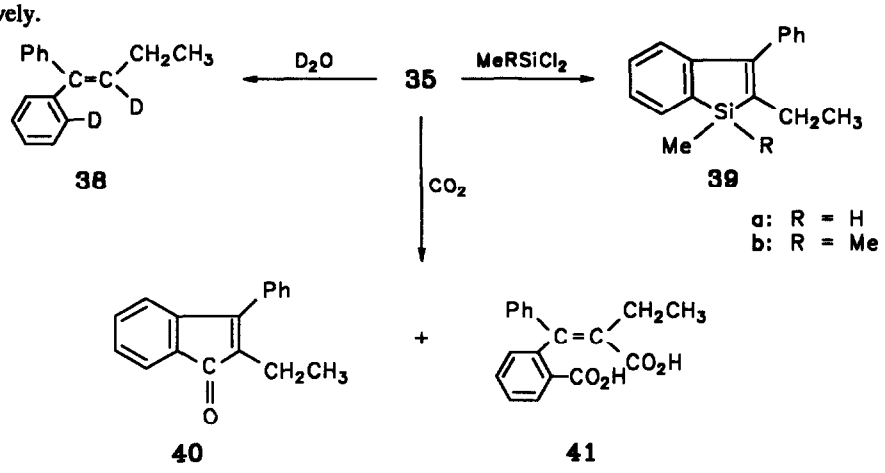
We started with the symmetrically substituted methylenecyclopropane **32b**. As the corresponding reaction with (diphenylmethylene)cyclobutane had yielded a dilithiumorganic compound which was unstable at room temperature[21] -20°C was chosen as the reaction temperature. Upon the addition of 10.0 mmol (diphenylmethylene)cyclopropane (**32b**) in dry diethyl ether at that temperature to a suspension of excess lithium dust (2% sodium) in diethyl ether under argon only after half an hour a yellow-green coloration could be observed slowly turning to yellow-brown. Derivatization with dimethyl sulfate after 5 hours still yielded 8% starting material **32b** besides 62% of 1,1-diphenyl-2-methyl-1-pentene (**36**) and 6% hydrolysis product **33**. In addition two monomethyl substituted products (7% and 17%) could be detected by GC/MS analysis.



At room temperature rearrangement of the primarily formed presumably doubly bridged 1,3-dilithio compound **34** to the 1,4-double-bridge **35** takes place, the mechanism of this interesting 1,6-proton shift being unknown. According to the ^{6}Li, ^{6}Li INADEQUATE experiment[22] the next higher homologue of **35**, (E)-2-lithio-1-phenyl-1-(2-lithiophenyl)-1-pentene,[21] is a dimer and the same will be true for **35**. In perdeutero diethyl ether as the solvent the rearrangement **34** → **35** can be conveniently followed by ^{1}H NMR spectroscopy the α methylene triplet at δ = -0.55 ppm (^{3}J = 7.0 Hz) being slowly replaced by a methyl triplet at δ = 1.1 ppm (^{3}J = 7.6 Hz). Characteristic for **35** is also the down-field shift to δ = 8.05 of the

aromatic proton ortho to the lithium. The driving force for the rearrangement assisted by "agostic interactions"[23] obviously is the greater stability of a 1,4-double-bridge compared with a 1,3-double-bridge which according to calculations[24] accounts for about 10 kcal/mol (41.8 kJ/mol) in the gas phase. In addition lithium bound to an sp^2 center (aryllithium) is more stable than bound to an sp^3 center (alkyllithium) which brings another 14.4 kcal/mol (60.3 kJ/mol).[21,25]

The "E" character, i.e. the *cis* arrangement of the lithium atoms in **35** was also chemically verified by the reaction with dichlorosilanes and carbon dioxide yielding the five-membered ring compounds **39** and **40**, respectively.



Due to the fact that carbon dioxide was conducted slowly the dicarboxylic acid **41** is formed only as a side-product accompanied by traces of the two corresponding monocarboxylic acids. A trilithio compound speaking for an *inter*molecular mechanism of the 1,6-proton shift **34** → **35** could not be detected. In this connection also (perdeuterodiphenylmethylene)cyclopropane has been prepared and a 1:1 mixture of $[D_{10}]$**32b** and **32b** was treated with excess lithium dust for 14 hours at room temperature in diethyl ether as the solvent. In case of an *inter*molecular rearrangement besides $[D_{10}]$**35** and **35** also $[D_9]$**35** and $[D_1]$**35** should have been formed in a 1:1:1:1 ratio. However, due to a huge isotope effect[26] the reaction starting with $[D_{10}]$**32b** was much slower so that the results could not be interpreted unequivocally.

***Benzylidenecyclopropane* (32a)**

As expected the monophenyl substituted methylenecyclopropane (**32a**) reacted more slowly with lithium dust than (diphenylmethylene)cyclopropane (**32b**). In diethyl ether as the solvent 12 hours at -20°C were necessary instead of 5 hours with **32b**. 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 giving pure (E)-1-phenyl-1-butene (**42**) in 70% yield. Not even a trace of the (Z)-isomer could be detected.

Due to the agostic interaction of the lithium atom *cis* to the phenyl ring in **44** 1,6-proton shift again takes place yielding **45** which has been shown in three different runs upon working up with dimethyl sulfate (Table 1).

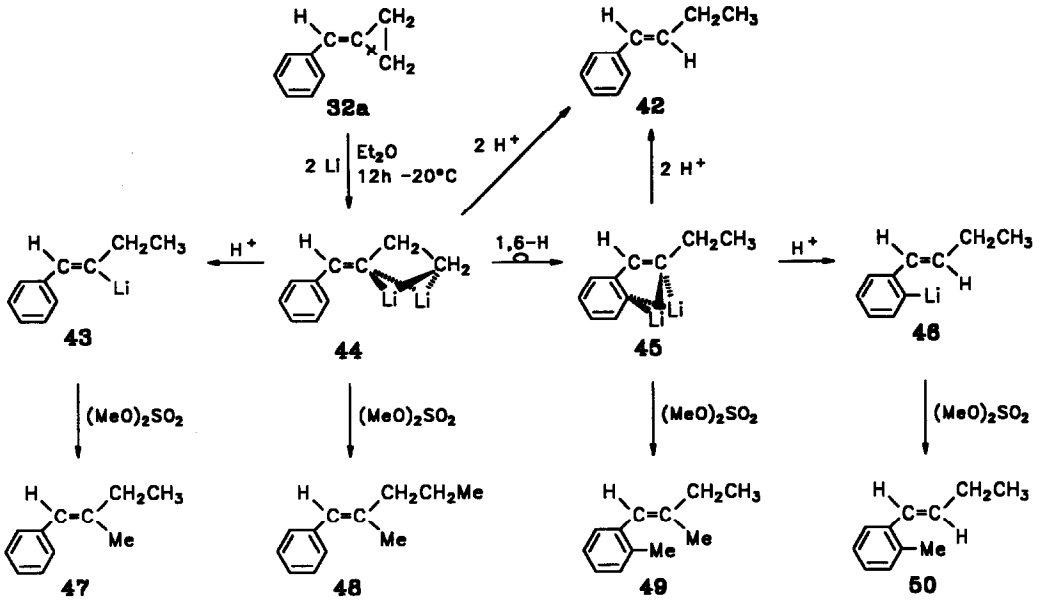
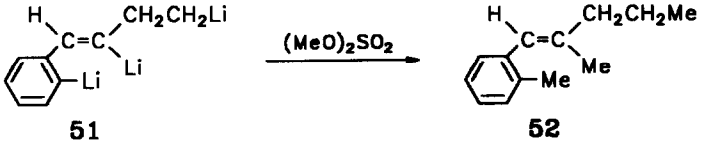


Table 1. GC/MS Analysis of the Cleavage and Rearrangement Products of **32a** worked up with Dimethyl Sulfate.

