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Polylithiumorganic Compounds - 23.[1]

3,4-Dilithio-1,2-butadienes by Addition of Lithium Metal to 1,4-Unsymmetrically Substituted Butatrienes

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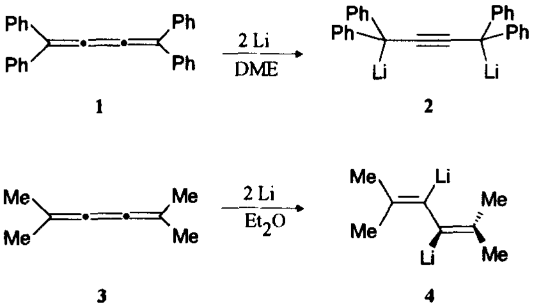
Abstract: *The synthesis of the highly reactive 1,4-unsymmetrically substituted butatrienes **12a-c** is described. When employing a strict synthetic protocol, these alkatrienes react with lithium metal to 3,4-dilithio-1,2-butadienes **20a-c** as stable intermediates. The structure of **20** is supported by IR and NMR spectroscopic evidence. The same dianionic intermediate can be prepared in one case by double deprotonation of the 1,2-butadiene **19**. Upon derivatization, either 3,4-disubstituted 1,2-butadienes **24**, 2,3-disubstituted 1,3-butadienes **25**, or 1,4-disubstituted 2-butynes **26** are formed, depending on the nature of the electrophile employed.*

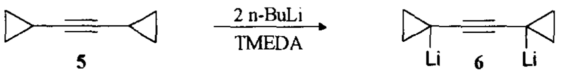
Introduction

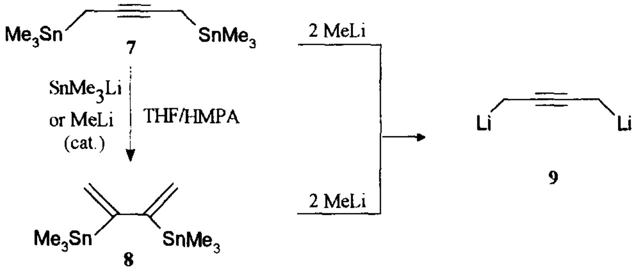
Reductive metalations of di- and tetra-aryl substituted butatrienes with alkali metals are known as far back as 1962.[3] Zweig and Hoffmann[4] as well as Day and coworkers[5-7] reported on the reductions of tetraarylbutatrienes; the reaction of 1,1,4,4-tetraphenylbutatriene (**1**) with lithium metal afforded the 1,4-dilithio-2-butyne derivative **2**, according to the products obtained after derivatization.[8] The reaction, however, proceeded only in poor yield and only when using 1,2-dimethoxyethane (DME) as solvent, in diethyl ether no reaction at all was observed.[4]



Tetra-alkyl substituted butatrienes, e.g. **3**, react in nearly quantitative yield in diethyl ether with commercially available lithium sand to the corresponding 2,3-dilithio-1,3-butadienes.[9,10] In these cases an apolar solvent like pentane works equally well. The electronic structure of **4** as a 2,3-dilithio-1,3-butadiene in the solid state and in solution was proved by an X-ray analysis of **4**[11] and by NMR investigations of solubilized crystals of **4** in perdeuterated diethyl ether or THF.[12,13] It has to be kept in mind that **4** is not a planar molecule, the cluster consisting of four 2,3-dilithio-1,3-butadienes **4** shows the two vinyllithium subunits to be nearly orthogonal to each other in the solid state.[11]

Besides reductive metalation of butatrienes the double metalation (hydrogen lithium exchange) of suitable precursors leads to the same dianionic intermediate. Köbrich and coworkers investigated in detail the mono- and dimetalation of differently substituted cyclopropylacetylenes.[14-16] It was found that dicyclopropylacetylene (**5**) can be metalated twice (to **6**) employing butyllithium in the presence of TMEDA (N,N,N',N'-tetramethylethylene diamine) and THF as solvent.[14] According to the products obtained after derivatization and NMR investigations[17] of the dilithio intermediate the 1,4-dilithio-2-butyne structure is reasonably assumed. Alkyl substituted cyclopropylacetylenes (as 1-cyclopropyl-1-propyne, 1-cyclopropyl-1-butyne, or 1-cyclopropyl-3-methyl-1-butyne) do react only with one equivalent of butyllithium even when using forcing reaction conditions.[15]

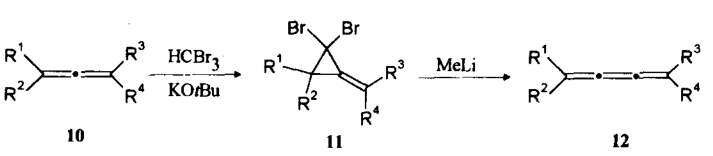




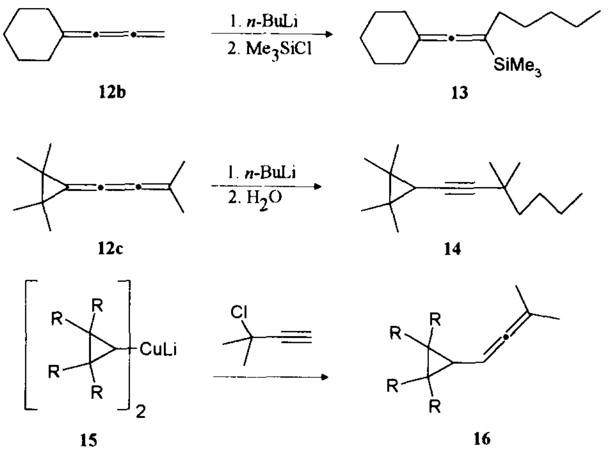
A third approach to the dianionic intermediate involves a double tin lithium exchange. Thus, starting from either 1,4-bis(trimethylstannyl)-2-butyne (**7**) or 2,3-bis(trimethylstannyl)-1,3-butadiene (**8**), which, by the way, is obtained by anion catalyzed isomerization of **7**, the same intermediate is obtained, which has been assigned the 1,4-dilithio-2-butyne structure **9**.[18a] A detailed NMR spectroscopic investigation of the oligo- or polymeric aggregates formed by **9** in solution confirms this assignment.[18b]

Obviously the dianionic intermediate can be best described as a 1,4-dilithio-2-butyne derivative **22** when the substituents in 1- and 4-position of the butatriene framework are stabilizing by either an increased p-character (**6**) or by resonance (**2**) or not destabilizing as in **9**. Alkyl substituents, on the other hand, destabilize the negative charge in 1- and 4-position, the 2,3-dilithio-1,3-butadiene structure of **4** was proved unambiguously, as described above. In this - admittedly simplifying - model, which does not consider the oligomeric nature of the polylithiumorganic species based on solvent and/or intermolecular aggregation or even intramolecular interactions of the lithium atoms, which might enhance the stability of polylithiumorganic compounds,[19-21] the question arises if a suitable choice of push and pull substituents would allow the synthesis of the hitherto unknown 3,4-dilithio-1,2-butadienes **20** or **23**, respectively. Here we report on our results in the reductive metalation of the unsymmetrically substitued butatrienes **12a-c** with lithium metal, and the attempted double deprotonation of the unsymmetrically substituted allenes **16a,b** and **19**.

