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Polylithiumorganic Compounds - 20.[1]

Stereoselective Synthesis of Vicinal Dilithioalkenes by Addition of Lithium Metal to Carbon-Carbon Triple Bonds

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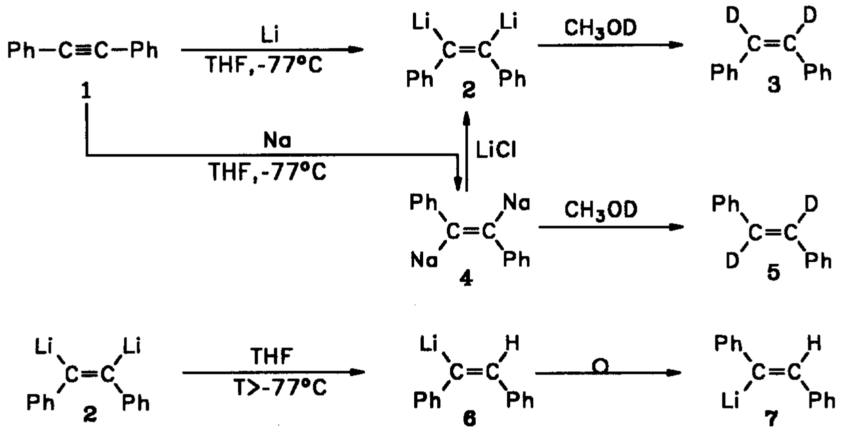
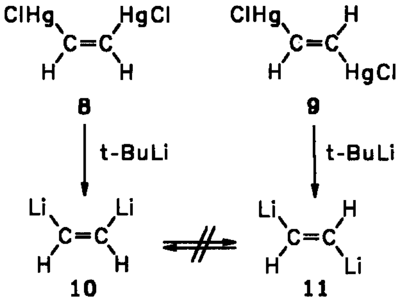
Abstract: *The reaction of various cyclic and acyclic alkynes with lithium dust (2% sodium) to form vicinal dilithioalkenes has been investigated: Aliphatic alkynes, e.g. 3-hexyne (27a), exclusively afford the corresponding (E)-dilithioalkenes, insoluble solids which are stable at room temperature and allow access to a variety of tetrasubstituted olefins in acceptable yields.*

Introduction

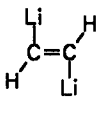
The first proof of a 1,2-dilithio-1-alkene as a stable intermediate in the reaction of carbon-carbon triple bonds with alkali metals has been reported by M. Szwarc et al.[3,4] Tolan (diphenylacetylene) (1) reacts with lithium metal at -77°C in THF to (Z)-1,2-dilithiostilbene (2) which, upon workup with methanol-d$_1$ forms (Z)-1,2-dideuterostilbene (3) exclusively. When employing sodium as reducing agent in the latter reaction, dideuterated (E)-stilbene (5) is the sole product. The high stability of the (Z)-configuration of the dilithioalkene 2 is demonstrated experimentally[3] by adding lithium chloride to the disodium compound 4 which transmetallates to 2 and, after workup with methanol-d$_1$, yields again (Z)-dideuterostilbene (3) only. (Z)-dilithiostilbene (2), however, is not stable at temperatures above -77°C and reacts with the solvent THF under formation of the corresponding monolithium compound, which isomerizes to the more stable (E)-lithiostilbene 7.[3]



1,2-Dilithioethylene is the simplest dilithioalkene possible, formed by the formal addition of lithium to acetylene. Both (E)- and (Z)-dilithioethylene (10) and (11), can be obtained[5] by using a double mercury lithium exchange reaction, an often used method in the synthesis of polylithiated hydrocarbons.[6] Thus, by treating the bis(chloromercurio) ethylenes **8** and **9** with *tert.*-butyllithium at -75°C both isomers can be obtained. These dilithioalkenes are configurationally stable, no isomerization can be observed. Upon warming up of the reaction mixtures, (Z)-1,2-dilithioethylene (**10**) is the less stable isomer, due to the easy *anti* elimination of lithium hydride.



Ab initio calculations[7] of the two isomers have found a distorted planar, partially bridged geometry **12** for the (E)-isomer, and the doubly bridged structure **13** for the (Z)-isomer to be the most stable ones. The (E)-isomer was recalculated[8] to be more stable by 3.8 kJ/mol. The barrier for the Z/E-isomerization was determined to be about 92 kJ/mol,[8] supposing a hypothetical gas phase reaction.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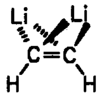
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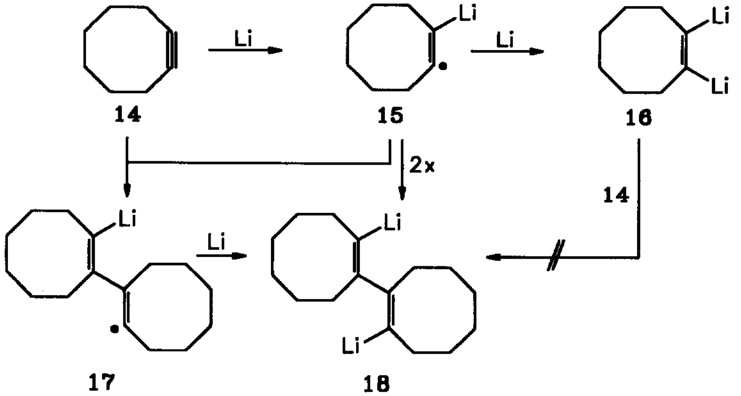
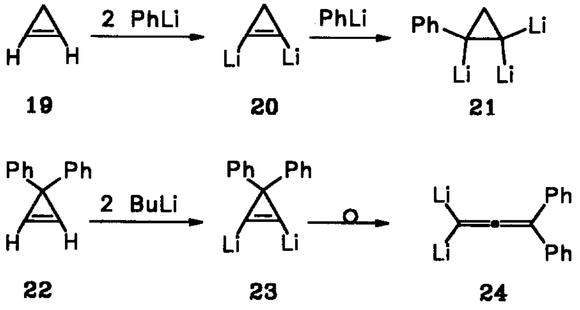
Cyclooctyne (**14**), which has a ring strain of about 50 kJ/mol[9] reacts readily with lithium metal at -35°C in diethyl ether[10,11] under formation of the soluble (Z)-1,2-dilithio-1-cyclooctene (**16**) and, as a side product, 2,2'-dilithio-1,1'-bicyclooctenyl (**18**). The amount of **18** depends strongly on the reaction conditions, especially on the quality of the lithium metal employed,[12] indicating that the radical anion **15** is a true intermediate in the reduction process. The addition of the dilithium compound **16** to the starting alkyne could be excluded experimentally,[12] despite reported additions of organolithium compounds to highly activated carbon-carbon triple bonds.[13] The solution of (Z)-1,2-dilithio-1-cyclooctene (**16**) in diethyl ether, however, is not stable at room temperature, it has a half-live of about one hour at 0°C and reacts with the solvent under protonation.[10]

The intermediacy of the smallest dilithiocycloalkene possible, 1,2-dilithio-1-cyclopropene (**20**), has been made plausible[14] in the reaction of the corresponding hydrocarbon cyclopropene (**19**) with phenyllithium, the high ring strain in this case being responsible for the high acidity of the vinylic protons. The dilithiocycloalkene is not stable towards the metalating agent and adds another equivalent of phenyllithium under formation of the trilithium compound **21**. More recently the interesting rearrangement of the diphenylsubstituted dilithiocyclopropene 23 to the geminal dilithioallene 24 has been reported.[15] The double deprotonation of vicinal vinylic protons, however, is obviously not applicable as a general approach to vicinal dilithioalkenes.