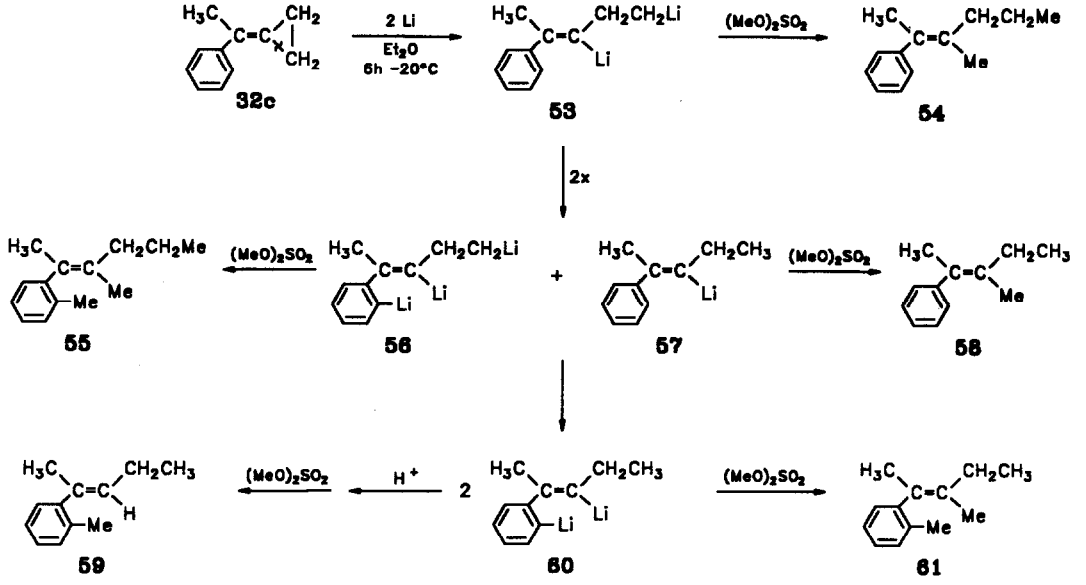
\Conditions / Compound \	3.5 h -20°C	12 h -20°C	3.5 h +20°C	Molecular Weight m/z
32a	84.3	2.1	0.0	130
42	1.3	10.6	67.3	132 (+ 2 H)
47	2.1	20.6	17.6	146 (+ H + Me)
48	12.3	48.3	0.3	160 (+ 2 Me)
49	0.0	7.0	10.3	160 (+ 2 Me)
50	0.0	5.0	3.6	146 (+ H + Me)
	0.0	2.6	0.4	146 (+ H + Me)
52	0.0	3.8	0.5	174 (- H + 3 Me)

Partial protonation of the dilithio compounds **44** and **45** by the solvent mainly leads to the monolithio compound **43** accompanied by some **46**, it is not known, however, which one of the mono-methyl side products (molecular weight = 146) corresponds to structure **50**. Here for the first time also a product with three methyl groups of the tentative structure **52** could be detected which speaks for an *inter*molecular character of the rearrangement **44** → **45**.



***α*-Methylbenzylidenecyclopropane (32c)**

It is remarkable that this compound is even more reactive towards lithium metal than (diphenylmethylene)cyclopropane (**32b**) the lithium again being forced stereoselectively into the *cis* position to the phenyl ring. The dark brown reaction mixture containing at -20°C a very fine yellow precipitate upon hydrolysis yields 63% pure (E)-2-phenyl-2-pentene without even a trace of the corresponding (Z)-product. Three runs under different conditions were worked up with dimethyl sulfate at -20°C (Table 2). This way it could be shown unequivocally that the 1,6-proton shift **53** → **60** indeed takes place by an *inter*molecular disproportionation/comproportionation mechanism via the trilithiumorganic compound **56**. Because decomposition by the solvent this time is very slow, the hydrolysis compound and monolithio compounds besides **57** are found only in trace amounts the structure of **59** being not certain.



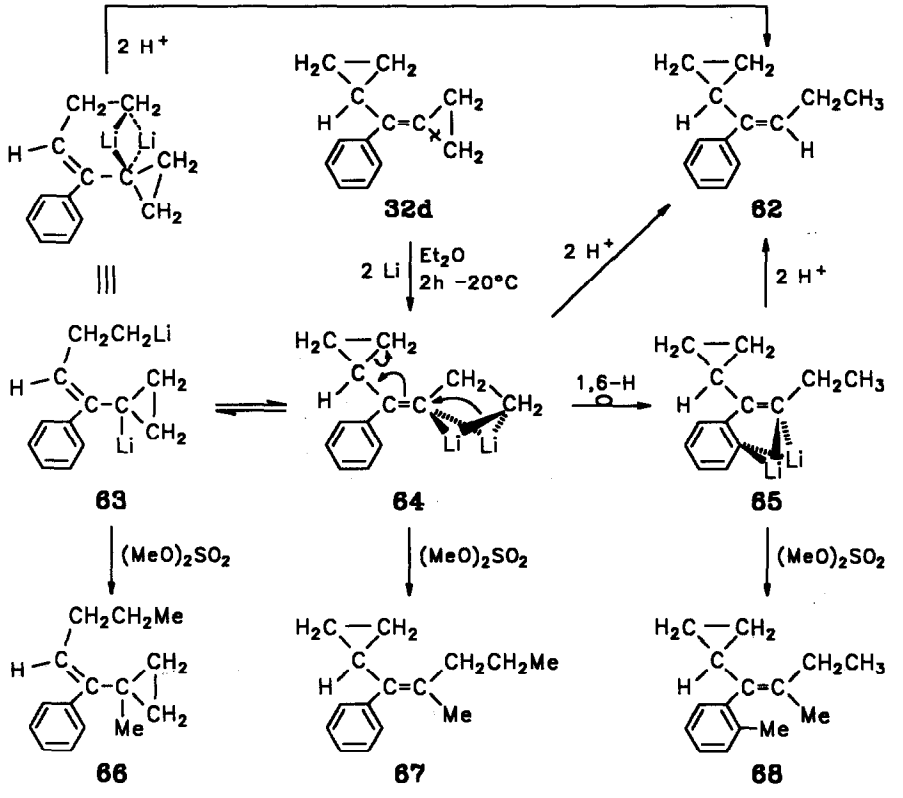
An expected vinyl-allyl-rearrangement[27] of **57** could not be deteced, the comproportionation **56** + **57** → 2 mol **60** obviously being faster.

Table 2. GC/MS Analysis of the Cleavage and Rearrangement Products of **32c** worked up with Dimethyl Sulfate.

\Conditions Compound \	6 h -20°C	5 h +5°C	5 h +20°C	Molecular Weight m/z
32c	0.0	0.0	0.0	144
54	46.8	2.1	0.0	174 (+ 2 Me)
55	17.8	24.2	2.1	188 (- H + 3 Me)
58	24.1	27.2	1.7	160 (+ H + Me)
59	0.0	0.0	13.2	160 (+ H + Me)
61	11.3	46.5	83.0	174 (+ 2 Me)

***α-Cyclopropylbenzylidenecyclopropane* (32d)**

Of all the benzylidenecyclopropane derivatives under investigation the α-cyclopropyl substituted **32d** interestingly is the most reactive. Filtration of the deep yellow-brown reaction mixture from the excess lithium dust after 5 hours at 0°C upon hydrolysis yielded 89% of (E)-1-cyclopropyl-1-phenyl-1-butene (**62**) proving again regioselectivity of the cyclopropane σ-bond scission. Even after 2 hours at -20°C no more starting material **32d** could be detected.



The reaction with dimethyl sulfate showed that in addition to the expected 1,6-proton shift **64** → **65** another rearrangement takes place leading - also in a stereoselective manner - to the dilithio compound **63**. The stereoselectivity of this ring-chain equilibrium speaks for a doubly bridged structure of **63**, too. Six runs under different conditions have been performed. Besides the dimethyl derivatives **66**, **67** and **68** of Table 3 small amounts of three mono- and trimethylated products, respectively, have been detected by GC/MS analysis which, however, were not fully characterized.

After 2.5 hours depending on the temperature both the rearrangement products **63** and **65** increase at the expense of **64** (Fig. 1). Only after very long periods of time also **63** decreases due to the irreversible character of the 1,6-proton shift **64** → **65**.