Starting materials



	R^1,R^2	R^3,R^4
a	Me	H
b	$(CH_2)_5$	H
c	Me	$(CMe_2)_2$



a) R=H, b) R=Me

Preliminary experiments with unsubstituted butatriene showed that this very reactive alkatriene can not be transformed to **9** upon treatment with lithium metal. When reacting a solution of butatriene in either pentane, diethyl ether, or THF with lithium metal complete polymerization could be observed when working at temperatures between -100 °C and +20 °C.[17] Additionally it is known that butatrienes with phenyl substituents on only one side (e.g. 4-methyl-1,1-diphenyl-1,2,3-pentatriene) tautomerize already during their synthesis to ene-allenes (4-methyl-1,1-diphenyl-1,2,4-pentatriene),[22] heterofunctionalized butatrienes are known to be unstable under the conditions of reductive metalation and eliminate e.g. alkali metal alkoxides[23] or react under reductive dimerization[7] and can therefore not be employed in our quest.

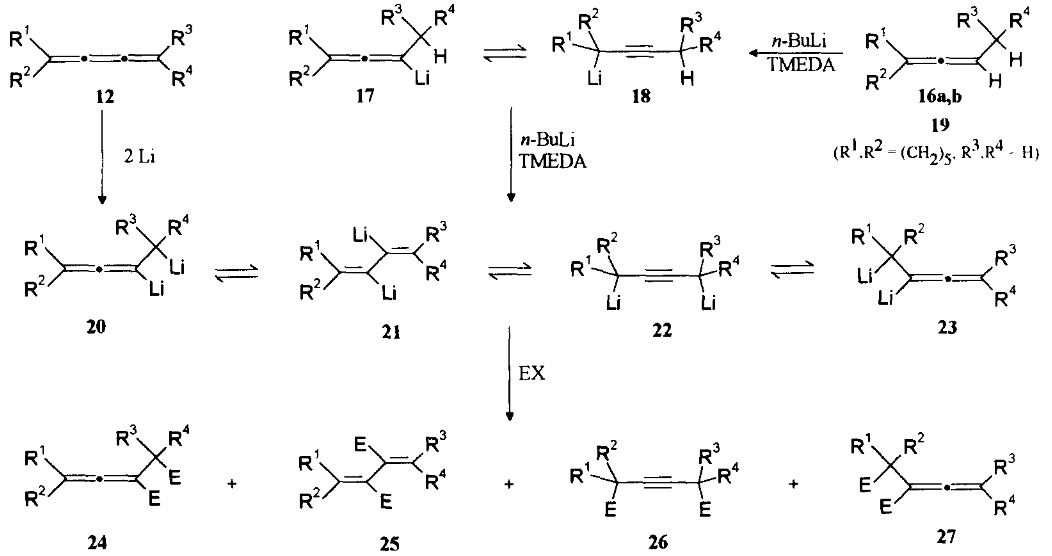
Thus we considered the reaction of the unfunctionalized hydrocarbons 4-methyl-1,2,3-pentatriene (**12a**),[24] 1,1-pentamethylenebutatriene (**12b**), and 1-(3-methyl-1,2-butadienylidene)-2,2,3,3-tetramethylcyclopropane (**12c**) with lithium metal, which fulfill the electronic requirements discussed above. These alkatrienes can be obtained in a uniform, optimized synthetic sequence - which is shorter as the sequence reported earlier for

12a[24] - from the corresponding allenes **10** and consists of carbene insertion to **11** and rearrangement of the carbenoids, which are formed upon treatment with methyllithium.

These butatrienes are very sensitive to acid, base, or radicals like oxygen; **12a** polymerizes even when stirred for a prolonged period at -60 °C with strict exclusion of air as a diluted solution in diethyl ether. **12c** is much more stable, at 20 °C a half-life of about 9 hours as a 0.1 M solution in diethyl ether is determined. With butyllithium, addition with formation of the allenes **13** and **14**, respectively, is observed, by attack to the least hindered end of the corresponding cumulene unit. This indicates quite clearly the high reactivity of the trienes, as a number of substituted allenes can be metalated with butyllithium without any formation of addition products.[25-28] The allenes **16a,b** were synthesized by copper(I) mediated coupling of the cyclopropyllithium compounds **15a,b** to 3-chloro-3-methyl-1-butyne; this reaction sequence is shorter than the synthesis described by Minter for **16a**.[29] The synthesis of 1,1-pentamethylene-1,2-butadiene **19** from 1-chloro-1-(2-propinyl)-cyclohexane is described elsewhere.[30]

Results and Discussion

When reacting a solution of either **12a** or **12b** with lithium metal employing conditions which proved successful in the synthesis of **4**, i.e. adding a solution of the triene **3** in diethyl ether to commercially available lithium sand in refluxing diethyl ether,[9] exclusive formation of polymeric material is observed.



	R^1,R^2	R^3,R^4
a	Me	H
b	$(CH_2)_5$	H
c	Me	$(CMe_2)_2$

EX = H_2O, D_2O, Me_3SiCl, Me_3SnCl, $(MeO)_2SO_2$, H_2CO, Me_2CO

However, the following experimental modifications allow the successful synthesis of **20a-c**:

i) instead of lithium sand highly reactive lithium dust, which contains 2 % of sodium,[31] is employed in a tenfold excess, ii) additionally the lithium dust is activated in the solvent by sonication in an ultrasonic bath, and iii) the highly diluted solutions of the butatrienes **12a-c** are added to the lithium metal as fast as possible, keeping the reaction temperature of the strongly exothermic reaction below 20 °C (at lower temperatures the competing polymerization becomes predominant; see also table 2). Under these conditions even 1,1,4,4-tetraphenylbutatriene (**1**) can be brought to reaction in diethyl ether.[17]

Table 1: Products Obtained upon Derivatization of the 3,4-Dilithio-1,2-butadienes **20a-c** with Various Electrophiles

entry	starting compound	reaction conditions[a]		electrophile	E	yield (%)[b]	relative ratio of isomers			
							24	**25**	**26**	**27**
1	**12a**	inverse addition	20 °C	Me$_3$SiCl	SiMe$_3$	70	100	-	-	-
2	**12a**		0 °C[c]	H$_2$O	H	83	14	86	-	-
3	**12a**		0 °C[c]	D$_2$O	D	82	11	89	-	-
4	**12a**		-20 °C	(MeO)$_2$SO$_2$	Me	73	0.5	99.5	-	-
5	**12a**	inverse addition	-20 °C	Me$_2$S$_2$	SMe	66	5	95	-	-
6	**12a**	inverse addition	-20 °C	Me$_3$SnCl	SnMe$_3$	20[d]	-	100	-	-
7	**12a**		-80 °C	Me$_2$CO[e]	CMe$_2$OH	60	20	-	80	-
8	**12a**		-40 °C	H$_2$CO[e]	CH$_2$OH	42	40	-	60	-
9	**12b**		20 °C	Me$_3$SiCl	SiMe$_3$	80	100	-	-	-
10	**12b**		0 °C	H$_2$O	H	65	13	87	-	-
11	**12b**		0 °C	D$_2$O	D	60	9	91	-	-
12	**12b**		-20 °C	(MeO)$_2$SO$_2$	Me	70	2	98	-	-
13	**19**	BuLi/TMEDA, 5h	20 °C	Me$_3$SiCl	SiMe$_3$	22[f]	100	-	-	-
14	**19**	BuLi/TMEDA		(MeO)$_2$SO$_2$	Me	25[g]	28	70	1	1
15	**12a**	addition of TMEDA		(MeO)$_2$SO$_2$	Me	63	27	70	2	1
16	**19**	addition of TMEDA		(MeO)$_2$SO$_2$	Me	63	31	67	1.5	0.5
17	**12c**	average of 3 experiments		H$_2$O	H	52[h]	56	8	36	-
18	**12c**	THF as solvent		H$_2$O	H	7[h]	57	-	43	-
19	**12c**			D$_2$O	D	36[h]	50	14	36	-
20	**12c**			(MeO)$_2$SO$_2$	Me	38[i]	-	-	-	-