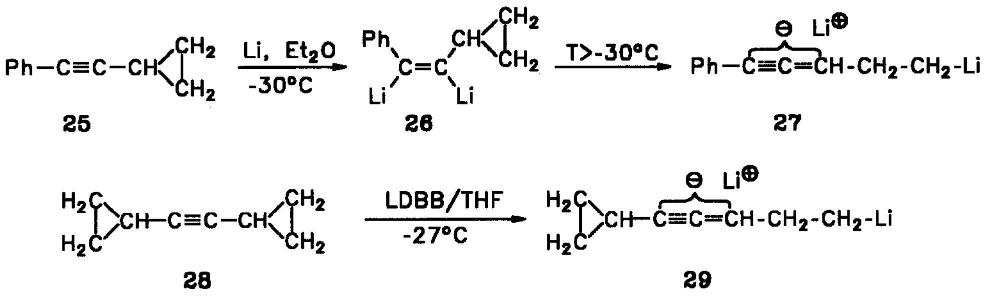


Cyclopropylacetylenes, as we have shown previously,[16] displace even another way of stabilization. When cyclopropylphenylacetylene (25) is treated with lithium metal at -30°C a stereoselective *cis* addition to the stable and soluble 26 is observed. When the reaction mixture is allowed to warm up, however, a ring-chain rearrangement occurs to the resonance stabilized dianion 27.



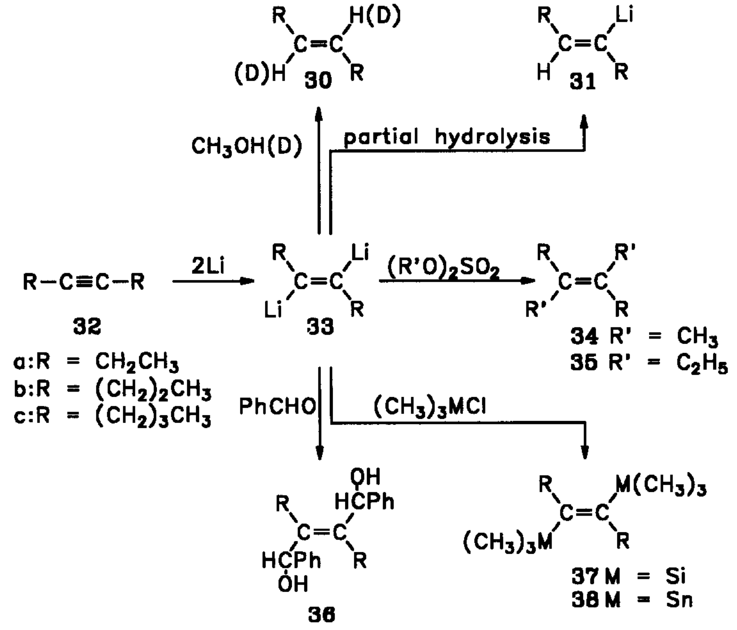
Dicyclopropylacetylene (28), on the other hand, does not react with lithium metal even when using forcing conditions,[12] probably due to the bulkiness of the two cyclopropyl substituents which do not allow an intensive contact of the triple bond and the metal surface. The reduction can be performed successfully when using catalytic amounts of lithium-4,4'-di-*tert.*-butylbiphenyl (LDBB),[17] in this case the vicinal dilithioalkene cannot be detected, the rearranged 29 is the observed product.[16]

Here, we report on our findings obtained in the reactions of the aliphatic internal alkynes 3-hexyne, 4-octyne, and 5-decyne (32a-c) and the cyclic alkynes cyclodecyne (51) and cyclododecyne (55) and our mechanistic investigations on the nature of the vicinal dilithioalkenes formed.



Results and Discussion

Even nonactivated internal aliphatic alkynes react cleanly with lithium metal. When a solution of the alkynes **32a-c** in diethyl ether is treated at room temperature with highly reactive lithium dust (2% sodium)[18] a greenish-silvery slurry is formed. Very efficient stirring and reaction times of up to 48 hours are necessary for the complete turnover of the alkyne. The vicinal dilithioalkenes **33a-c** formed are insoluble and cannot be separated from the excess of lithium metal employed. Upon hydrolysis of the reaction mixture only the corresponding (E)-alkenes **30a-c** are found, showing that a stereoselective *trans* addition of the lithium to the carbon-carbon triple bond has taken place. Not even a trace of the correspondig (Z)-isomers has been detected in the latter reactions.



Contrary to the reaction of cyclooctyne (**14**) dimeric products like **18** have not been identified. When quenching the reaction mixtures with methanol-d_1 a deuterium incorporation of up to 90% at both vinylic positions is observed. Therefore the stepwise reduction of the triple bond - even during the workup - can be excluded, as it is known[19] that radicals abstract preferably a hydrogen atom from methanol-d_1, which has been skilfully used as a probe for the differentiation between anionic and radical intermediates in the Grignard reaction.[20]

It is interesting to note that the reaction works in THF or hydrocarbons as cyclopentane as well, demonstrating the surface nature of the interaction between the alkyne and the metal. Attempts to dissolve the (E)-dilithioalkenes **33a-c** by using complexing additives like HMPA (hexamethylphosphoric triamide) or TMEDA (N,N,N',N'-tetramethylethylene diamine) failed and let to decomposition of the dilithium intermediate. **33a-c** were subjected to a number of electrophiles, the results are shown in Table 1. With decreasing reactivity of the electrophile the yield of disubstitution decreases as well, the dilithioalkenes then act as strong bases. The amount of products arising from the monolithium compounds **31a-c** increases. Contrary to the known Z/E-isomerization of phenyl substituted vinyllithium compounds,[21] alkyl substituted vinyllithium compounds are stable under the reaction conditions employed,[22] therefore always only one isomer of the corresponding derivative of **31a-c** is found with the alkyl groups in *trans* position to each other.