Table 3. GC/MS Analysis of the Main Cleavage and Rearrangement Products of **32d** worked up with Dimethyl Sulfate

\Conditions / Compound \	2.5 h -20°C	23 h -20°C	2.5 h 0°C	2.5 h +10°C	2.5 h +20°C	2.5 h -20°C and 21 h +20°C
62	1.7	1.7	2.2	2.6	3.1	8.5
66	8.2	3.1	8.2	22.5	39.9	32.8
67	64.3	71.1	59.0	27.9	4.5	0.6
68	2.4	2.5	2.9	9.2	19.2	27.6

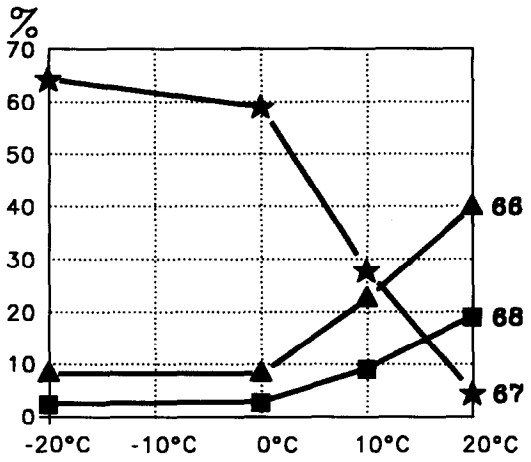
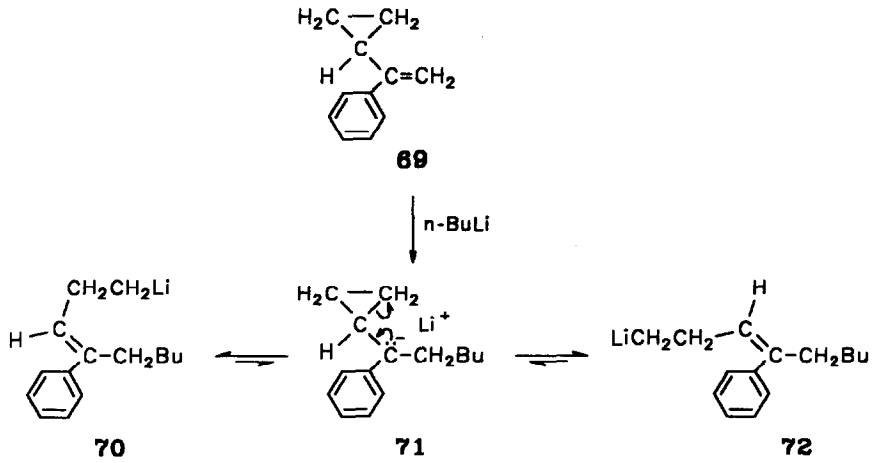


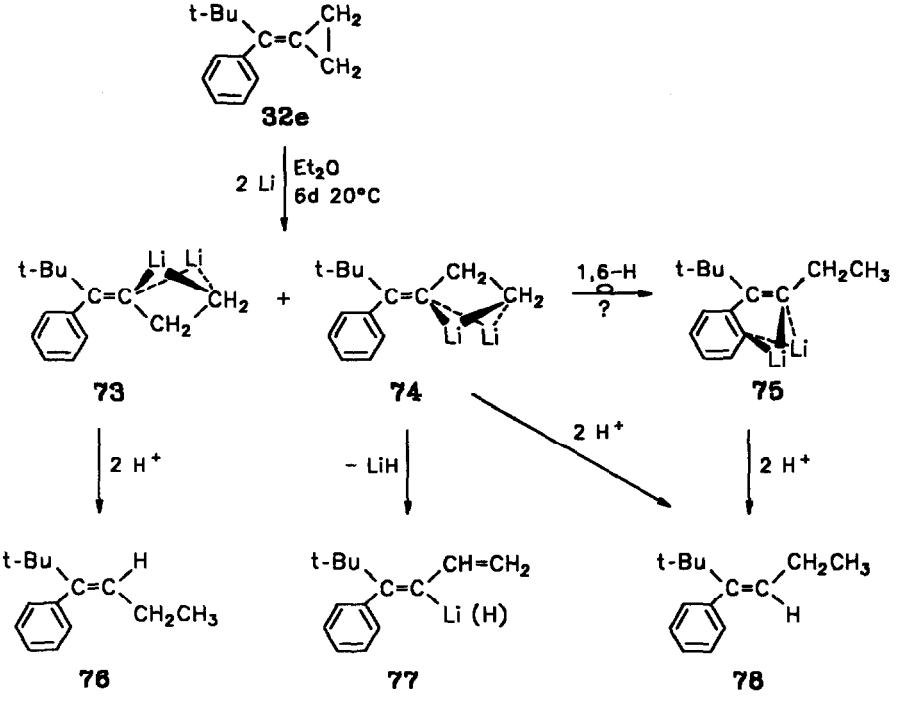
Figure 1. Distribution of the Different Cleavage and Rearrangement Products depending on the Temperature after 2.5 h, respectively.

In connection with the stereochemistry of the ring-chain rearrangement **64** → **63** the addition of *n*-butyllithium to *α*-cyclopropylstyrene (**69**) has to be mentioned which in contrast yields a 1:1 mixture of the two open-chain monolithio compounds **70** and **72**.[28]



***α-tert-Butylbenzylidenecyclopropane* (32e)**

The reactivity of the *α-tert*-butyl substituted benzylidenecyclopropane **32e** towards lithium dust is extremely low. Even after 44 hours at room temperature 17% of the starting material was still present. During these long reaction times most of the lithiumorganic reaction products were protonated by the solvent so that the expected 1,6-proton shift **74** → **75** could not been detected, the hydrolysis product **78** being the same.



On the other hand, for the first time regioselectivity here was not complete, although the (E)-product **78** again is strongly favored despite the *cis*-standing *tert*-butyl group. (Table 4).

Table 4. GC/MS Analysis of the Cleavage Products of **32e** after Hydrolysis.

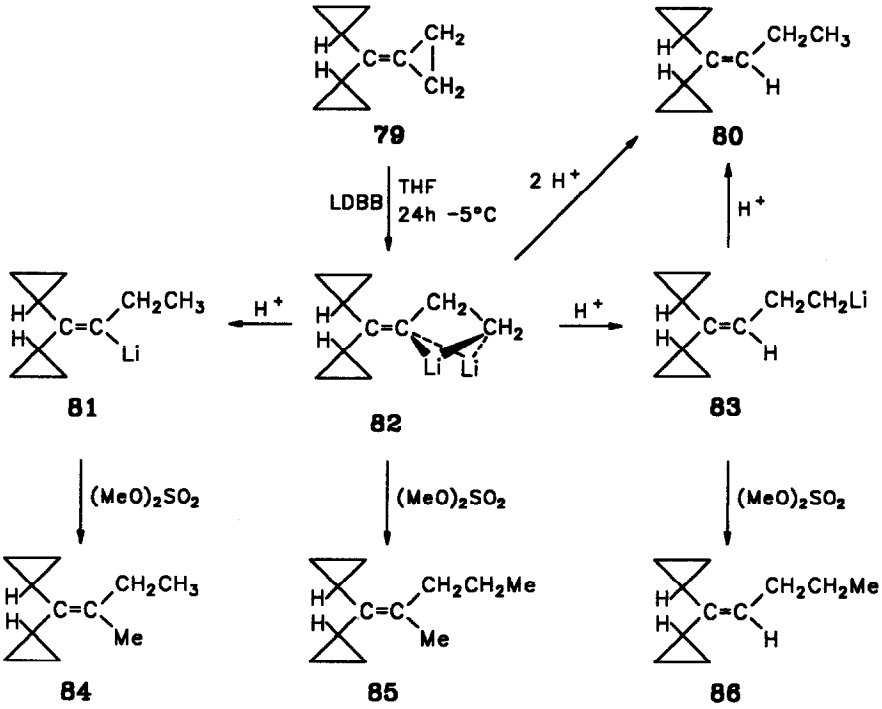
\Conditions Compound \	23 h 20°C	44 h 20°C	6 d 20°C
32e	35.7	17.0	0.0
76	0.7	1.8	3.5
77(H)	10.0	15.3	9.1
78	53.6	66.3	78.1

While the structure **77** is tentative, the unknown (E) and (Z)-2,2-dimethyl-3-phenyl-3-hexenes **78** and **76** have been prepared for comparison (7:1) by a Wittig reaction starting from pivalophenone and propylidenetriphenylphosphorane, the stereochemistry being found out by NMR spectroscopy using NOE and the $^{3}J(^{13}C, ^{1}H)$ coupling between the vinyl proton and the ipso carbon of the phenyl group.

***(Dicyclopropylmethylene)cyclopropane* (79)**

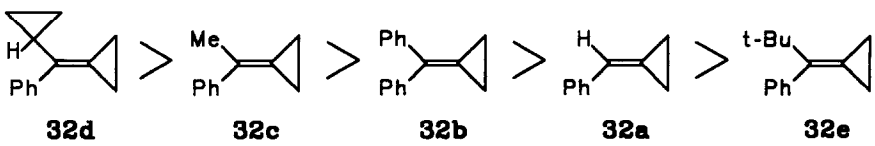
The high reactivity of α-cyclopropylbenzylidenecyclopropane (**32d**) towards lithium metal raised the question whether the replacement of the phenyl ring by a second cyclopropyl group would also lead to a reactive methylenecyclopropane derivative. This, however, is not the case. Even sonication of **79** with lithium dust in boiling diethyl ether or THF was not successful.