[a] if not stated otherwise a solution of the electrophile in diethyl ether is added to a solution of the organolithium compound in diethyl ether, inverse addition indicates that the organolithium compound is added to a solution of the electrophile [b] not optimized yield of isolated mixture of isomers [c] the yield and the ratio of isomers does not change upon inverse addition [d] besides 45 % of polymeric material and 5 % of products of hydrolysis [e] PhCHO and Ph$_2$CO do not afford any products of substitution [f] besides 75 % of **35b**, **E** = **SiMe$_3$** [g] besides products of monometalation [h] for the amount of other products in these reactions see table 3 [i] due to the complexity of the reaction mixture not analyzed in detail, with methyl iodide only traces of **24-27** are formed, besides mainly polymeric material

The reaction mixtures, which have a greenish-yellow color in the initial phase of the reaction, turn red and are filtered off from the excess of lithium metal; Gilman double titration[32] indicates a content of dilithium intermediate in the order of 73 to 87 %. Yields do not improve upon working in THF, in hydrocarbons like pentane or pentane/diethyl ether mixtures (1:1) as solvent mainly polymeric material is formed. This might be due to the insolubility of the dilithio compound **20** in the apolar solvent, which deactivates the metal surface and acts as polymerization seed. Even under these optimized reaction conditions butatriene, the simplest 1,2,3-alkatriene, polymerizes faster than reacting with the lithium metal, equally so in DME or 1,4-dioxane as solvent.[17]

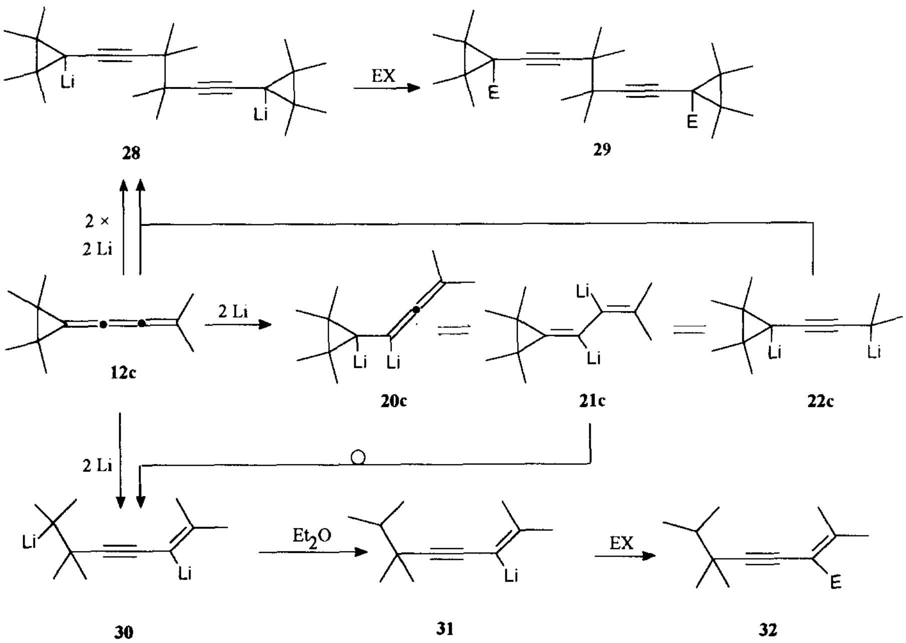
When solutions of **20a** are stored at room temperature a solid separates already after a few minutes from the reaction mixture which consists mainly of the dilithio intermediate **20a** itself, however, solutions stored for several weeks show a complex product composition upon work-up with e.g. dimethyl sulfate or trimethylsilyl chloride; here, besides intra- and intermolecular transmetalation, eliminiation of lithium hydride (indicated by the formation of trimethylsilane), another reaction mechanism responsible for the decompositon of **20a** is observed. In THF as solvent (half-life time of ca. 10 h at 20 °C) or similarily upon addition of TMEDA to an ethereal solution of **20a**, the same complex reaction mixture is found. For **20b** a half-life time of 30 h at 20 °C in diethyl ether is found, in THF the value is estimated to be less than 25 min by Gilman double titration,[32] here solvent cleavage[23] has to be taken into account.

Solutions of the dilithio compounds **20a-c** (and their corresponding follow-up products) are brought to reaction with various electrophiles, the isomeric products obtained are shown in table 1. Upon hydrolysis and deuterolysis of the reaction mixtures mainly butadiene derivatives **25** are formed, as is the case when the workup is performed with dimethyl sulfate. The allenic structure **24** is formed to a small extent only, ratios of **25** : **24** are in the order of 6 : 1 up to 200 : 1 (entries 2-4, 10-12). The same tendency of product distribution is observed when derivatizing the 3,4-dilithio-1,2-butadiene **20a** with either dimethyl disulfide or trimethylstannyl chloride (entries 5 and 6). It is of importance to know that the ratio under discussion so far is independent on the mode of workup (i.e. adding the electrophile slowly to the organolithium compound: normal addition; or adding the organolithium compound to an excess of electrophile: inverse addition). Furthermore the ratio is not effected by the time elapsed between the synthesis of the dilithio intermediate **20a,b** and the time of derivatization (that is after storage for 3 days at 20 °C, not considering a slightly decreased yield), rendering the observed ratio an intrinsic character of the dilithio species. Here, as in many other cases,[33,34] the compounds obtained upon derivatization do not reflect the true nature of the dilithium intermediate **20**, but depend on either the kind of derivatization mechanism or the electronic and steric requirements of the electrophile. In general the following model can be applied which is based on the energy difference of the highest occupied and lowest unoccupied orbitals of the reactants, the concept of hard and soft acids and bases (Pearson's concept).[35] Thus, when looking at the tautomeric structures **20** to **22** (structure **23** with one tertiary anionic center can be neclected in this discussion, which is also evident from table 1) the hardest base is **21**, the softest **22**. The assignment is based on the number of carbanionic atoms with sp^2 character, which have the lower polarizability. This simple assumption would predict the preferential formation of butadiene derivatives **25** with the hard electrophiles water, deuterium oxide and dimethyl sulfate, which is indeed the case. This concept holds also true for the reaction with the soft electrophiles formaldehyde and acetone, here

1,4-disubstituted butynes **26** are obtained. In all cases derivatives with allene structure **24**, derived from the base with an intermediate hardness are formed to a varying amount, which either shows that the differences of the reacting centers are only marginal or demonstrate the unrigorousness of the HSAB concept.[36]

The products isolated after the work-up with the soft electrophiles dimethyl disulfide and trimethylstannyl chloride seem not to fit into the proposed model, the detection of moderate amounts of hexamethyldistannane, however, show quite clearly that the derivatization mechanism has changed and should be best described by an electron transfer of the dilithiobutadiene to the electrophile and subsequent recombination of the radical anion and the radical derived from the electrophile (i.e. the very stable $Me_3Sn\bullet$[37] and MeS• derived from homolytic cleavage of the weak sulfur sulfur bond of dimethyl disulfide[38]). Thus, the crucial intermediates which determine the structure of the isolated isomer **24**, **25** or **26** have radicaloid character and are not compatible with the model under discussion.[39] The single electron-transfer mechanism is, by the way, responsible that substitution products in the reaction of **12a** with benzaldehyde or benzophenone are not formed: upon addition of benzophenone to the solution of **12a**, free of lithium metal, an intense blue coloration (benzophenone ketyl!) is observed and the two radical anions do not recombine to afford **25/26a, E = CPh$_2$OH**.[40]

With trimethylsilyl chloride the preferential formation of the allenic structure **24** is observed. The reaction with the hard electrophile ("fat proton") should lead to a butadienic derivative, instead the allene is formed by attack at the sterically least hindered side, the terminal methylene carbanionic center of **20a** and **20b**. The second derivatization step occurs than, again kinetically controlled, with the harder allenic center and not in the propargylic position.