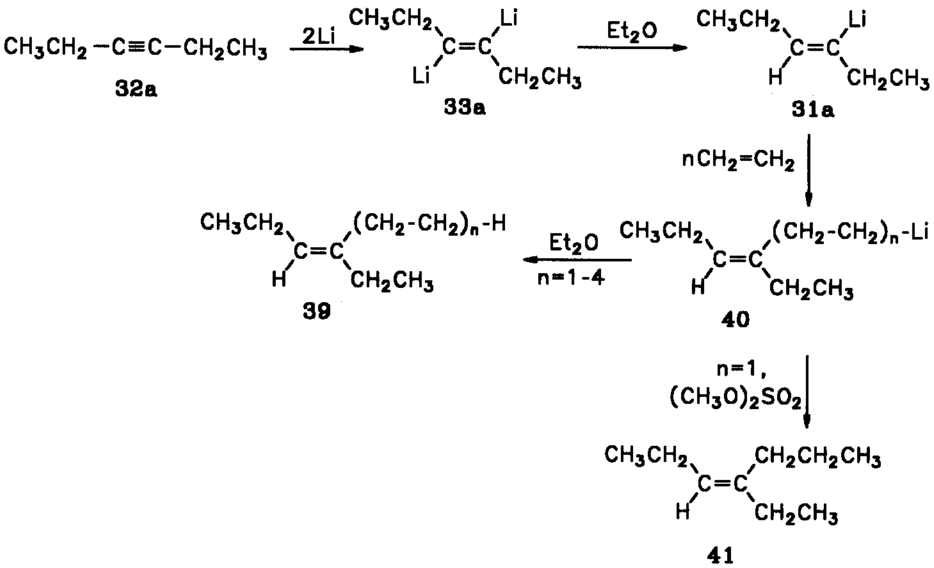
It should be noted here that unsymmetrically substituted internal alkynes as a matter of course react in the same way with lithium metal, the reaction mixture still being more complex, as two different vinyllithium compounds are formed upon partial hydrolysis, as was shown for 3-octyne.[10] If bulky groups are connected to the triple bond, as in the case of di-*tert.*-butylacetylene, no reaction with lithium dust can be observed, even when using forcing conditions.[10]

Table 1. Products of Derivatization of the Dilithioalkenes **33a-c**.

entry	alkyne	electrophile	product	yield[a] (%)	other products
1	**32a**	$(CH_3O)_2SO_2$	**34a**	78 (69)	12% of **42**
2	**32a**	$(C_2H_5O)_2SO_2$	**35a**	70[b]	14% **39,n=1**
3	**32a**	$(CH_3)_3SiCl$	**37a**	29 (21)	10% deriving from **31a**
4	**32a**	$(CH_3)_3SnCl$	**38a**	20	not determined
5	**32a**	PhCHO	**36a**	22 (16)[c]	not determined
6	**32b**	CH_3OD	**30b**	88[d]	85% d_2, 13%d_1, 2%d_0
7[10]	**32b**	$(CH_3O)_2SO_2$	**34b**	73	11% deriving from **31b**
8	**32b**	$(CH_3)_3SiCl$	**37b**	26[b]	13% deriving from **31b**
9[10]	**32c**	CH_3OD	**30c**	85	64%d_2, 30%d_1, 6%d_0
10	**32c**	$(CH_3)_3SiCl$	**37c**	28 (25)	7% deriving from **31c**

[a] the yields given are not optimized and have been determined by GC analysis using n-alkanes as internal standards, numbers in brackets are isolated compound. [b] purified for spectroscopical analysis by preparative gas chromatography. [c] a mixture of meso and d,l compound was expected, the isolated compound, however, shows only one set of signals in the ^1H nmr and ^{13}C nmr spectrum. [d] the reaction mixture was filtered and the remainder carefully washed before quenching with CH_3OD, the filtrate only contained 2% of **32b** and 3% of **30b**.

Furthermore the stability of the dilithioalkene **33a** was investigated. After reacting a solution of 3-hexyne (**32a**) in diethyl ether with an excess of lithium metal for 664 hours and subsequent workup with dimethyl sulphate still a small amount (7%) of (E)-3,4-dimethyl-3-hexene (**34a**) was found, thereby a half-life of about 260 hours in diethyl ether can be calculated. n-Butyllithium for comparison has a half-life of 150 hours[23] in the same solvent. Besides mainly polymeric material (51%), 10% of (E)-3-methyl-3-hexene (**42**), and 5% of (E)-3-hexene (**30a**), a series of hydrocarbons (**39**,n=1-4 and **41**) in 11, 8, 2, 1, and less than 1% respectively, was identified, which allows to understand the main pathway of decomposition of the vicinal dilithioalkenes in diethyl ether: The dilithioalkene deprotonates slowly the solvent to ethylene and lithium ethoxide.[24] The even more stable, soluble vinyllithium compound **31a** reacts then under insertion of up to four ethylene molecules,[25] which are again protonated by the solvent. Only **40**,n=1 is present to such an extent that it can be detected as methyl derivative by the workup with dimethyl sulphate. There is no evidence, however, for the elimination of lithium hydride, a well known decomposition pathway of polylithiumorganic compounds,[26] especially in the case of geminal dilithioalkanes.[27] In the following experiment described, the product of lithium hydride elimination **43** was obtained independently by deprotonation of the starting alkyne **32a** and was shown to be stable and detectable under the reaction conditions.

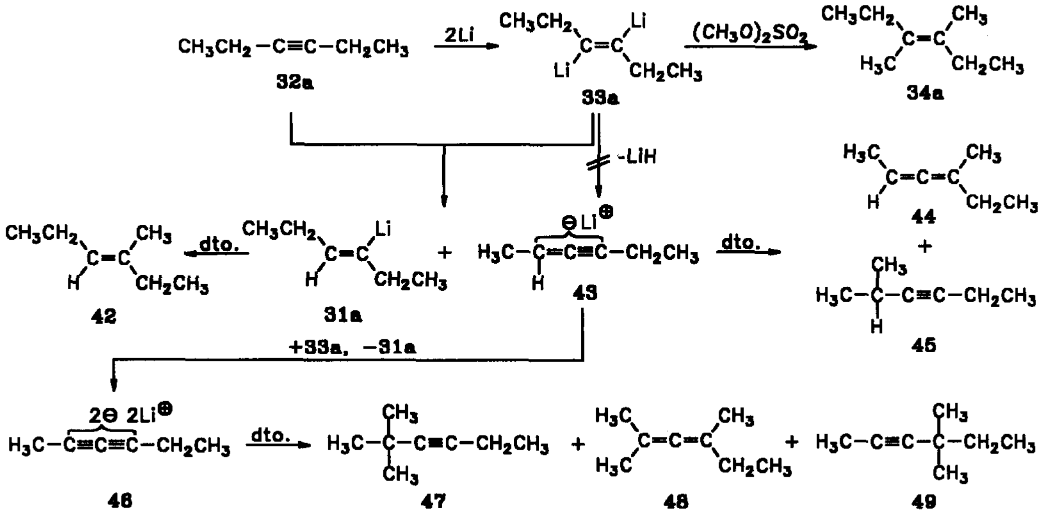


The latter result shows clearly the high stability of the (E)-dilithioalkenes. A major drawback is the presence of the excess of lithium metal during the workup, as side reactions have to be anticipated and are responsible for the but moderate yields in Table 1. It is known, for example, that organotin compounds react with lithium metal.[28] Therefore we attempted the synthesis of the (E)-dilithioalkene **33a** by using equimolar amounts of lithium metal, for comparison half an equivalent of lithium metal was employed and the alkyne was treated with butyllithium, as deprotonation products were expected. The results are shown in Table 2.