On the other hand, the reaction worked by using lithium 4,4'-di-*tert*-butylbiphenyl (LDBB)[16] instead of lithium the reductive cleavage being nearly complete after 24 hours at -5°C in THF as the solvent. Upon working up with dimethyl sulfate as usual besides 3% starting material **79** and 29% 1,1-dicyclopropyl-1-butene (**80**) one dimethylated product **85** (24%) and two monomethylated products **84** (41%) and **86** (3%) could be detected. Hydrolysis yielded 85% **80** as the sole product. In contrast to **32d** products of ring-chain rearrangements seem not to be formed at least under the reaction conditions used.



Reaction Mechanism

Lithium metal will react with benzylidenecyclopropanes **32** first by a single electron transfer (SET) reaction and this has to be the rate determining step. The sequence of falling reactivity reported in this paper shows that not only electronic but also steric effects of the α-substituents come into play.



According to MNDO calculations[29] the radical anion of **32a** solvated with two molecules of water has the structure **87** in a nearly bisected[30] conformation with the lithium atom at C2 oriented syn to the phenyl ring (Fig. 2). Besides coordination with C2 (Li-C2 = 1.99 Å, Li-C1 = 2.30 Å) there is a remarkable interaction of the lithium atom with the phenyl ring (Li-C6 = 2.43 Å) especially with the proton at C6 (2.23 Å). 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 "E" derivative **44** being formed stereoselectively. Wether the second lithium atom immediately attacks C3 (C4) or first C1 followed by an anionic cyclopropylcarbinyl-allylcarbinyl rearrangement[31,32] **88** → **44** is not known.

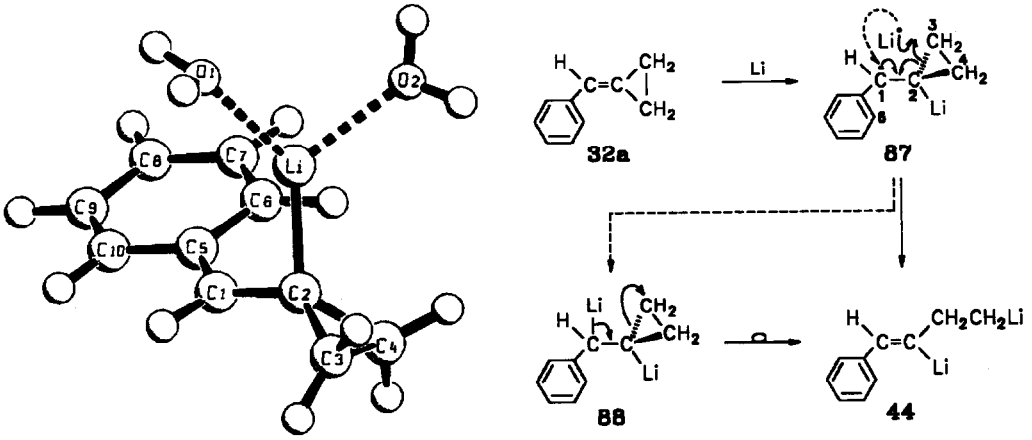


Figure 2. MNDO Geometry of the Radical Anion **87**·2 H_2O

The reaction of 2,2-dimethylmethylenecyclopropane (**91**) with lithium metal[9] where the scission of definitely only one cyclopropane σ-bond had been found, was also treated calculationally. For the primarily formed radical anion **12** three molecules of water were used to simulate solvation, for the presumably doubly bridged dilithio compounds **13**, **90** and **15** only two per lithium.[23] (Fig. 3-6)

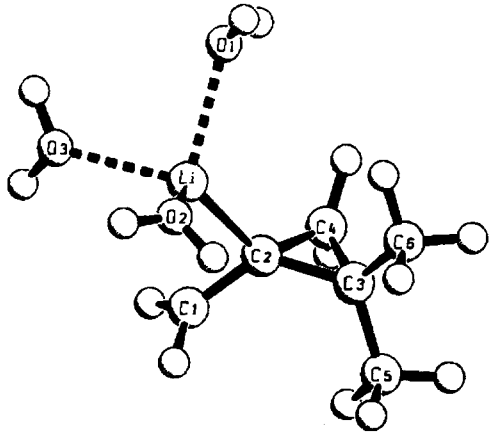


Figure 3. MNDO Geometry of the Radical Anion **12** ·3 H_2O

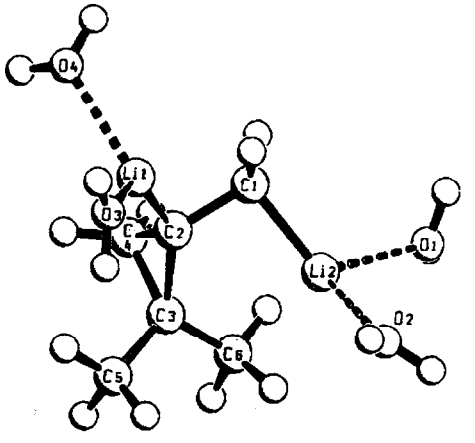
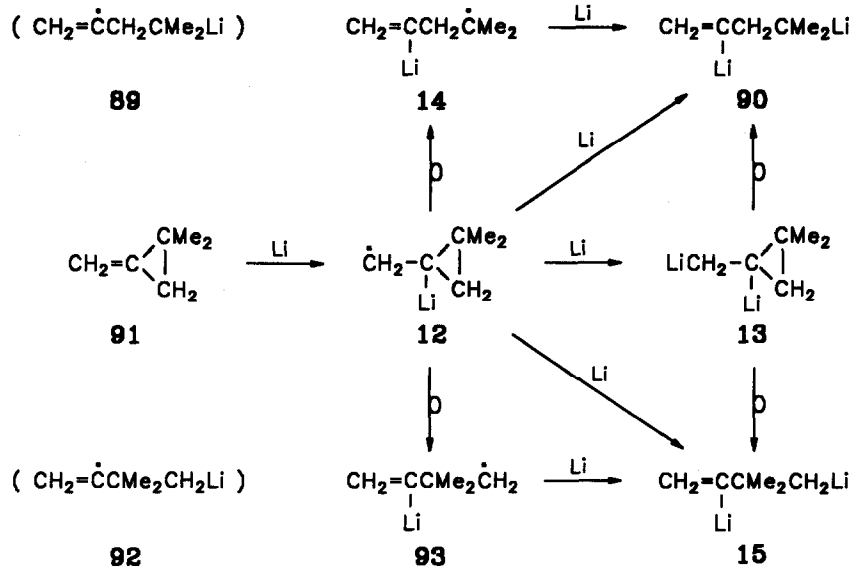


Figure 4. MNDO Geometry of the Vicinal Dilithio Compound **13** ·4 H_2O



According to the MNDO calculations[29] the lithium atom in the radical anion **12** (Fig. 3) again is coordinated mainly to C2 of the cyclopropane ring leaving the single electron at C1. (Li-C2 = 1.99 Å; Li-C1 = 2.37 Å; C1-C2 = 1.44 Å instead of 1.33 Å in **91**). As to be expected the distance C1-C2 in **13** (Fig. 4) is even longer (1.53 Å; Li1-C2 = 1.90 Å; Li1-C1 = 2.38 Å; Li2-C1 = 1.93 Å; Li2-C2 = 2.26 Å). In the open-chain dilithio compounds **90** (Fig. 5) and **15** (Fig. 6) C1-C2 again has double bond character (1.36 Å) and the double-bridge is more pronounced in **90** (Li1-C2 = 1.94 Å; Li1-C3 = 2.51 Å; Li2-C3 = 2.04 Å; Li2-C2 = 2.27 Å) than in **15** (Li1-C2 = 1.91 Å; Li1-C4 = 3.74 Å; Li2-C4 = 1.93 Å; Li2-C2 = 2.42 Å).

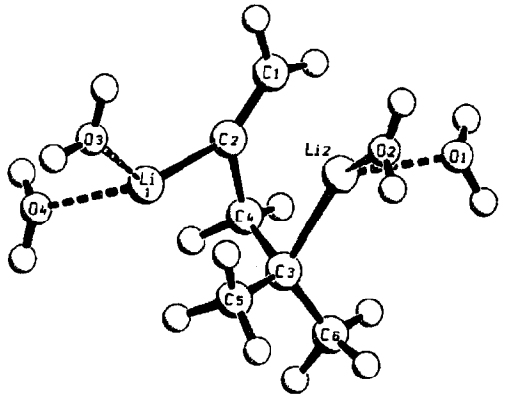


Figure 5. MNDO Geometry of the 1,3-Dilithio Compound **90** ·4 H_2O

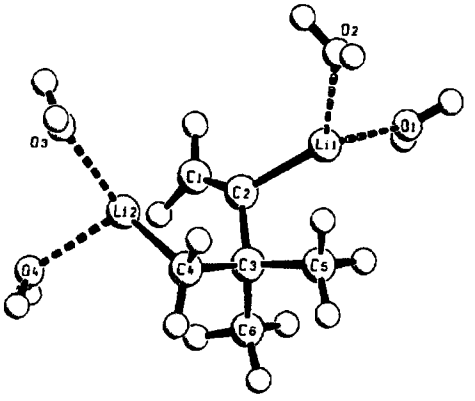


Figure 6. MNDO Geometry of the 1,3-Dilithio Compound **15** ·4 H_2O

The *energies* calculated by the MNDO method, however, were not in accord with the experimental results leading to **90** as the most stable dilithiumorganic 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)[33] yielding the very plausible values of Figure 7. The obviously wrong MNDO energies are included.