In the case of the 1,2-dilithio-3,4-butadiene **20c** - the solutions of which are not as stable as those of **20a** or **20b** and show a time-dependent product distribution upon derivatization with a remarkable increase of follow-up products even after only a few hours at 20 °C - several different reaction pathways are observed. Besides the monomeric isomers deriving from the dilithium compounds **20c** - **22c** the product of ring-opening[41-43] to the more stable ene-yne dianion **30** is evolved. This is evident from the isolation of the derivatives **32**, as the tertiary carbanionic center reacts immediately with the solvent. For **30** and **31** only one tautomeric structure is pictured as products deriving from a 4,6-dilithio-1,2,3-butatrienyl or a 4-lithio-1,2,3-butatrienyl system have not been found. Another follow-up product, not observed in the reaction of **12a** and **12b** with lithium metal, is the dimeric structure **28**, with two independent propargylic systems, formed by reductive dimerization.

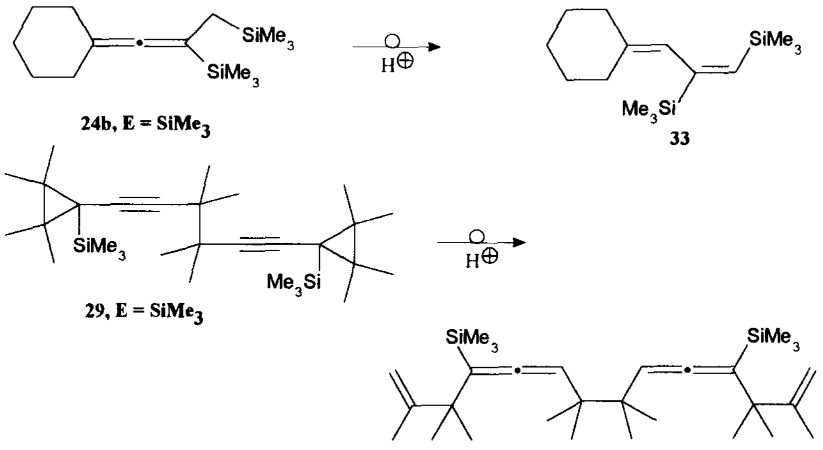
In order to shed light upon the question in which way these dimers are formed, the experiments described in the following were performed. One part of a freshly prepared solution of **20c** in diethyl ether was hydrolyzed with water, other aliquots were freed from the solvent and brought to reaction with the butatriene **12c** in either THF with 5 % of diethyl ether, pure diethyl ether, or a pentane/diethyl ether mixture (5 : 1). The amount of dimer **29, E = H** found in these reactions less the amount of dimer found in the original mixture (about 10%, see entry 7 in table 2) afforded the following numbers: 58 % (THF), 22 % (diethyl ether), 5 % (pentane/diethyl ether). Furthermore, performing the addition of lithium metal to **12c** in a pentane/diethyl ether mixture (5 : 1) the amount of dimer was determined to be 25 %.

Table 2: Product Distribution in the Reaction of **12c** with Lithium Metal and Subsequent Derivatization

			compounds (yield in %)					not identified	
entry	reaction condition	E	**24c**	**25c**	**26c**	**32**	**29**	volatile	remainder
1	Et_2O as solvent	H	27	5	16	18	a)	3	32
2	Et_2O as solvent	H	29	4	19	19	a)	3	26
3	Et_2O as solvent	H	24	5	16	18	a)	2	34
4	addition at +5 °C	D	18	5	13	24	a)	7	33
	Et_2O as solvent		95 %d_2	85 %d_2	50 %d_2	95 %d_1			
	relative amount		30	8	22	40			
5	addition at -10 °C	D	8	4	11	31	a)	2	44
	relative amount		15	7	20	58			
6	addition at -20 °C	D	1	3	7	24	a)	2	63
	relative amount		3	9	20	68			
7	Et_2O as solvent	H	27	b)	17	18	9.5c)	7	21.5
8	THF as solvent	H	4	b)	3	19.5	45	1	27.5
9	THF as solvent	$SiMe_3$	d)	d)	d)	5	43	d)	52

a) the amount of **29** is given, together with the non-volatile mainly polymeric material under the heading remainder b) not analyzed in detail, the amount is summarized together with other not-identified volatile products c) this small amount could only be determined by employing seeding crystals of **29, E = H** d) not analyzed in detail, the amount is summarized under the heading remainder

So **28** is formed by the addition of the dilithium intermediate to the butatriene itself, which is much easier in the more polar solvent THF than in the less polar solvents due to the activation (a smaller degree of aggregation) of the reactive species. Furthermore the large amount of dimer **28** observed when performing the addition of lithium metal in the apolar solvent discloses another dimerization mechanism, based on the intermediate radical anions (either the radical anions react with each other or with the starting butatriene to **28**). In the apolar solvent the life-time of the radical anion is higher, the second reduction step (electron transfer to the negatively charged radical anion) forming the dianion, is slowed down. Another aspect of this reaction is the ring-opening product **30**, which might be taken as evidence for the ring-opening of the intermediate radical anion. As can be seen from table 2 the relative amount of the product **32** increases when decreasing the reaction temperature, thereby increasing the life-time of the radical anion.[44]



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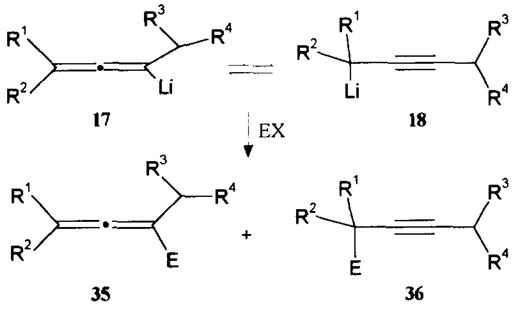
When performing the work-up with trimethylsilyl chloride special care has to be taken to exclude any traces of acid during the derivatization and the work-up, as is demonstrated in the observed acid catalyzed rearrangement[45] of **24b, E = SiMe$_3$** and **29, E = SiMe$_3$** to **33** and **34** respectively, thereby pretending, for example, the dimerization of the product of ring-opening. This rearrangement is not observed simply upon heating, neither does **29, E = H** show the rearrangement under similar conditions.