Table 2. **Products in the Reaction of 3-Hexyne (32a) with 0.5 and 1 Equivalent of Lithium Metal.**

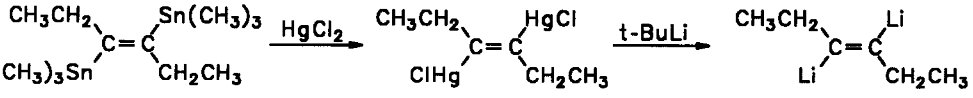
compound[a]	yield[b] (%) 1[c] ratio 32a/Li=1/1	 2[c] ratio 32a/Li=1/2	 3[d] ratio 32a/butyllithium=1/2.5
3-hexyne **32a**	12.6	15.3	-
(E)-3-hexene **30a**	5.5	7.3	-
(E)-3-methyl-3-hexene **42**	2.6	14.3	-
(E)-3,4-dimethyl-3-hexene **34a**	-	3.5	-
4-methyl-2,3-hexadiene **44**	7.1	5.4	21.3
2-methyl-3-hexyne **45**	1.2	0.5	6.6
unidentified isomer to **44** and **45**	-	-	0.9
4,4-dimethyl-2-hexyne **49**	0.4	1.5	4.7
2,4-dimethyl-2,3-hexadiene **48**	2.8	5.9	33.2
2,2-dimethyl-3-hexyne **47**	0.5	1.4	6.3

[a] in order of elution, no other mono- and dimethyl derivatives have been found. [b] yields have been determined by GC analysis using an internal standard, the remainder is not volatile and probably of polymeric nature. [c] reaction time 7 days. [d] reaction time 5 days.



The dilithioalkene **33a**, which is formed to a small extent only, reacts with the starting material **32a** under protonation to the monoanion **43**, and in a second step to the dianion **46**, both being resonance stabilized. Therefore two monomethyl and three dimethyl derivatives are found, when the reaction mixture is quenched with dimethyl sulphate. Surprisingly 3-hexyne (**32a**) can be metallated twice with n-butyllithium contradictory to the exclusive monometalation reported earlier.[29]

This procedure, however, is obviously not a useful method of obtaining vicinal dilithioalkenes free of lithium metal, but we were successful in synthesizing **33a** by metal metal exchange reaction: The tin compound **38a** was treated with mercury chloride[30] and the insoluble 3,4-bis(chloromercurio)-3-hexene (**50**) was treated with an excess of *tert.*-butyllithium to **33a**. This reaction was performed under various conditions, the results are summarized in Table 3.



38a **50** **33a**

Table 3. Reaction Conditions and Products in the Synthesis of **33a** by Lithium Mercury Exchange.

entry	1	2	3[a]	4[b]
solvent	Et_2O	pentane	pentane	Et_2O
electrophile	$(C_2H_5O)_2SO_2$	$(C_2H_5O)_2SO_2$	$(C_2H_5O)_2SO_2$	$(CH_3O)_2SO_2$
maximum reaction temperature	0°C	20°C	20°C	20°C
product	71% **35a**	44% **35a**	52% **35a**	64% **34a**
product of monosubstitution	13%	6%	5%	not determined

[a] the reaction mixture was decanted and the remainder washed and quenched with diethyl sulphate, the decanted solution and the combined washings were independently quenched with diethyl sulphate and 4% of **35a** were obtained. [b] in a blind experiment (*tert.*-butyllithium/diethyl ether/dimethyl sulphate) an isomeric and coeluting hydrocarbon to **42** is formed, therefore the yield of **42** could not be determined exactly.

When an excess of *tert.*-butyllithium is added to a slurry of **50** in the appropriate solvent and allowed to warm up to the temperatures given in Table 3 a color change of the colorless suspension to a greenish black is observed already at -60°C in diethyl ether and at -10°C in pentane. The yields too are better using the more polar solvent. From these results the following conclusions can be drawn: The dilithioalkene **33a** is a stable insoluble compound at room temperature, the presence of metallic lithium is not necessary for the stability. The stepwise mercury lithium exchange can be excluded in entry 1 and 4 as *tert.*-butyllithium reacts violently with diethyl ether already at about -30°C,[23] and in entry 3 as the excess of *tert.*-butyllithium was decanted. Entry 4 shows clearly that no isomerization at all occurs during the whole reaction sequence, the 3,4-dimethyl-3-hexene (**34a**) is obtained as pure (E)-isomer.

As a consequence of the different behaviour of cyclooctyne (**14**), which forms the soluble (Z)-dilithioalkene **16** and simple aliphatic internal alkynes, which form insoluble (E)-dilithioalkenes, we put our investigation forward to the reaction of cyclodecyne (**51**) and cyclododecyne (**55**). We choose these cycloalkynes as **51** still exhibits a small ring strain of about 10-15 kJ/mol,[9] and **55** has been used as a model compound for an unstrained cycloalkyne,[31] on the other hand, both compounds are available with a reasonable expenditure by well-known literature procedures.[32,33] Both cycloalkynes are treated with lithium dust in diethyl ether using the same conditions as employed for the aliphatic alkynes. The results of the products obtained after hydrolysis are summarized in Table 4.

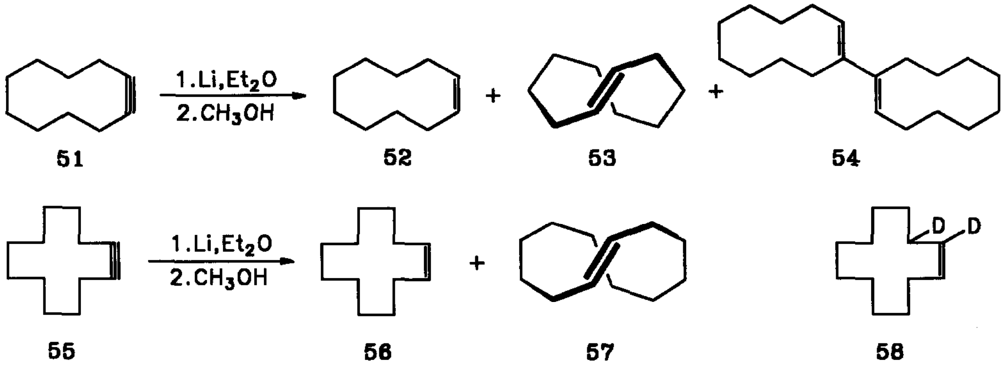


Table 4. Reaction of the Cycloalkynes 51 and 55 with Lithium Metal and Subsequent Hydrolysis.

compound[a]	entry 1 reaction of 51 in Et_2O for 24 hours	entry 2 reaction of 55 in Et_2O for 36 hours
starting alkyne	3% of 51	32% of 55
(Z)-cycloalkene	35% of 52	16% of 56
(E)-cycloalkene	2% of 53	39% of 57
Z/E-ratio	95:5[b]	27:73[c]
dimeric product	26% of 54	-
not identified	15%	4%

[a] the remainder is non volatile and and probably of polymeric nature. [b] determined by GC analysis. [c] determined by GC analysis and ^{13}C nmr spectroscopy.