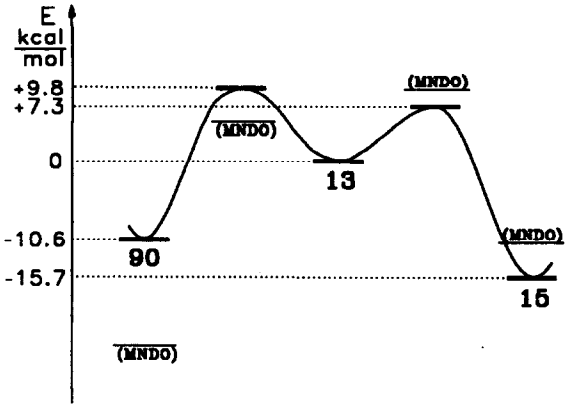


Figure 7. Energies of the Dilithio Compounds (·4 H_2O) according to ab inito Calculations (STO-3g)

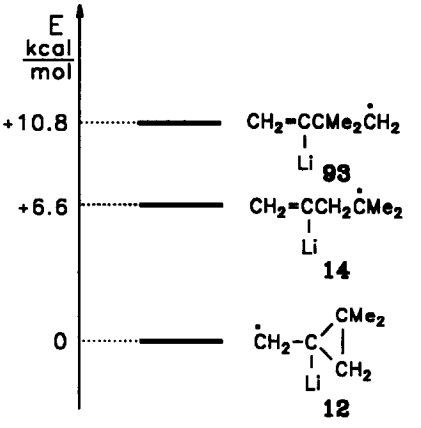
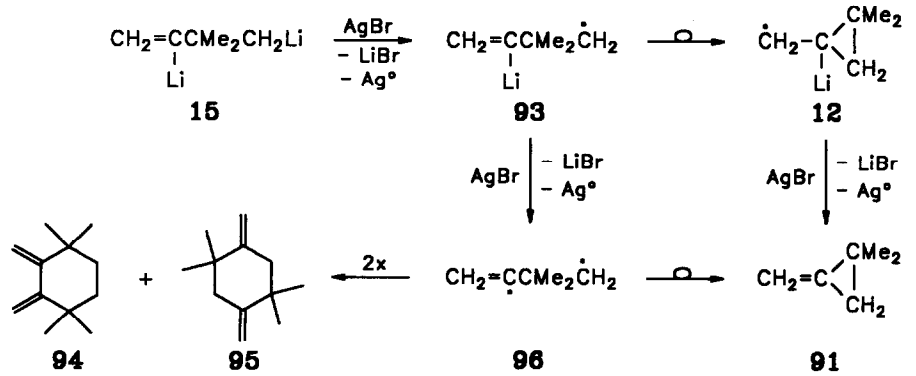


Figure 8. Energies of the Radical Anions (·3 H_2O) (STO-3g)

It is interesting that according to these ab inito calculations (STO-3g)[33] the most stable radical anion is the cyclic one **12** (Fig. 8). Of the open-chain radical anions only **14** and **93** have to be discussed, **89** and **92** (in brackets) are much less stable. As before the radical anions were calculated complexed with three, the dilithio compounds with four molecules of water.

The higher stability of the cyclic radical anion **12** compared with **93** was confirmed chemically by treating the open-chain dilithiumorganic compound **15** with silver bromide or copper(I) chloride yielding back the methylenecyclopropane derivative **91**.



On the other hand, also traces of the dimers **94** and **95** could be detected which speaks for the diradical **96** as an intermediate.

Experimental

General Methods. All reactions with air sensitive compounds were carried out under an atmosphere of dried argon (99.996%). Diethyl ether and tetrahydrofuran (THF) were purified by adsorptive filtration over aluminium oxide (basic, activity I) and distilled under argon from sodium-benzophenone ketyl. Dimethyl sulfate was distilled and stored over molecular sieve (3Å). Mass spectra (MS) were obtained on a Hewlett-Packard GC-Mass Spec 5988a (5% phenylmethylsilicon quartz capillary); m/e values are reported, followed by the relative intensity in parantheses. Nuclear Magnetic Resonance (^1H, ^2H, and ^{13}C) spectra were recorded on the Bruker instruments WP-80, AC-200, and AMX-400. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Coupling constants (J) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s(singlet), d(doublet), t(triplet), q(quartet), quint(quintet), sext(sextet), m(multiplet).

Preparation of the Starting Materials

Cyclopropyltriphenylphosphonium bromide (**29**):[19] In a 2 l three-necked flask equipped with a magnetic stirring bar, a reflux condenser, and a 500 ml dropping funnel 204.24 g (0.44 mol) (3-bromo-propyl)triphenylphosphonium bromide (**28**)[18] were suspended in 450 ml of water and 440 ml (0.44 mol) 1 N NaOH was introduced at 80°C within 5 h. After 2 h reflux and 12 h stirring at room temperature the mixture (pH = 8) was extracted three times with 300 ml chloroform, respectively, the combined extracts being dried over magnesium sulfate. Three fourth of the solvent was distilled off and the phosphonium salt was precipitated by adding diethyl ether until cloudy followed by standing over night to give 153.32 g (0.40 mol, 91%) **29** as a white solid: m.p. 188-189°C [Lit.[34] 189-190°C]. ^1H NMR (80 MHz, $CDCl_3$) δ 0.6 (m, 2 H, syn-cyclopropyl), 1.8 (m, 2 H, anti-cyclopropyl), 3.4 (m, 1 H, cyclopropyl), 7.8 (m, 15 H, phenyl). The product was dried at 120°C for several hours at oil vacuum and before use in the Wittig reaction it was appropiate to grind it finely in a mortar and stor it under argon after drying again.

α-tert-Butylbenzylidenecyclopropane (**32e**): 76.66 g (0.20 mol) **29** were suspended under argon in 300 ml of dry THF and 24.68 g (0.22 mol) potassium *tert*-butoxide were added. The yellow mixture was stirred for 2 h at 60°C, and then at the same temperature 24.33 g (0.15 mol) pivalophenone (**30e**) in 25 ml THF was added dropwise within 30 min. The color turned to dark brown with the formation of a light precipitate while stirring for 50 h at 45°C. Finally 200 ml water was added at room temperature and the aqueous layer extracted with 100 ml diethyl ether and 100 ml n-pentane, respectively, the combined organic extracts being dried over magnesium sulfate. After removing the solvent under vacuum on a rotary evaporator at temperatures not exceeding 60°C the crude brown oil was vigorously stirred three times with 200 ml warm hexane, respectively, leaving a granular residue of triphenylphosphine oxide. The crude product containing still some **30e** was best purified by chromatography on aluminium oxide (basic, activity I) with hexane as the eluent followed by distillation under vacuum to give 11.37 g (61.0 mmol, 41%) **32e** as a colorless, liquid of b.p. 105-106°C (10 Torr). MS (70 eV): m/z 186 (M^+, 2), 171(31), 143(54), 130(46), 129(100), 128(57), 115(38), 91(29), 77(25), 57(38), 41(28). Anal. calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74; found: C, 90.37; H, 9.75. ^1H NMR (200 MHz, $CDCl_3$) δ 0.8 (m, 2 H, cyclopropyl), 1.2 (s, 9 H, *tert*-butyl) 1.4 (m, 2 H, cyclopropyl), 7.2 (m, 5 H, phenyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.5, 6.2, 30.2, 36.9, 118.45, 125.9, 127.4, 129.2, 138.6, 143.3.

The same procedure was used for the synthesis of benzylidenecyclopropane (**32a**) itself and the other starting materials **32b-d** as well as **79** and **26** prepared in the literature[18,35-37] in a somewhat different manner.