Deprotonation of suitable allenes is another approach to 1,2-dilithio-3,4-butadienes **20**, provided that they show sufficient acidity. So the allenes **16a,b** and **19** are treated with *n*-butyllithium in hydrocarbons like hexane, pentane, or cyclopentane together with one equivalent of TMEDA per mole of metalating agent. When adding either diethyl ether or THF to the reaction mixtures or employing more than one equivalent of TMEDA the product mixtures obtained upon derivatization are much more complex, and even under these conditions or when using *s*- or *t*-butyllithium and reaction times of up to 72 h at 30 °C in the case of **16a** and **16b** not more than one position of the cyclopropyl allenes is metalated (typical product mixtures are given in table 3). Only the monosubstituted allene **19** can be metalated twice (entries 13 and 14 in table 1), especially the spectroscopic data discussed below prove that indeed the same intermediate, i.e. the 1,2-dilithio-3,4-butadiene **20b** is formed, either by the metalation of **19** or by reductive metalation of **12b**. This excludes the formation of QUADACs (Quasi Dianion Complexes)[46] consisting of the monometalated allene and the metalating agent butyllithium, pretending, due to the finding of disubstituted derivatives, the formation of dilithium compounds. The same product distribution is observed when adding TMEDA to the reaction mixtures obtained by adding lithium to **12b** (compare entries 14-16 in table 1); the differences in reactivity of the nucleophilic carbon centers are thereby diminished affording even products deriving from **23**. So far no explanation has been forwarded to explain the fact that cyclopropylallenes or cyclopropylalkynes[15] can only be metalated once, which has been observed in the reaction of 2-butyne with butyllithium as well.[47]



	R^1,R^2	R^3,R^4
a	Me	$(CH_2)_2$
b	$(CH_2)_5$	H
c	Me	$(CMe_2)_2$

EX = H_2O, D_2O, $(MeO)_2SO_2$, Me_3SiCl

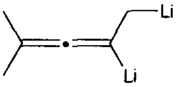
Table 3: Hydrocarbons Obtained Upon Metalation of the Allenes **16a** and **16b** and **19** after Derivatization

entry	starting allene	reaction conditions[a)]	E	yield (%)	ratio of isomers
1	**16a**	10 eq. BuLi, 20 eq. TMEDA	D	88	**35a** : **36a** = 91 : 9[b)]
2	**16b**	10 eq. BuLi, 20 eq. TMEDA	D	81	**35c** : **36c** = 95 : 5[b)]
3	**16a**	10 eq. BuLi, 10 eq. TMEDA	Me	85	**35a** only
4	**19**	10 eq. BuLi, 10 eq. TMEDA	$SiMe_3$	75[c)]	**35b** only

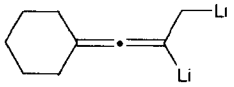
[a)] in all cases in hexane as solvent [b)] When employing less than 1 equivalent of TMEDA the product with alkyne-structure is not detected [c)] For the products of dimetalation see entries 13 and 14 in table 1

IR and NMR spectroscopic investigations

The accessability of structural information by NMR spectroscopy is hampered by the very low solubility of **20a** and **20b** in diethyl ether, however, samples of the 1,2-dilithio-3,4-butadienes prepared in diethyl ether, which are repeatedly freed from the solvent and solubilized in perdeuterated diethyl ether, deliver informative spectra: the ^1H NMR spectrum (80 MHz) of **20a** shows two singlets at 1.59 ppm and 1.69 ppm, in a ratio of 1 : 3, thus corresponding to the methylene group and the two identical methyl groups. There is no evidence for the butadienic structure **21a**, as no olefinic signals are observed in the region between 5 and 6 ppm, which has been reported for similar organolithium compounds like vinyllithium, propenyllithium or 2,4-dilithio-1-butene.[48] Even when considering an enhanced shielding in the double negatively charged species the signals for the olefinic proton are only slightly shifted upfield and are found at 4.8 ppm as in the dilithiated 2-butene.[49] Similarily for **20b** at 400 MHz in perdeuterated diethyl ether two broad multiplets are found at 1.63 ppm for 6 alicyclic methylene protons and the two protons of the methylene group α to the lithium and at 2.21 ppm for the 4 alicyclic allyl protons. These data would be in accordance with the 2-butyne structure **22b** as well, however, the ^{13}C NMR spectrum of **20b** at 100 MHz in perdeuterated diethyl ether at room temperature (the solubility of **20a** is indeed too low to record a ^{13}C NMR spectrum) proves the allenic structure, as signals at 200.4, 124.1 and 113.1 ppm are observed for the allenic subunit, besides signals at 83.2 (methylene group α to the lithium), 32.6, 28.4, and 27.2 (ring carbons) ppm.



20a

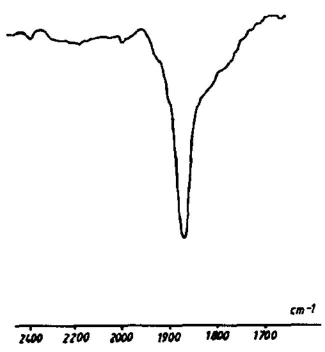


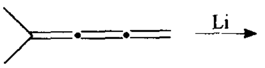
20b

Independently the allenic structure of the 1,2-dilithio-3,4-butadiene is concluded when looking at the IR spectra of solutions of **20a-c** in diethyl ether. Here medium to strong absorption bands are observed at about 1860 cm^{-1} for **20a** and **20b**, which correspond to typical absorptions of allenes at 1800 - 2000 cm^{-1}. In the case of **20c** additional bands are observed originating from the dimeric structure **28** and the ene-yne **31** which are present in solutions of **20c** as well. For symmetry reasons no absorptions are observed for either **4** or **9**, monometalated dicyclopropylacetylene shows the typical C,C triple bond absorption at about 2180 wavenumbers.[15] More interestingly the double metalation of propyne affords a species which absorbs in the same region as the 1,2-dilithio-2,4-butadienes synthesized. The similarity of the IR spectra of **20b** either obtained by reductive metalation or by metalation with Buli/TMEDA is obvious and needs no further comment. It is interesting to note that dilithiopropyne shows an absorption at 1870 cm^{-1} too.[50]

Figure 1: IR spectra in the Region of 1650 - 2250 cm^{-1} Obtained by a) Reduktive Metalation of **12a** in Diethyl Ether b) Reduktive Metalation of **12b** in Diethyl Ether c) Metalation of **19** with BuLi/TMEDA in Pentane d) Reduktive Metalation of **12c** in Diethyl Ether

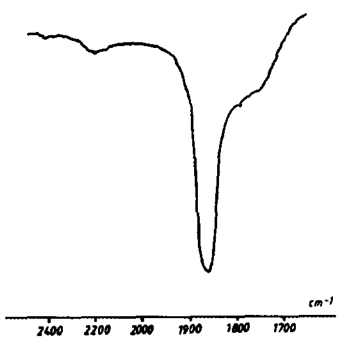
Fig. 1a)

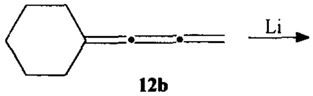




12a

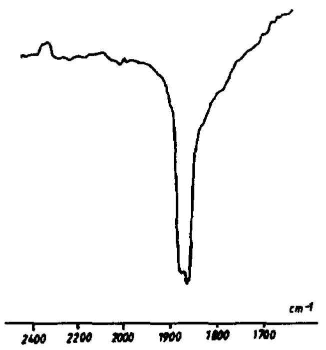
Fig. 1b)

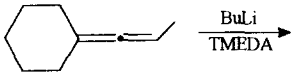




12b

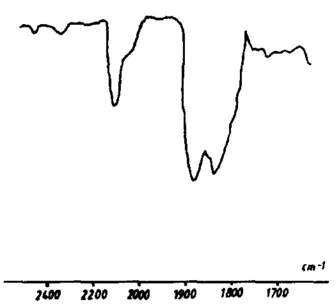
Fig. 1c)





19

Fig. 1d)



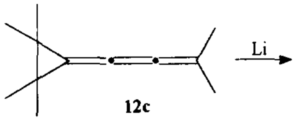


Table 4: Characteristic Absorption Bands in the Region of 1650 - 2250 cm^{-1}[a)]