It is interesting to note that only in the reaction of cyclodecyne (51) the product of dimerization 54 is obtained. This can be easily understood as the π^*-orbitals (LUMO) of the strained cycloalkynes 14 and 51 are not degenerated, especially the energy of the $\pi_{||}^*$-orbital parallel to the ring plane is lowered as much as 1.1 eV in the case of 14, compared to an unstrained aliphatic alkyne.[9] Therefore the primarily formed radical anion (in the reaction of cyclooctyne: 15) can be considered more stable and longer living so that a substantial amount of 18 and 54 is found. The Z/E-ratios determined in the above reactions are similar to those obtained in the investigations of the thermodynamic stabilities of the cycloalkenes,[35] the reported values are 94:6 for 52/53 and 35/65 for 56/57 respectively.

To answer the question if there is a relation between the geometry of the dilithioalkenes and the solubility, cyclododecyne (**55**) was reacted with lithium metal and, after filtration of the reaction mixture, filtrate and remainder were independently quenched with methanol-d_1. The results are given in Table 5.

Table 5. Reaction of Cyclododecyne (**55**) with Lithium Metal and Subsequent Deuterolysis.

	entry 1	entry 2
compound[a]	reaction of **55** in Et_2O for 48 hours[b]	reaction of **55** in pentane for 20 hours
<u>filtrate</u>		
cyclododecyne **55**	25% (undeuterated)	15%
(Z)-cyclododecene **56**	14% (about 30% d_1, 70% d_0)	-
(E)-cyclododecene **57**	37% (about 30% d_1, 70% d_0)	-
not identified	8%	12%
<u>remainder</u>		
(Z)-cyclododecene **58**	-	52% (1% d_0, 4% d_1, 93% d_2, 2% d_3)[c]
not identified[d]	5%	4 %

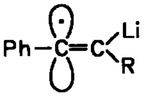
[a] the remainder is non volatile and and probably of polymeric nature. [b] when reducing the reaction time, similar results were obtained, the amount of **55**, however, increases remarkably. [c] when repeating this experiment 4% d_1, 92% d_2, and 4% d_3 were found for **58**. [d] containing traces of **55**, **57**, and in entry 1, of **56** as well.

From these results the clear conclusion can be drawn, that both (E)- and (Z)-1,2-dilithio-1-cyclododecene are soluble in diethyl ether and react even faster with the solvent as being generated. We were, however, much surprised when we switched to the less acidic solvent pentane and a shorter reaction time (entry 2), here, besides traces of unidentified material and starting material, the only insoluble product was (Z)-cyclododecene **58**. The structure of **58** was unambiguously proved by ^1H, ^2H, and ^{13}C nmr data, together with the mass spectroscopical evidence. The isomerization of 1,2-dilithio-1-cyclododecene to the resonance stabilized and insoluble 2,3-dilithio-1-cyclododecene, however, is not very probable, as inter- and intramolecular metalation reactions require polar solvents.[35] Thus isomerization of the sluggishly reacting cycloalkyne **55** to 1,2-cyclododecadiene, catalyzed by a primarily formed lithiumorganic intermediate has to be taken into account. Addition of lithium metal to the allene and subsequent workup with methanol-d_1 would lead directly[36] to **58** and has not been excluded experimentally.

Conclusions

From all these pieces of evidence a general picture of the addition of lithium to carbon carbon triple-bonds can be drawn. In a first reduction step an intermediate vinyl radical anion **59**/**60** or **61** respectively, is formed, which already defines the geometry of the dilithioalkene. Analogous to the known differentiation between σ- and π-radicals,[37,38] we conceive the formation of σ- and π-radical anions, having comparable stabilities as the corresponding alkenes itself. The geometry of the dilithioalkene is determined at this step, as the Z/E-isomerization of the dilithioalkenes was experimentally disproved.[5] In strained cycloalkynes the cycloalkene radical anion is stabilized due to the release of ring strain and therefore the formation of dimeric products is posssible.

59 **60**



61

In alkyl substituted vinyl radical anions, which are sp^2 hybridized, a very fast inversion (59 $\rightleftharpoons$ 60) takes place, in the next reduction step the thermodynamically stable (E)-dilithioalkene is formed. Phenyl substituted radical anions as 61 are sp hybridized and planar,[39] this radical anion reacts further by lithium attack to the more stable (Z)-dilithioalkene,[40] as additional stabilization by a doubly bridged structure as in **13** has to be anticipated and Z/E isomerization is possible even at low temperatures as demonstrated by the transmetalation of **4** to **2**.[3,4]

Summary

Simple internal aliphatic alkynes react with an excess of lithium metal quantitatively and stereoselectively to vicinal (E)-dilithioalkenes, which owe their stability at room temperature to their insolubility in the solvents employed. If necessary, these (E)-dilithioalkenes can be obtained free of lithium metal by using the mercury lithium exchange procedure. By treating the dilithioalkenes with a number of electrophiles the corresponding (E)-olefins are yielded. (Z)- and (E)-dilithiocycloalkenes, as far as we know, are soluble under the same reaction conditions and show fast deprotonation of the solvent or other side reactions.

Experimental

General Methods. All reactions with air sensitive compounds were carried out under an atmosphere of dried argon (99.996%). Etherial solvents were purified by adsorptive filtration over basic aluminium oxide (activity I) and freshly distilled under argon from sodium-benzophenone ketyl. Pentane, cyclopentane, and the commercially available alkynes **32a-c** were freshly distilled from sodium prior to use. Mass spectra were obtained on a Varian MAT 112 (OV 101 capillary); m/z values are reported followed by the relative intensity in parantheses. Nuclear Magnetic Resonance (^{1}H, ^{2}H, and ^{13}C) spectra were recorded on the Bruker instruments WP 80 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), m(multiplet). Separations of the reaction mixtures were performed using a prepaprative gas chromatograph (Hupe und Busch, HP 1075c prep. GC) using the following packings: 10% SE30 on Chromosorb W45/60, 15% SE52 on Chromosorb W60/80, 10% DEGS on Chromosorb W45/60, 20% DEGS on Chromosorb W60/80, and 20% Carbowax 1000 on Chromosorb W45/60. For the analysis of the low boiling mixtures of unsaturated hydrocarbons 15% SE30 on Chromosorb W80/100 and 10% of a saturated solution of $TlNO_3$ in PEG 400 on Chromosorb P NAW45/60 were employed. For analytical gas chromatography a Siemens L350 with a Spectra Physics 4001 integrator and a HP 5890 with a HP 3396A integrator, both with FID, were employed.

General procedure for the synthesis of the (E)-dilithioalkenes 33a-c. In a 150 ml Schlenk flask, equipped with a reflux condenser, a dropping funnel, and a mercury filled outlet, 10 mmol of the alkyne in about 20 ml of solvent were efficiently magnetically stirred with 50 mmol of lithium dust (2% sodium)[18] at room temperature. The reaction can be upscaled, in this case, however, the alkyne has to be added slowly to the suspension of the lithium dust at 0°C. When quenching with dialkyl sulphate, the reaction mixture was cooled to -40°C and a solution of the dialkyl sulphate was added dropwise. The reaction mixture was then allowed to warm to room temperature and was then, after cooling down to -40°C again, treated with 25% aqueous ammonia in order to destroy excess dialkyl sulphate. The aqueous layer was extracted several times with ether and the combined organic phases were washed with saturated ammonium chloride solution and brine, dried over magnesium sulphate, and the solvent removed. The crude product was, after recondensing, analyzed several times by either using the internal or an added external standard and subsequently subjected to GC-MS analysis.