Benzylidenecyclopropane (**32a**): Yield 43% of a colorless liquid recondensed at ca. 50°C (5 Torr) [Lit.[18] b.p. 58-59°C (3 Torr)]. MS (70 eV): m/z 130 (M^+, 54), 129(100), 128(62), 127(25), 115(67), 63(19), 51(47), 50(30), 39(38), 27(20). ^1H NMR (200 MHz, $CDCl_3$) δ 1.2 and 1.4 (2 m, 4 H, cyclopropyl), 6.7 (m, 1 H, vinyl), 7.4 and 7.6 (2 m, 5 H, phenyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.5, 4.2, 118.2, 124.2, 126.6, 126.65, 128.4, 138.2. The product is unstable at higher temperatures polymerizing above 60°C. It is also decomposed during chromatography on neutral and basic aluminium oxide and was therefore purified by recondensing within 2 days at temperatures lower than 60°C (5 Torr).

(Diphenylmethylene)cyclopropane (**32b**): Yield 75% of white crystals: m.p. 65-66°C (n-hexane) [Lit.[18] 64.5-65.5°C] MS (70 eV): m/z 206 (M^+, 47), 205(77), 203(60), 191(100), 189(40), 129(43), 115(43), 91(43), 88(34), 51(47). ^1H NMR (200 MHz, $CDCl_3$) δ 1.4 (s, 4 H, cyclopropyl), 7.35 (m, 10 H, phenyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 3.55, 124.35, 126.8, 128.05, 128.3, 129.95, 140.9.

α-Methylbenzylidenecyclopropane (**32c**): Yield 80% of a colorless liquid of b.p. 95-96°C (11 Torr) [Lit.[35] 65-66°C (2 Torr)]. MS (70 eV): m/z 144 (M^+, 14), 143(13), 129(100), 128(67), 127(19), 115(24), 77(18), 63(16), 51(28), 39(27). ^1H NMR (200 MHz, $CDCl_3$) δ 1.1 and 1.5 (2 m, 4 H, cyclopropyl), 2.2 (m, 3 H, methyl), 7.3 and 7.65 (2 m, 5 H, phenyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.45, 5.8, 19.7, 120.5, 122.4, 125.4, 126.5, 128.1, 140.5. The product is decomposed during chromatography on basic aluminium oxide and partly rearranged to 1-cyclopropyl-1-phenylethene during preparative gas chromatography. It is therefore best purified by vacuum distillation or simply by recondensation at 70°C (oil pump).

α-Cyclopropylbenzylidenecyclopropane (**32d**): Yield 60% of a colorless liquid of b.p. 124-125°C (12 Torr) [Lit.[35] 100°C (2 Torr)]. MS (70 eV): m/z 170 (M^+, 8), 155(49), 153(30), 142(48), 141(83), 129(85), 128(100), 115(62), 51(46), 39(50), 27(27). ^1H NMR (200 MHz, $CDCl_3$) δ 0.75 (m, 4 H, α-cyclopropyl) 1.2 (m, 4 H, cyclopropyl), 1.75 (m, 1 H, α-cyclopropyl), 7.25 and 7.8 (2 m, 5 H, phenyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 1.4, 2.3, 5.9, 14.7, 118.75, 125.9, 126.4, 127.4, 127.9, 141.2. The product was purified by chromatography on aluminium oxide (neutral, activity I) using n-pentane as the eluent followed by distillation.

(Dicyclopropylmethylene)cyclopropane (**79**): Yield 69% of a colorless liquid of b.p. 95°C (40 Torr) [Lit.[36] 98-99°C (45 Torr)]. MS (70 eV): m/z 134 (M^+, 5) 105(19), 91(100), 79(28), 77(39), 65(16), 53(16), 51(31), 41(32), 39(62), 27(17). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.6 (m, 8 H), 1.0 (s, 4 H), 1.4 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.7, 4.7, 14.3, 111.8, 129.2.

Cyclopropylidenecyclobutane (**26**): Yield 29% of a colorless liquid of b.p. 57-58°C (85 Torr) [Lit.[37] 54-60°C (83 Torr)]. MS (70 eV): m/z 94 (M^+, 18), 91(19), 79(100), 77(58), 66(29), 65(29), 40(24), 39(48), 28(17), 27(17). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.0 (quint, ^5J = 2.3 Hz, 4 H, cyclopropyl), 2.0 (quint, ^3J = 7.9 Hz, 2 H, cyclobutyl), 2.75 (tquint, ^3J = 7.9 Hz, ^5J = 2.3 Hz, 4 H, cyclobutyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 1.9, 17.5, 31.2, 109.9, 128.5.

Reductive Metalation Reactions

General Procedure: In a 100 ml three-necked flask equipped with a magnetic stirring bar, a dropping funnel, an internal thermometer, and an argon inlet 0.30 g (43.2 mmol) lithium dust (2% sodium)[38] was suspended in 50 ml of dry diethyl ether and a solution of 10.0 mmol of the methylenecyclopropane derivative in 10 ml of ether was added dropwise under the conditions mentioned in the Theoretical Part and in the Tables. Depending on the temperature the reaction started sooner or later indicated by the appearing coloration. Finally the reaction was stopped by filtration from the excess lithium metal through glass wool dried before by heating in vacuum.

In case of derivatization with dimethyl sulfate the reaction mixture was cooled to -20°C and a solution of 5 ml dimethyl sulfate in 10 ml diethyl ether was added. After decolorization and stirring for 2 h at room temperature the mixture was stirred for another 3 h with 25% aqueous ammonia in order to destroy excess dimethyl sulfate. The aqueous phase was extracted several times with ether and the combined organic phases dried over magnesium sulfate. After removing the solvent under vacuum on a rotary evaporator at temperatures not exceeding 60°C the crude reaction product was recondensed from the nonvolative residue the latter seldom exceeding 20% of the total amount. The reaction mixture was analyzed by GC/MS, most products in addition being characterized by NMR spectroscopy after separation by preparative gas chromatography. Unknown compounds like **76** and **78** have been prepared for comparison.

(Diphenylmethylene)cyclopropane (32b) as the Starting Material

1,1-Diphenyl-1-butene (**33**): MS (70 eV): m/z 208 (M^+, 62), 193(48), 179(23), 178(33), 165(34), 130(42), 129(29), 115(100), 91(49), 77(19). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.0 (t, ^3J = 7.6 Hz, 3 H, methyl), 2.1 (quint, ^3J = 7.6 Hz, 2 H, methylene), 6.05 (t, ^3J = 7.6 Hz, 1 H, vinyl), 7.2 (m, 10 H, phenyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 23.2, 126.7, 126.8, 127.2, 128.0, 128.1, 129.8, 131.5, 140.2, 141.05, 142.75. The compound was synthesized for comparison by dehydration of 1,1-diphenylbutanol with sulfuric acid.

1,1-Diphenyl-2-methyl-1-pentene (**36**): MS (70 eV): m/z 236 (M^+, 62), 207(66), 191(17), 179(17), 178(26), 165(26), 129(100), 128(27), 115(25), 91(80). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9 (t, ^3J = 7.2 Hz, 3 H, methyl), 1.5 (m, 2 H, methylene), 1.8 (s, 3 H, $=CCH_3$), 2.1 (m, 2 H, $=CCH_2$), 7.2 (m, 10 H, phenyl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.5, 21.6, 37.4, 126.0, 126.9, 127.9, 128.0, 128.3, 129.5, 129.6, 134.9, 137.7, 143.4.

(E)-2-Methyl-1-(2-methylphenyl)-1-phenyl-1-butene (**37**): MS (70 eV): m/z 236 (M^+, 100), 221(53), 179(85), 178(36), 143(53), 129(69), 128(38), 115(29), 105(29), 91(52). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.1 (t, ^3J = 7.5 Hz, 3 H, methyl), 1.75 (s, 3 H, $=CCH_3$), 2.2 (s, 3 H, $ArCH_3$), 2.2 (m, 2 H, $=CCH_2$), 7.2 (m, 9 H, aryl). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.35, 18.9, 19.7, 27.6, 125.6, 125.9, 126.45, 127.8, 129.2, 129.7, 130.0, 135.8, 135.9, 136.7, 142.1.

(E)-2-Deutero-1-(2-deuterophenyl)-1-phenyl-1-butene (**38**): Yield 62% of a colorless oil of b.p. 58-60°C (50 Torr). MS (70 eV): m/z 210 (M^+, 100), 195(75), 180(45), 166(37), 132(37), 131(51), 130(36), 117(66), 116(92), 92(50). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.0 (t, ^3J = 7.6 Hz, 3 H, methyl), 2.1 (q, ^3J = 7.6 Hz, 2 H, methylene), 7.2 (m, 9 H, phenyl). ^{2}H NMR (61 MHz, $CDCl_3$) δ 6.4 (s, vinyl), 7.55 (s, phenyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 23.1, 126.7, 126.8, 126.9(t), 127.1, 127.9, 128.0, 128.05, 130.0, 131.2(t), 140.2, 141.8, 142.6.