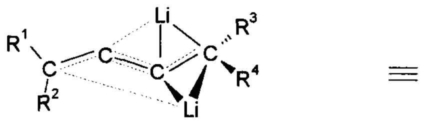
compound	solvent	wavenumber in cm^{-1}
20a[b)]	diethyl ether	1865
20b[b)]	diethyl ether	1860
20b[b)]	TMEDA/pentane	1865
dimetalation of **19**[b)]	TMEDA/pentane	1880/1865
4[b)]	diethyl ether	---
20c[b)]	diethyl ether	2110 and 1880/1840
monometalation of **5**[15]	THF	2180
6[15]	THF	---
$C_3H_2Li_2$ (by metalation of propyne[50)])	hexane	1870

a) the polymeric material obtained from the butatrienes **12a-c** which is a side product in the redutive metalation shows no absorption in this region b) all the IR and NMR samples under investigation in this work show only minute amounts of products of hydrolysis (less than 5 %) after derivatization with either dimethyl sulfate or trimethylsilyl chloride

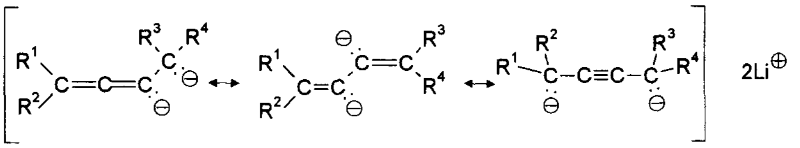
Conclusions

For the understanding of reactivity of organolithium compounds solid state structures are helpful, however, the actually more stable and reacting species in solution might be different to those obtained by crystallization; aggregation and structure in solution are much more important for the understanding of the isolated products **24a-c** to **27a-c**, which are formed in two consecutive, kinetically controlled reactions of a dilithium compound and a substituted monolithium compound. In a few cases even two different structures of one and the same organolithium compound in the solid state have been observed,[51a,b] for this phenomenon the term 'lithiotropy' has been coined by Boche et al.[51a] Furthermore, a detailed NMR spectroscopic investigation of simple allenyl-propargyllithium reagents has led Reich and coworkers to the assumption of an equilibrium between allenyl- and propargyllithium structures, this equilibrium is mainly shifted to the side of the allenyllithium compound even when introducing alkyl substituents at the lithiated carbon atom.[52a]

However, these findings can not be taken as a rationale for the regioselectivity observed upon derivatization of the 3,4-dilithio-1,2-butadienes. The results presented here show clearly that the composition of the product mixture is largely dependent on the nature of the electrophile and thus the type of derivatization mechanism. To a smaller extent the polarity and complexing properties of the solvent have to be considered. Moreover, the assumption of an equilibrium between the tautomers **20** $\rightleftharpoons$ **21** $\rightleftharpoons$ **22** $\rightleftharpoons$ **23** is not neccessary at all. The system is best described by formula **37**, which summarizes three mesomeric structures and is in accordance with calculated structures of similar dilithiobutadienes.[19] The fourth mesomeric structure, which corresponds to tautomer **23** can be neclected, its importance is only small with respect to the experimental and spectroscopic results obtained. Formula **37** considers as well the fact that the allenyl anion system is bent, by up to 15°, which is proved by calculations and X-ray structures of allenyllithium and sodium compounds.[52b] Additionally structure **37** allows for an intramolecular and stabilizing interaction of the two lithium atoms.[19-21]



37



Experimental

General Methods. All reactions with air sensitive compounds were carried out under an atmosphere of dried argon (99.996 %). Ethereal solvents were purified by adsorptive filtration over basic aluminium oxide (activity I) and freshly distilled under argon from sodium-benzophenone ketyl. Pentane and cyclopentane were freshly distilled from lithium aluminium hydride 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. High resolution mass spectra were recorded on a Varian MAT 311 A. Nuclear Magnetic Resonance (^{1}H, and ^{13}C) spectra were recorded on the Bruker instruments WP 80 and WH 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), m(multiplet), br (broad signal). Separations of the reaction mixtures were performed using a preparative gas chromatograph (Hupe und Busch, HP 1075c prep. GC). For analytical gas chromatography a Siemens L350 (FID) with a Spectra Physics 4001 integrator with Silicon OV 101 (30 m, WAG Griesheim) and 5 % Phenylmethylsilicon (25 m, Hewlett Packard) capillary columns were employed. IR spectra were recorded on either a Perkin Elmer PE 580 or a Beckman Acculab 4. IR absorption bands are given in cm^{-1}. Elemental analyses were performed by the Mikroanalytisches Labor Beller (Göttingen).

Highly reactive lithium dust (2 % sodium).[19] All operations were performed under an atmosphere of argon! 50.0 g of lithium and 1.0 g of sodium were heated in 1.5 l of viscous paraffin oil (Roth) together with a few drops of oleic acid to the melt (m.p. 180.5 °C). Then the metal was suspended with a high speed stirrer (20000 r.p.m., Tornado ET 20) for 90 min; the stirring was continued for a few seconds while removing the heating source. The suspension of lithium powder was then allowed to cool and collect on the surface (about ten days). Most of the paraffin was sucked off through teflon tubing and the lithium dust suspended with pentane (free of alkenes), filtered through a G4 glas sinter frit and washed carefully several times with pentane.

Starting materials

2,2-Dibromo-3,3-dimethyl-1-methylenecyclopropane (**11a**).[53] A suspension of 16.8 g (0.15 mol) of potassium-*tert.*-butoxide and 10.0 g (0.15 mol) of **10a**[54] in 100 ml of pentane under argon was stirred for 10 min at 0 °C. Then a solution of freshly distilled bromoform (38.0 g, 0.15 mol) in 100 ml of pentane was added at 0-5 °C during a period of 1 h, whilst efficiently stirring the reaction mixture by means of a mechanical stirrer. The stirring was continued at 20 °C for 5 h, the reaction mixture diluted with 200 ml of pentane and the solution separated from the remaining solid with the help of a centrifuge; the solvent was evaporated at 0 °C and the crude product was isolated by bulb-to-bulb distillation (0.01 Torr, 60 °C maximum bath temperature). 2,2-Dibromo-3,3-dimethyl-1-methylenecyclopropane was obtained after fractional distillation: 28.4 g (0.12 mol, 79 %); b.p. 65-67 °C (20 Torr). Boiling point and spectroscopic data were in accordance with literature data.[53]

4-Methyl-1,2,3-pentatriene (**12a**).[24] To a solution of 63 ml (0.10 mol) of a 1.6 M solution of methyllithium in diethyl ether (Merck) were added dropwise 12.0 g (0.05 mol) of **11a** in 25 ml of diethyl ether at -70 °C. The reaction mixture was allowed to warm to room temperature and the butatriene **12a** was isolated by a double bulb-to-bulb distillation (0.01 Torr, 0 °C bath temperature) as a solution in diethyl ether. The yield was determined by gas chromatography using cyclohexane as standard: 2.8 g (36 mmol, 72 %). **^{1}H NMR** (80 MHz, CDCl$_3$, diethyl ether as impurity) δ 1.87 (t, ^6J = 1.5 Hz, 6 H, methyl), 4.78 (m, 2 H, vinyl). **IR** 2070, ν (C=C=C=C).