(E)-3,4-Dimethyl-3-hexene (**34a**): Reaction scale 1.6 g (19.5 mmol) **32a** and 0.5 g (72 mmol) of lithium metal: 1.5 g (13.4 mmol) of a colorless liquid of b.p. 108-113°C (15 Torr), b.p.[41] 115-116°C (15 Torr). **MS** (70eV): m/z 112 (M$^+$, 54), 97(17), 83(100), 69(34), 56(17), 55(90), 43(14), 41(47), 29(13). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 0,95 (t, ^3J = 7.6 Hz, 6 H, methyl), 1.64 (s, 6 H, methyl), 2.03 (q, ^3J = 7.6 Hz, 4 H, allyl).**^{13}C NMR** (20 MHz, CDCl$_3$) δ 12.6, 17.2, 27.5, 129.1. *(E)-3-Methyl-3-hexene* (**42**): **MS** (70 eV): m/z 98 (M$^+$, 50), 83(28), 70(21), 69(100), 67(11), 56(27), 55(84), 53(10), 41(91), 39(19).

(E)-3,4-Diethyl-3-hexene (**35a**): Reaction scale 0.8 g (10 mmol) **32a** and 0.25 g (36 mmol) of lithium metal. The crude product was recondensed and purified by preparative gas chromatography. **MS** (70 eV): m/z 140 (M$^+$, 18), 111(19), 83(11), 70(8), 69(100), 55(54), 43(8), 41(32), 39(10), 29(13). **^{1}H NMR**[42] (80 MHz, CDCl$_3$) δ 0.96 (t, ^3J = 7.5 Hz, 12 H, methyl), 2.03 (q, ^3J = 7.5 Hz, 8 H, allyl). **^{13}C NMR** δ 13.6, 24.1, 135.6. *3-Ethyl-3-hexene*: (**39,n=1**): **MS** (70 eV): m/z 112 (M$^+$, 15), 84(7), 83(44), 70(7), 69(9), 56(7), 55(100), 41(32), 39(13). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 0.80-1.50 (m, 9 H, methyl), 1.80-2.50 (m, 6 H, allyl), 5.09 (t(br.), ^3J = 6.9 Hz, 1 H, vinyl). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 12.9, 13.4, 14.8, 20.8, 23.1, 29.2, 124.6, 142.2.

(E)-Bis(trimethylsilyl)-3-hexene (**37a**): Reaction scale: 0.7 g (8.5 mmol) **32a** and 0.5 g (72 mmol) of lithium metal. 0.4 g (1.8 mmol) of a colorless liquid with b.p. 86-89°C (15 Torr). **MS** (70 eV): m/z 228 (M$^+$, 1), 140(7), 125(6), 111(8), 73(100), 59(14), 45(10). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 0.17 (s, 18 H, SiMe$_3$), 0.93 (t, ^3J = 7.3 Hz, 6 H, methyl), 2.03 (q, ^3J = 7.3 Hz, 4 H, allyl). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 1.6, 16.3, 30.2, 155.0. *(E)-3-Trimethylsilyl-3-hexene* (**31a**, SiMe$_3$ instead of Li): **MS** (70 eV): m/z 156 (M$^+$, 11), 141(35), 99(25), 87(32), 83(13), 73(100), 59(38), 45(11).

(E)-4,5-Bis(trimethylsilyl)-4-octene (**37b**): Reaction scale: 2.0 g (18 mmol) **32b** and 0.5 g (72 mmol) of lithium metal. After removing the solvent in vacuo, the reaction mixture was recondensed and **37b** was isolated from the colorless crude product (3.0 g) by preparative gas chromatography. **MS** (70 eV): m/z 256 (M$^+$, 6), 241(4), 182(7), 168(8), 153(7), 125(17), 108(11), 73(100), 59(11), 45(8). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 0.16 (s, 18 H, SiMe$_3$), 0.91 (m, 6 H, methyl), 1.25 (m, 4 H, methylene), 2.18 (m, 4 H, allyl). **^{13}C NMR** (20 MHz, CDCl$_3$) δ 1.5, 14.2, 25.1, 40.2, 154.0. *(E)-4-Trimethylsilyl-4-octene* (**31b**, SiMe$_3$ instead of Li): **MS** (70 eV): m/z 184 (M$^+$, 10), 169(40), 127(15), 113(13), 110(38), 101(14), 99(23), 85(11), 73(100), 59(42), 45(11).

(E)-5,6-Bis(trimethylsilyl)-5-decene (**37c**): Reaction scale: 8.0 g (60 mmol) **32c** and 1.7 g (243 mmol) of lithium metal. The crude product was fractionated through a short Vigreux column at 0.1 Torr and crystallizes at m.p. 40-43°C, m.p.[43] 46-47°C. 3.6 g (13 mmol) of **37c**. **MS** (70 eV): m/z 284 (M$^+$, 1), 269(1), 182(2), 136(8), 112(2), 73(100), 59(12), 45(10), 43(2). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 0.15 (s, 18 H, SiMe$_3$), 0.85 (t, $^3J \approx$ 7.5 Hz, 6 H, methyl), 1.05-1.50 (m, 8 H, methylene), 2.00-2.40 (m, 4 H, allyl). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 1.5, 14.1, 25.1, 34.0, 37.7, 153.8. *(E)-5-Trimethylsilyl-5-decene* (**31c**, SiMe$_3$ instead of Li). **MS** (70 eV): m/z 212 (M$^+$, 1), 198(12), 197(3), 138(16), 99(5), 92(4), 81(4), 73(100), 59(28), 45(11).

(E)-3,4-Bis(trimethylstannyl)-3-hexene (**38a**): Reaction scale: 4.1 g (50 mmol) **32a** and 2.0 g (290 mmol) of lithium metal. After removing the solvent in vacuo, the crude product was recondensed and then distilled: 4.1 g (10 mmol) **38a**, b.p. 65-68°C (0.2 Torr), m.p. 35-37°C. **MS** (70 eV): m/z 404-416 (M^+, 1), 389-401(3), 243-251(36), 228-234(1), 161-169(100), the observed isotopic patterns are in accordance with the calculated patterns. **Anal.** calc. for $C_{12}H_{28}Sn_2$: C, 35.18; H, 6.89; found: C, 35.26; H, 6.67. **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.18 (s, 18 H, $SnMe_3$), 0.92 (t, ^3J = 7.2 Hz, 6 H, methyl), 2.24 (q, ^3J = 7.2 Hz, 4 H, allyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ -7.1, 15.9, 35.4, 155.6.