2-Ethyl-1-hydro-1-methyl-3-phenylbenzosilole (**39a**): Yield 42% of a colorless oil of b.p. 80-84°C (40 Torr). MS (70 eV): m/z 250 (M^+, 18), 223(18), 222(81), 221(100), 207(25), 121(14), 119(17), 105(28), 53(23), 43(32). High res. MS: calcd. for $C_{17}H_{18}Si$: 250.11776, found: 250.11761. ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.5 (d, ^3J = 4.1 Hz, 3 H, $SiCH_3$), 1.1 (t, ^3J = 7.5 Hz, 3 H, methyl), 2.3 (m, 2 H, methylene), 4.75 (q, ^3J = 4.1 Hz, 1 H, SiH), 7.2 (m, 9 H, aryl). ^{13}C NMR (100 MHz, $CDCl_3$) δ -6.5, 15.55, 23.5, 123.3, 126.0, 127.0, 128.3, 128.95, 129.9, 132.25, 134.6, 138.0, 143.7, 152.0, 153.9.

1,1-Dimethyl-2-ethyl-3-phenylbenzosilole (**39b**): Yield 40% of a colorless oil of b.p. 100-103°C (40 Torr). MS (70 eV): m/z 265(24), 264(M^+, 100), 249(41), 233(31), 205(48), 204(31), 135(84), 121(19), 59(56), 43(24). High res. MS: calcd. for $C_{18}H_{20}Si$: 264.13351, found: 264.13323. **Anal.** calcd. for $C_{18}H_{20}Si$: C, 81.76; H, 7.62; found: C, 81,71, H, 7.50. ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.3 (s, 6 H, $SiMe_2$), 0.95 (t, ^3J = 7.5 Hz, 3 H, methyl), 2.2 (q, ^3J = 7.5 Hz, 2 H, methylene), 7.2 (m, 9 H, aryl). ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.4, 15.15, 23.4, 123.0, 125.9, 127.2, 128.1, 129.0, 129.6, 131.3, 137.6, 138.2, 145.6, 151.0, 152.4.

2-Ethyl-3-phenylinden-1-one (**40**): Yield 19% of bright yellow crystals of m.p. 88-89°C (ethanol) [Lit.[39] 87-88°C]. **MS** (70 eV): m/z 235(17), 234(M^+, 100), 233(51), 219(52), 191(34), 189(35), 165(23), 101(22), 94(26), 51(17). ^{1}**H NMR** (80 MHz, $CDCl_3$) δ 1.1 (t, ^3J = 7.5 Hz, 3 H, methyl), 2.35 (q, ^3J = 7.5 Hz, 2 H, methylene), 7.2 (m, 9 H, aryl). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 14.0, 16.7, 120.7, 122.4, 127.75, 128.15, 128.7, 129.1, 131.0, 132.7, 133.1, 136.6, 145.8, 154.6, 198.2.

Benzylidenecyclopropane (32a) as the Starting Material

(E)-1-Phenyl-1-butene (**42**): Yield 70%. **MS** (70 eV): m/z 132(M^+, 43), 131(10), 118(10), 117(100), 116(10), 115(42), 91(28), 78(7), 77(8), 51(8). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 1.1 (t, ^3J = 7.5 Hz, 3 H, methyl), 2.2 (ddq, ^3J = 7.5 Hz, ^3J = 6.25 Hz, ^4J = 1.3 Hz, 2 H, methylene), 6.25 (dt, ^3J = 15.9 Hz, 3 J = 6.25 Hz, 1 H, vinyl), 6.35 (dt, ^3J = 15.9 Hz, ^4J = 1.3 Hz, 1 H, vinyl), 7.25 (m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 13.6, 26.0, 125.9, 126.7, 128.4, 128.8, 132.6, 138.0.

(E)-2-Methyl-1-phenyl-1-butene (**47**): **MS** (70 eV): m/z 146 (M^+, 45), 131(100), 129(15), 117(16), 116(16), 115(29), 91(48), 51(22), 39(29), 27(21).

(E)-2-Methyl-1-phenyl-1-pentene (**48**): **MS** (70 eV): m/z 160 (M^+, 34), 131(100), 129(17), 116(17), 115(27), 91(46), 51(16), 41(18), 39(26), 27(21).

(E)-2-Methyl-1-(2-methylphenyl)-1-butene (**49**): **MS** (70 eV): m/z 160 (M^+, 56), 145(100), 131(25), 130(23), 128(26), 115(30), 105(27), 91(23), 39(34), 27(25).

(E)-1-(2-Methylphenyl)-1-butene (**50**): a) **MS** (70 eV): m/z 146 (M^+, 30), 117(100), 116(11), 115(48), 104(30), 91(30), 51(24), 39(36), 29(11), 27(27). b) **MS** (70 eV): m/e 146 (M^+, 45), 131(100), 129(15), 117(16), 116(16), 115(29), 91(48), 51(22), 39(29), 27(21).

α-Methylbenzylidenecyclopropane (32c) as the Starting Material

(E)-2-Phenyl-2-pentene (hydrolysis product): Yield 63%. **MS** (70 eV): m/z 146 (M^+, 32), 131(100), 129(16), 117(11), 116(17), 115(26), 91(44), 77(17), 51(12), 39(11). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 1.05 (t, ^3J = 7.45 Hz, 3 H, methyl), 2.0 (dt, ^4J = 1.3 Hz, ^5J = 0.75 Hz, 3 H, $=CCH_3$), 2.2 (dqq, ^3J = 7.45 Hz, ^3J = 7.0 Hz, ^5J = 0.75 Hz, 2 H, $=CCH_2$), 5.8 (tq, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1 H, vinyl), 7.3 (m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 14.0, 15.6, 22.0, 125.6, 126.4, 128.1, 130.2, 134.1, 144.0.

(E)-3-Methyl-2-phenyl-2-hexene (**54**): **MS** (70 eV): m/z 174 (M^+, 42), 145(100), 129(23), 128(22), 117(49), 115(29), 91(39), 77(22), 39(21), 27(22).

(E)-3-Methyl-2-(2-methylphenyl)-2-hexene (**55**): **MS** (70 eV): m/z 188 (M^+, 56), 159(100), 145(27), 131(59), 129(39), 128(36), 117(28), 115(32), 105(28), 91(28). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 1.0 (t, ^3J = 7.6 Hz, 3 H, methyl), 1.35 (m, 3 H, =CMe), 1.5 (m, 2 H, methylene), 1.85 (m, 3 H, $=CCH_3$), 2.2 (s, 3 H, ArMe), 2.2 (m, 2 H, $=CCH_2$), 6.95 and 7.15 (2 m, 4 H, aryl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 14.0, 19.0, 19.3, 19.8, 21.3, 35.6, 125.7, 126.0, 128.3, 129.7, 130.0, 131.1, 135.0, 145.2.

(E)-3-Methyl-2-phenyl-2-pentene (**58**): **MS** (70 eV): m/z 160 (M^+, 49), 146(18), 145(100), 131(33), 128(18), 117(35), 115(27), 105(20), 91(44), 77(20). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 1.05 (t, ^3J = 7.5, 3 H, methyl), 1.55 (q, ^5J = 1.5 Hz, 3 H, =CMe), 1.95 (m, 3 H, $=CCH_3$), 2.2 (q, ^3J = 7.5 Hz, methylene), 7.2 (m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 12.5, 19.4, 20.2, 27.3, 125.7, 127.9, 128.4, 129.65, 133.0, 145.5.

(E)-3-Methyl-2-(2-methylphenyl)-2-pentene (**61**): **MS** (70 eV): m/z 174 (M^+, 78), 159(100), 145(46), 131(27), 129(29), 128(31), 117(51), 115(32), 105(21), 91(25). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 1.05 (t, ^3J = 7.65 Hz, 3 H, methyl), 1.4 (q, ^5J = 1.5 Hz, 3 H, =CMe), 1.85 (qt, ^5J = 1.5 Hz, ^5J = 1.0 Hz, 3 H, $=CCH_3$), 2.15 (s, 3 H, ArMe), 2.2 (m, 2 H, methylene), 6.95 and 7.1 (2 m, 4 H, aryl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 12.6, 18.8, 18.9, 19.5, 26.7, 125.7, 126.0, 128.3, 129.0, 129.7, 132.8, 135.0, 145.0.