2,2-Dibromo-1-methylene-spiro[2.5]octane (**11b**).[55] The synthesis was performed as described for **11a**. 36.5 g (0.34 mol) of 1,1-pentamethylene-1,2-propadiene (**10b**)[56], 39.2 g (0.35 mol) of potassium-*tert.*-butoxide, and 88.5 g (0.35 mol) of bromoform afforded 72.8 g (0.26 mol, 77 %) of **11b**; b.p. 65-67 °C (0.3 Torr). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 1.54/1.75 (m, 10 H, methylene), 5.40/5.67 (2 × s, 2 H, vinyl).

1,1-Pentamethylene-1,2,3-butatriene (**12b**). The synthesis was performed as described for **12a**. 28 g (0.10 mol) of **11b** and 126 ml (0.20 mol) of a 1.6 M solution of methyllithium in diethyl ether afforded 7.3 g (60 mmol, 61 %) of **12b**. The butatriene polymerizes upon isolation and was isolated and employed in further reactions as a solution in diethyl ether. **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.64 (m, 6 H, methylene), 2.31 (m, 4 H, allyl), 4.92 (quint, ^6J = 1.0 Hz, 2 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 25.8, 27.6, 35.1, 85.5, 126.6, 153.1, 166.1. **MS** (70 eV): m/z 120 (M^+, 100), 105(51), 92(40), 91(93), 79(50), 78(33), 77(48), 67(54), 52(41), 39(38). **IR** 2065, ν(C=C=C=C).

2,2-Dibromo-3,3-dimethyl-1-(2,2,3,3-tetramethylcyclopropylidene)-cyclopropane (**11c**). A suspension of 1.50 g (10 mmol) of 1-(2-methyl-1-propylidene)-2,2,3,3-tetramethylcyclopropane (**10c**)[57] and 2.90 g (30 mmol) of sodium *tert.*-butoxide in 150 ml of pentane were stirred for 10 min at 0 °C under argon. At this temperature 3.80 g (15 mmol) of bromoform in 30 ml of pentane were added dropwise during 1 h. After stirring for 3 h at room temperature the solid was separated by means of a centrifuge and the solvent of the remaining solution was evaporated in vacuo (10-15 Torr). The brown remainder was purified by adsorptive filtration through silica gel; recrystallization from pentane afforded **11c** as colorless crystals: 2.61 g (8.1 mmol, 81 %); m.p. 75-80 °C (dec.). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.19/1.29/1.45 (3 × s, 3 × 6 H, methyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.4, 20.6, 23.6, 24.4, 25.0, 32.5, 36.8, 122.6, 141.6. **MS** (70 eV): m/z 322 (M^+ for $^{79}Br^{81}Br$, 4), 162(100), 147(66), 121(69), 119(50), 105(75), 91(61), 55(52), 44(48), 41(90). **Anal.** calc. for $C_{12}H_{18}Br_2$: C, 44.75; H, 5.63; found: C, 44.60; H, 5.75.

1-(3-Methyl-1,2-butadienylidene)-2,2,3,3-tetramethylcyclopropane (**12c**). To a solution of 4.30 g (13.4 mmol) of **11c** in 500 ml of diethyl ether were added dropwise at -70 °C 40 ml (64 mmol) of a 1.6 M solution of methyllithium in diethyl ether. The reaction mixture was allowed to warm to -10 °C and stirred at this temperature for 10 min. Then 100 ml of oxygen-free water were added carefully and the organic layer was washed with oxygen-free water and dried over magnesium sulfate at -40 °C for 1 h. The solution was filtered and the solvent evaporated in vacuo (10-15 Torr) at 0 °C. **12c** was isolated by bulb-to-bulb distillation (0.001 Torr, 20 °C maximum bath temperature): 1.22 g (7.5 mmol, 56 %). The solid polymerized at room temperature within a few min, even when stored under argon; **12c** was employed in subsequent reactions as a solution in diethyl ether. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.23 (s, 12 H, cyclopropyl-methyl), 1.90 (s, 6 H, allyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.0, 24.4, 28.0, 111.0, 120.7, 143.3, 163.8. **MS** (70 eV): m/z 162 (M^+, 48), 147(74), 119(67), 107(36), 105(100), 91(83), 79(35)77(46), 55(37), 41(74). **IR** 2065, ν (C=C=C=C).

1-Cyclopropyl-3-methyl-1,2-butadiene (**16a**):[30] A solution of cyclopropyllithium[58] [from 6.20 g (0.89 mol) of lithium sand and 30.5 g (0.252 mol) of cyclopropyl bromide in 200 ml diethyl ether] was treated with 24.00 g (0.126 mol) of copper(I) iodide and 12.92 g (0.126 mol) of 3-chloro-3-methyl-1-butyne[59] and afforded 8.71 g (81 mmol, 64 %) of **16a**. B.p. 50-51 °C (39 Torr), b.p.[53] 43-43.5 °C (30 Torr). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.31/0.65 (2 × m, 4 H, cyclopropyl-methylene), 1.18 (m, 1 H, cyclopropyl-methine), 1.69 (d, ^5J = 2.9 Hz, 6 H, methyl), 4.79 (br m, 1 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 6.8, 10.0, 20.9, 93.1, 96.8, 200.8. **MS** (70 eV): m/z 108 (M^+, 22), 93(100), 91(73), 79(39), 77(96), 67(24), 65(33), 51(27), 41(65), 39(76). **IR** 3090, s, ν(cyclopropyl), 1955, ν(C=C=C).

1-(3-Methyl-1,2-butadienyl)-2,2,3,3-tetramethylcyclopropane (**16b**). Starting from tetramethylcyclopropyllithium[54] [from 44.60 g (0.252 mol) of 1-bromo-2,2,3,3-tetramethylcyclopropane[60] and 6.20 g (0.89 mol) of lithium in 200 ml of diethyl ether] the reaction with 24.00 g (0.126 mol) of copper(I) iodide and 12.92 g (0.126 mol) of 3-chloro-3-methyl-1-butyne[59] afforded 10.95 g (69 mmol, 53 %) of **16b**; b.p. 59-61 °C (26 Torr). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.80 (d, ^3J = 8.0 Hz, 1 H, cyclopropyl-methine) 0.99/1.11 (2 × s, 2 × 6 H, cyclopropyl-methyl), 1.69 (d, ^5J = 3.0 Hz, 6 H, allyl), 4.77 (m, 1 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.5, 21.0, 23.4, 23.5, 33.0, 86.2, 94.2, 203.7. **MS** (70 eV): m/z 164 (M^+, 13), 149(100), 121(31), 107(63), 97(37), 91(33), 57(30), 55(65), 43(28), 41(45). **IR** 1955, ν(C=C=C). **Anal.** calc. for $C_{12}H_{20}$: C, 87.73; H, 12.27; found: C, 87.90; H, 12.13.

*Addition of butyllithium to the alkatrienes **12b** and **12c**.*

1,1-Pentamethylene-3-trimethylsilyl-1,2-octadiene (**13**). A solution of 1.98 g (16 mmol) of **12b** in 100 ml of diethyl ether was added at -70 °C to 83 ml (132 mmol) of a 1.6 M solution of butyllithium in hexane (Metallgesellschaft). The reaction mixture was allowed to warm to room temperature during 2 h and then added dropwise to 21.70 g (200 mmol) of trimethylsilyl chloride in diethyl ether and stirred for 30 min at room temperature. This mixture was dropped into an excess of a saturated solution of sodium bicarbonate at 0 °C, the organic layer was washed with water, dried over magnesium sulfate and the solvent evaporated in vacuo. The remaining oil was fractionated to afford 2.88 g (11.5 mmol, 72 %) of **13**, b.p. 53-55 °C (0.1 Torr). **^{1}H NMR** (400 MHz, C_6D_6) δ 0.13 (s, 9 H, $SiMe_3$), 0.89 (t, ^3J = 6.8 Hz, 3 H, methyl), 1.30/1.53 (2 × m, 10 H, methylene), 1.97 (t, ^3J = 7.3 Hz, 2 H, allyl), 2.10 (m, 4 H, allyl). **^{13}C NMR** (100 MHz, C_6D_6) δ -0.9, 14.3, 23.0, 26.8, 28.2, 29.5, 30.1, 31.8, 31.9, 95.5, 97.4, 201.9. **MS** (70 eV): m/z 250 (M^+, 14), 194(15), 179(12), 176(9), 153(17), 148(12), 91(10), 73(100), 59(14), 45(14). **Anal.** calc. for $C_{16}H_{30}Si$: C, 76.72; H, 12.07; found: C, 76.78; H, 12.21.