(E)-2,3-Diethyl-1,4-diphenyl-2-buten-1,4-diol (**36a**): Reaction scale: 0.8 g (10 mmol) **32a** and 0.50 g (72 mmol) of lithium metal. To the suspension of the dilithioalkene **33a** a solution of 7.5 g (70 mmol) benzaldehyde in 30 ml of diethyl ether was slowly added at 0°C and the reaction mixture heated to reflux for 3 hours. After adding of about 30 ml of water the aqueous layer was acidified with diluted hydrochloric acid, saturated with sodium chloride, and extracted with diethyl ether/THF (3:1). The combined organic phases were washed with brine and the solvent removed in vacuo. The remaining oil was subjected to column chromatography on basic aluminium oxide (activity I) with THF as solvent, 0.45 g (1.6 mmol) **36a** were obtained and recrystallized from methanol/pentane m.p. 177-180°C. The NMR data obtained from the crude product gave no evidence for another isomer. **MS** (70 eV): m/z 249 (M^+, 58), 173(35), 143(28), 131(13), 115(15), 107(32), 105(100), 91(43), 79(37), 77(43). **Anal.** calc. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; found: C, 81.22; H, 8.43. **^{1}H NMR** (80 MHz, DMSO-d_6) δ 0.80 (t, ^3J = 7.4 Hz, 6 H, methyl), 1.65-2.45 (m, 4 H, allyl), 5.33 (d, ^3J = 4.4 Hz, 2 H, OH), 5.61 (d, ^3J = 4.4 Hz, 2 H, methine) 7.20-7.40 (m, 10 H, phenyl). **^{13}C NMR** (20 MHz, DMSO-d_6) δ 16.0, 20.0, 70.3, 125.6, 126.2, 127.8, 138.6, 144.7.

Investigation of the decomposition of 33a in diethyl ether: Reaction scale: 0.8 g (10 mmol) **32a** and 0.4 g (57 mmol) of lithium metal, reaction time 664 hours at room temperature, workup as described above, separation was performed by preparative gas chromatography. Besides **34a** and **39,n=1** were found: *4-Ethyl-3-octene* (**39,n=2**): **MS** (70 eV): m/z 140 (M^+, 16), 98(19), 83(24), 71(60), 69(66), 56(13), 55(100), 43(12), 41(38), 39(11). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.80-1.20 (m, 9 H, methyl), 1.20-1.50 (m, 4 H, methylene), 1.80-2.25 (m, 6 H, allyl), 5.09 (t(br.), ^3J = 6.9 Hz, 1 H, vinyl). **^{13}C NMR** (20 MHz, $CDCl_3$) δ 12.9, 14.1, 14.8, 20.9, 22.9, 29.5, 29.9, 30.9, 125.1, 140.6. *(E)-4-Ethyl-3-decene* (**39,n=3**): **MS** (70 eV) m/z 168 (M^+, 12), 98(37), 83(42), 70(90), 69(59), 67(13), 57(13), 56(18), 55(199), 43(20), 41(36). *(E)-4-Ethyl-3-dodecene* (**39,n=4**): **MS** (70 eV): m/z 196 (M^+, 4), 98(48), 97(15), 83(33), 70(100), 69(56), 57(22), 55(98), 43(27), 41(45). *(E)-4-Ethyl-3-heptene* (**41**): **MS** (70 eV): m/z (126 (M^+, 16), 97(33), 83(17), 70(9), 69(35), 56(9), 55(100), 41(29), 39(11).

Reaction of 3-hexyne (32a) with an equimolar amount of lithium. Entry 1: 2.4 g (29 mmol) **32a** and 105 mg (15 mmol) of lithium metal were reacted in 30 ml of diethyl ether for 7 days at room temperature, whereby a white solid was formed. The derivatization with dimethyl sulphate was performed as above. Entry 2: 1.2 g (15 mmol) **32a** and 105 mg (15 mmol) of lithium metal were reacted in 20 ml of diethyl ether at room temperature for 7 days. Together with the white solid there were still small amounts of metal present. Entry 3: 1.6 g (20 mmol) **32a** in 30 ml of diethyl ether were cooled down to -80°C and 35 ml of a 1.5M solution of n-butyllithium (53 mmol) in hexane were added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for another 5 days. After 3 days a white precipitate was formed which could not be filtered off. Derivatization with an excess of dimethyl sulphate was performed as described above:

4-Methyl-2,3-hexadiene (**44**)[44]: **MS** (70 eV): m/z 96 (M^+, 67), 81(99), 79(24), 67(47), 65(20), 55(33), 53(33), 41(100), 39(61). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.02 (t, ^3J = 7.5 Hz, 3 H, methyl), 1.63 (d, ^3J = 7.5 Hz, 3 H, methyl), 1.68 (d, $^5J \approx 3.0$ Hz, 3 H, methyl), 1.93 (dq, ^3J = 7.5 Hz, $^5J \approx 3.0$ Hz, 2 H, allyl), 5.01 (m, 1 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 12.2, 15.0, 19.1, 27.0, 85.1, 100.5, 201.5.

2-Methyl-3-hexyne (**45**)[45]: **MS** (70 eV): m/z 96 (M^+, 54), 81(100), 79(37), 67(37), 65(15), 55(26), 53(58), 41(66), 39(36). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.03 (t, ^3J = 7.5 Hz, 3 H, methyl), 1.25 (d, ^3J = 7.1 Hz, 6 H, methyl), 2.17 (m, 2 H, methylene), 1.90-2.30 (m(br.), 1 H, methine).

2,2-Dimethyl-3-hexyne (**47**)^{45}: **MS** (70 eV): m/z 110 (M^+, 37), 95(100), 93(12), 81(16), 77(15), 67(64), 55(56), 53(24), 41(43), 39(21). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.11 (t, ^3J = 7.6 Hz, 3 H, methyl), 1.20 (s, 9 H, methyl), 2.16 (q, ^3J = 7.6 Hz, 2 H, methylene).
2,4-Dimethyl-2,3-hexadiene (**48**): **MS** (70 eV): m/z 110 (M^+, 100), 95(72), 81(65), 79(17), 77(19), 67(73), 55(61), 53(59), 41(71), 39(42). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.96 (t, ^3J = 7.3 Hz, 3 H, methyl), 1.63 and 1.64 (s, 3 H and 6 H, methyl), 1.90 (q, ^3J = 7.3 Hz, 2 H, allyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 12.5, 19.3, 21.0, 27.4, 94.4, 98.8, 198.4.
4,4-Dimethyl-2-hexyne (**49**)^{45}: **MS** (70 eV): m/z 110 (M^+, 17), 95(30), 81(100), 80(12), 79(13), 67(18), 55(18), 53(23), 41(26), 39(15). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.95 (t, $^3J \approx$ 7.0 Hz, 3 H, methyl), 1.14 (s, 6 H, methyl), 1.39 (q, $^3J \approx$ 7.0 Hz, 2 H, methylene), 1.85 (s, 3 H, methyl).