α-Cyclopropylbenzylidenecyclopropane (32d) as the Starting Material

(E)-1-Cyclopropyl-1-phenyl-1-butene (**62**): Yield 89%. **MS** (70 eV): m/z 172 (M^+, 12), 157(21), 143(37), 129(100), 128(75), 115(67), 91(42), 77(29), 51(23), 39(33), 27(29). **Anal.** calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36; found: C, 90.85; H, 9.34. ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 0.3 and 0.8 (2 m, 4 H, cyclopropyl), 1.1 (t, ^3J = 7.45 Hz, 3 H, methyl), 1.7 (m, 1 H, cyclopropyl), 2.4 (quint, $^3J \approx$ 7.4 Hz, 2 H, methylene), 5.7 (td, ^3J = 7.3 Hz, ^4J = 1.8 Hz, 1 H, vinyl), 7.25 (m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 6.45, 11.4, 14.1, 21.8, 126.1, 127.25, 127.6, 133.4, 139.95, 142.7.

(E)-1-(1-Methylcyclopropyl)-1-phenyl-1-pentene (**66**): **MS** (70 eV): m/z 200 (M^+, 8), 157(93), 143(73), 129(100), 128(71), 115(67), 91(70), 41(40), 39(38), 29(46), 27(48). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 0.55 and 0.65 (2 m, 4 H, cyclopropyl), 1.0 (t, ^3J = 7.3 Hz, 3 H, methyl), 1.4 (s, 3 H, methyl), 1.5 (sext, ^3J = 7.3 Hz, 2 H, methylene), 2.4 (q, ^3J = 7.3 Hz, 2 H, allyl), 5.9 (t, ^3J = 7.3 Hz, 1 H, vinyl), 7.3 and 7.5 (2 m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 14.2, 15.4, 17.3, 22.8, 26.2, 31.1, 126.1, 126.2, 127.8, 132.3, 142.6, 142.9.

(E)-1-Cyclopropyl-2-methyl-1-phenyl-1-pentene (**67**): **MS** (70 eV): m/z 200 (M^+, 10), 157(29), 143(43), 129(100), 128(58), 115(46), 91(48), 41(37), 39(35), 29(38), 27(41). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 0.1 and 0.6 (2 m, 4 H, cyclopropyl), 1.0 (t, ^3J = 7.55 Hz, 3 H, methyl), 1.4 (s, 3 H, methyl), 1.5 (sext, ^3J = 7.55, 2 H, methylene), 1.85 (m, 1 H, cyclopropyl), 2.3 (m, 2 H, allyl) 6.9 and 7.3 (2 m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 4.8, 13.2, 14.1, 20.5, 21.4, 35.8, 125.8, 127.6, 129.8, 132.4, 135.8, 140.9.

(E)-1-Cyclopropyl-2-methyl-1-(2-methylphenyl)-1-butene (**68**): **MS** (70 eV): m/z 200 (M^+, 13), 157(23), 143(100), 142(22), 141(24), 129(61), 128(58), 115(42), 105(24), 41(34), 39(31). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ -0.1, 0.2, and 0.55 (3 m, 4 H, cyclopropyl), 1.15 (t, ^3J = 7.5 Hz, 3 H, methyl), 1.4 (s, 3 H, $=CCH_3$), 1.85 (m, 1 H, cyclopropyl), 2.15 (s, 3 H, $ArCH_3$), 2.35 (m, 2 H, methylene), 6.8 and 7.15 (2 m, 4 H, aryl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 3.9, 4.3, 12.3, 12.8, 19.3, 19.7, 26.6, 125.0, 126.2, 129.4, 132.3, 133.6, 133.7, 139.5.

α-*tert*-Butylbenzylidenecyclopropane (32e) as the Starting Material

(Z)-3-Phenyl-2,2-dimethyl-3-hexene (**76**): **MS** (70 eV): m/z 188 (M^+, 30), 159(27), 131(100), 129(20), 117(57), 115(28), 91(55), 57(46), 41(31), 29(18). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 0.85 (t, ^3J = 7.6 Hz, 3 H, methyl), 1.15 (s, 9 H, t-Bu), 1.6 (quint, ^3J = 7.6 Hz, 2 H, methylene), 5.5 (t, ^3J = 7.6 Hz, 1 H, vinyl), 7.05 and 7.2 (2 m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 14.5, 22.5, 29.7, 35.7, 125.8, 125.9, 127.3, 129.8, 146.8, 149.8.

(E)-3-Phenyl-2,2-dimethyl-3-hexene (**78**): **MS** (70 eV): m/z 188 (M^+, 24), 159(25), 131(100), 129(26), 117(60), 115(36), 91(63), 57(47), 41(39), 29(25). ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 1.0 (t, ^3J = 7.6 Hz, 3 H, methyl), 1.15 (s, 9 H, t-Bu), 2.35 (quint, ^3J = 7.6 Hz, 2 H, methylene), 5.1 (t, ^3J = 7.6 Hz, 1 H, vinyl), 7.05 and 7.22 (2 m, 5 H, phenyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 14.8, 23.2, 31.6, 35.3, 125.5, 127.2, 128.7, 132.6, 146.8, 148.8.

The latter two compounds (1:7) have been prepared for comparison by a Wittig reaction starting with pivalophenone (**30e**) and n-propyltriphenylphosphonium bromide using dimsyl sodium (methylsulfinyl carbanion) in DMSO as the base. Separation was achieved by preparative gas chromatography. **Anal.** calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; found: C, 89.15; H, 10.85.

(Dicyclopropylmethylene)cyclopropane (79) as the Starting Material

Here lithium 4,4'-di-*tert*-butylbiphenyl (LDBB)[16] has been prepared first by adding 0.79 g (3.0 mmol) di-*tert*-butylbiphenyl to a suspension of 0.28 g (40.0 mmol) lithium dust (2% sodium)[38] in 50 ml of dry THF at -5°C. At the same temperature 1.34 g (10.0 mmol) **79** in 10 ml THF was added dropwise to the blue-green mixture, which was stirred for 24 h at -5°C being then worked-up as usual.

1,1-Dicyclopropyl-1-butene (**80**)[40]: Colorless liquid of b.p. 96-97°C (40 Torr). **MS** (70 eV): m/z 136 (M^+, 28), 107(27), 93(47), 91(54), 79(100), 77(51), 67(42), 55(27), 41(39), 39(42). **Anal.** calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84; found: C, 88.04; H, 12.07. ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 0.3, 0.5, and 0.65 (3 m, 8 H, cyclopropyl), 1.0 (t, ^3J = 7.3 Hz; 3 H, methyl), 1.0 and 1.7 (2 m, 2 H, cyclopropyl) 2.1 (quint, $^3J \approx$ 7.3 Hz, 2 H, methylene), 5.1 (t, $^3J \approx$ 7.3 Hz, ^{1}H, vinyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 4.4, 4.8, 12.4, 12.8, 14.5, 20.7, 125.4, 138.7.

1,1-Dicyclopropyl-2-methyl-1-butene (**84**): **MS** (70 eV): m/z 150 (M^+, 17), 107(22), 105(49), 93(46), 91(100), 79(99), 77(58), 67(38), 65(24), 41(31), 39(32).

1,1-Dicyclopropyl-2-methyl-1-pentene (**85**): **MS** (70 eV): m/z 164 (M^+, 3), 121(69), 107(35), 105(41), 93(100), 91(93), 79(99), 77(62), 67(35), 55(35), 41(36).

1,1-Dicyclopropyl-1-pentene (**86**): **MS** (70 eV): m/z 150 (M^+, 5), 121(89), 107(24), 93(100), 91(64), 79(77), 77(53), 67(33), 55(32), 41(28), 39(25).

Cyclopropylidenecyclobutane (26) as the Starting Material

The same procedure was used as for (dicyclopropylmethylene)cyclopropane (**79**) yielding 54% of *(1-Methylbutyliden)cyclobutane* (**27**, Me instead of Li): **MS** (70 eV): m/z 124 (M^+, 38), 109(49), 95(49), 81(86), 68(46), 67(100), 55(38), 41(51), 39(36), 27(29). **Anal.** calcd. for C_9H_{16}: C, 87.02; H, 12.98; found: C, 87.02; H, 13.18. ^{1}**H NMR** (200 MHz, $CDCl_3$) δ 0.85 (t, ^3J = 7.3 Hz, 3 H, methyl), 1.35 (sext, ^3J = 7.3 Hz, 2 H, methylene), 1.45 (s, 3 H $=CCH_3$), 1.85 (t, ^3J = 7.3 Hz, 2 H, $=CCH_2$), 1.9 (quint, ^3J = 7.9 Hz, 2 H, cyclobutyl), 2.6 (t, ^3J = 7.9 Hz, 4 H, cyclobutyl). ^{13}**C NMR** (50 MHz, $CDCl_3$) δ 13.8, 15.4, 15.9, 20.8, 29.1, 29.2, 34.4, 125.8, 132.6.

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