3,4-Bis(chloromercurio)-3-hexene (**50**): To a solution of 3.0 g (11 mmol) of mercury chloride in 50 ml of dry acetone were added 1.5 g (3.7 mmol) **38a** at room temperature . After 30 min the white precipitate formed was filtered off, washed with hot acetone and dried over phosphorus pentoxide. 1.9 g (3.4 mmol = 94%) of the light-sensitive **50** with m.p. > 320°C were isolated. **50** could only be solubilized to a small extent upon warming in DMSO, thereby crude NMR data could be obtained, **50**, however slowly decomposed in this solvent. **MS** (70 eV): m/z 549-560 (M^+, <0.1), 315-323(25), 82(87), 67(100), the observed isotopic patterns are in accordance with the calculated patterns. **Anal.** calc. for $C_6H_{10}Hg_2Cl_2$ C, 13.00; H, 1.76; Hg, 72.38; Cl, 12.79; found (C, H, Hg, Cl = 100%): C, 12.95; H, 1.76; Hg, 72.85; Cl, 12.44. **^{1}H NMR** (80 MHz, DMSO-d_6) δ 0.91 (t, ^3J = 7.1 Hz, 6 H, methyl), 1.64 (q, ^3J = 7.1 Hz, 4 H, allyl). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 16.0, 35.2, 157.1.

Lithium mercury exchange. Entry 1: The reaction was performed in the same apparatus as described above, instead of the dropping funnel a rubber septum was used and the reagents were added via a gas tight syringe. 300 mg (0.55 mmol) **50** were suspended by magnetical stirring in 6 ml diethyl ether and cooled to -80°C, then 5 ml of a 1.1M solution of *tert.*-butyllithium (5.5 mmol) in pentane was added dropwise. The temperature of the reaction mixture was allowed to rise slowly to 0°C, at -60°C a color change to a greenish black was observed, at about -30°C ethylene formed by the decompositon of the solvent by the excess of *tert.*-butyllithium evolved. The workup with diethyl sulphate was performed as described above, the crude mixture was analyzed by gas chromatography using n-decane as external standard. Found 55 mg (0.39 mmol = 71%) **35a** and 8 mg (0.07 mmol =13%) **39,n=1**.
Entry 2: 350 mg (0.63 mmol) **50** in 5 ml pentane and 4 ml of a 1.1M *tert.*-butyllithium solution (4.4 mmol) in pentane were reacted as described in entry 1. The color change was observed at -10°C, the formation of gaseous products was not observed, when the reaction temperature was allowed to rise to room temperature. Found: 39 mg (0.28 mmol = 44%) **35a** and 4 mg (0.04 mmol = 6%) **39,n=1**.
Entry 3: 300 mg (0.55 mmol) **50** in 10 ml pentane were reacted analogous with 14.5 ml of a 1.1M solution of *tert.*-butyllithium (16 mmol) in pentane. After reaching room temperature and settling of the solid, the solution was decanted (attempts to filtrate the whole reaction mixture were not successful), the solid suspended with another portion of pentane (5 ml) and decanted again. The combined solutions and the solid were derivatized independently. Found in solution: 3 mg (0.02 mmol = 4%) **35a**, **39,n=1** not detected. Solid: 40 mg (0.29 mmol = 52%) **35a** and 4 mg (0.03 mmol = 5%) **39,n=1**.
Entry 4: 300 mg (0.55 mmol) **50** in 6 ml diethyl ether were reacted as described in entry 1 with 3 ml of a 1.1M solution of *tert.*-butyllithium (3.3 mmol) in pentane. Derivatization was performed with an excess of dimethyl sulphate in diethyl ether. Found 35 mg (0.31 mmol = 57%) **34a**, the corresponding (Z)-isomer was not detected.

Reaction of the cycloalkynes 51 and 55. Entry 1: 0.9 g (7mmol) **51** were magnetically stirred with 0.3 g (43 mmol) of lithium metal in 20 ml diethyl ether for 24 hours at room temperature. The reaction mixture was then cooled down to -80°C and quenched with a 10% solution of methanol in diethyl ether. The crude mixture was analyzed after the usual workup by GC-MS coupling and the Z/E-ratio was determined by gas chromatography. The main product **52** was isolated by preparative gas chromatography.

(Z)-Cyclodecene (**52**)[32,46]: **MS** (70 eV): m/z 138 (M^+, 30), 96(37), 95(48), 82(69), 81(70), 68(58), 67(100), 55(81), 54(87), 41(53). **^1H NMR** (80 MHz, $CDCl_3$) δ 1.03-1.80 (m, 12 H, methylene), 2.07-2.42 (m, 4 H, allyl), 5.20-5.60 (m, 2 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.9, 25.1, 26.1, 26.9, 129.9.

(E)-Cyclodecene (**53**): **MS** (70 eV): m/z 138 (M^+, 23), 96(26), 95(41), 82(57), 81(77), 68(53), 67(100), 55(83), 54(88), 41(59).

1,1-Bicyclodecenyl (**54**): **MS** (70 eV): m/z 274 (M^+, 29), 125(80), 107(45), 95(75), 94(45), 93(63), 82(86), 81(100), 79(55), 67(86), 55(61).

Entry 2: 1.0 g (6 mmol) **55** were treated with 0.3 g (43 mmol) lithium metal in 20 ml diethyl ether for 36 hours at room temperature. The hydrolysis was performed identical to entry 1. The Z/E-ratio was determined by GC analysis and the crude reaction mixture subjected to GC-MS coupling. The mixture of **56** and **57** was isolated by preparative gas chromatography and the Z/E-ratio confirmed by integration of the ^{13}C NMR spectrum, the signals were assigned by comparison with literature data.[46]

(Z)-cyclododecene (**56**)[46]: **MS** (70 eV): 166 (M^+, 31), 96(67), 95(46), 82(87), 81(71), 68(48), 67(100), 55(87), 54(66), 41(71). **^1H NMR** (80 MHz, $CDCl_3$) mixture of **56** and **57** δ 0.90-1.70 (m, 16 H, methylene), 1.92-2.20 (m, 4 H, allyl), 5.23-5.48 (m, 2 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.8, 22.1, 24.0, 24.4, 27.0, 130.4. *(E)-cyclododecene* (**57**)[46]: **MS** (70 eV): 166 (M^+, 29), 96(61), 95(44), 82(92), 81(70), 68(47), 67(100), 55(94), 54(71), 41(73). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 24.6, 25.0, 25.6, 26.3, 32.1, 131.4.

(Z)-cyclododecene-d_2 (**58**): 0.3 g (2mmol) **55** were reacted with 0.25 g (36 mmol) of lithium metal for 20 hours at room temperature. The reaction mixture was filtered, the remainder suspended in pentane and quenched with methanol-d_1 at -80°C. The crude reaction mixture was analyzed by GC-MS coupling and the main product isolated by preparative gas chromatography. **^1H NMR** (80 MHz, $CDCl_3$) δ 1.40 (s(br.), 16 H, methylene), 1.95-2.30 (m, 3 H, allyl), 5.40 (t(br.), 1 H, vinyl). **^2H NMR** (61.4 MHz, $CDCl_3$) δ 2.11 (s(br.) 1 D, allyl), 5.36 (s(br.), 1D, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.1, 23.5(t), 23.9, 24.4, 24.6, 26.9, 27.0, 129.9(t), 130.2.

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