1-(3,3-Dimethyl-1-heptinyl)-2,2,3,3-tetramethylcyclopropane (**14**). The reaction was performed as described for **13**, starting with 100 ml (160 mmol) of a 1.6 M solution of butyllithium in hexane and 2.59 g (16 mmol) of **12c**. Then 20 ml of water were added and the organic layer was washed neutral with brine, dried with magnesium sulfate and the solvent evaporated in vacuo. The remaining oil was fractionated and afforded 1.80 g (8.2 mmol, 51 %) of **14**; b.p. 61-63 °C (0.06 Torr). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.83 (s, 1 H, cyclopropyl-methine), 0.92 (t, ^3J = 6.9 Hz, 3 H, methyl), 1.07/1.10/1.18 (3 × s, 3 × 6 H, 6 methyl), 1.28-1.45 (m, 6 H, 3 × methylene). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.3, 18.3, 22.5, 23.4, 24.7, 25.5, 27.8, 29.7, 31.5, 43.7, 76.7, 88.6. **MS** (70 eV): m/z 220 (M^+, 17), 163(68), 121(100), 107(62), 91(36), 69(61), 57(79), 55(54), 43(71), 41(95). **IR** 3085, ν(cyclopropyl), 2230, ν(C≡C).

General procedure for the synthesis of the 3,4-dilithio-1,2-butadienes **20a-c**. All operations were performed under an atmosphere of argon! Lithium dust was activated by sonication in a small volume of diethyl ether for 3 to 5 h in an ultrasonic cleaning bath. Then a 0.1 M solution of the freshly prepared butatrienes **12a-c** in either diethyl ether or a diethyl ether/THF mixture (1 : 1, v/v) was added as fast as possible to the magnetically stirred lithium suspension, keeping the temperature of the mixture between 15 to 20 °C by cooling with an ice/water bath. After complete addition the reaction mixture was stirred for another 10 min at 15 °C and filtered through a glas sinter frit from excess lithium metal. The content of dilithium compound was determined by double Gilman titration.[32]

1,2-Dilithio-4-methyl-2,3-pentadiene **20a**. From 2.80 g (36 mmol) of **12a** in 360 ml of diethyl ether and 2.50 g (0.36 mol) of lithium metal a 0.031 to 0.033 M solution of **20a** was obtained (86-91 %).

3,4-Dilithio-1,1-pentamethylene-1,2-butadiene **20b**. From 6.72 g (56 mmol) of 1,2-pentamethylene-1,2,3-butatriene (**12b**) in 560 ml of either diethyl ether or THF and 3.92 g (0.56 mol) of lithium metal a 0.044 to 0.045 M solution of **20b** was obtained (78-81 %).

1-(1,2-Dilithio-(3-methyl-1,2-butadienyl)-2,2,3,3-tetramethylcyclopropane **20c**. From 10.04 g (62.0 mmol) of **12c** and 620 ml of diethyl ether a 0.035 to 0.040 M solution of **20c** was obtained (57-65 %). When employing THF as solvent, the molarity was determined to be 0.019 to 0.025 M (31-40 %).

1,2-Bis(trimethylsilyl)-4-methyl-2,3-pentadiene (**24a, E = SiMe$_3$**). The derivatization of a solution of 30 mmol of **20a** in 400 ml of diethyl ether was performed as described for compound **13** with 13.0 g (0.12 mol) of trimethylsilyl chloride in 100 ml of diethyl ether. After the work-up and fractional distillation 5.71 g (25 mmol, 84 %) of **24a, E = SiMe$_3$** were obtained, b.p. = 115-120 °C (12 Torr). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.03/0.06 (2 × s, 2 × 9 H, 2 × $SiMe_3$), 1.24 (s, 2 H, methylene), 1.64 (s, 6 H, methyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ -1.30, -1.25, 16.7, 20.2, 83.4, 90.6, 205.0. **MS** (70 eV): m/z 226 (M^+, 27), 211(10), 153(13), 152(20), 133(62), 132(50), 123(45), 113(33), 73(100), 45(25). **Anal.** calc. for $C_{12}H_{26}Si_2$: C, 63.63; H, 11.57; found: C, 63.66; H, 11.54.

1,2-Bis(trimethylsilyl)-4,4-pentamethylene-2,3-butadiene (**24b, E = SiMe$_3$**). As described above from 30 mmol of **20b** in 400 ml of diethyl ether and 13.0 g (0.12 mol) of trimethylsilyl chloride were obtained 6.30 g

(24 mmol, 79 %) of **24b, E = SiMe$_3$**, b.p. 59-61 °C (0.08 Torr). **^{1}H NMR** (80 MHz, CDCl$_3$) δ 0.02/0.06 (2 × s, 2 × 9 H, 2 × SiMe$_3$), 1.24 (s, 2 H, methylene-SiMe$_3$), 1.53 (m, 6 H, ring-methylene), 2.08 (m, 4 H, ring-allyl). **^{13}C NMR** (100 MHz, C$_6$D$_6$) δ -1.0, -0.9, 17.5, 27.3, 28.2, 32.2, 91.2, 96.5, 202.2. **MS** (70 eV): m/z 266 (M$^+$, 5), 192(5), 169(6), 119(3), 118(5), 96(8), 74(8), 73(100), 59(5), 45(11). **Anal.** calc. for $C_{15}H_{30}Si_2$: C, 67.59; H, 11.34; found: C, 67.69; H, 11.32.

2-Methyl-2,3-pentadiene (**24a, E = H**) *and 4-methyl-1,3-pentadiene* (**25a, E = H**).
The derivatization of a solution of 15 mmol of **20a** in 150 ml of diethyl ether with water and the work-up was performed as described for compound **14**. The crude mixture was isolated by bulb-to-bulb distillation; 1.03 g (12.5 mmol, 83 %) of the isomeric hydrocarbons **24a, E = H** and **25a, E = H**. GC-MS analysis of the reaction mixture afforded the following relative amounts: 11.9 % of **24a, E = H**, 71.5 % of **25a, E = H**, 1.2 % not identified, 15.4 % non-volatile, mainly polymeric material. Characterization of **24a, E = H: ^{1}H NMR-** and **^{13}C NMR** spectrum were in accordance with literature data.[61,62] **MS** (70 eV): m/z 82 (M$^+$, 100), 81(10), 79(24), 67(95), 65(48), 54(21), 53(35), 51(8), 41(57), 39(48). Characterization of **25a, E = H: ^{1}H NMR** and **^{13}C NMR** spectrum were in accordance with literature data.[63,64] **MS** (70 eV): m/z 82 (M$^+$, 100), 81(37), 79(28), 67(97), 65(34), 54(42), 53(39), 51(17), 41(55), 39(54).

1,2-Dideuterio-4-methyl-2,3-pentadiene (**24a, E = D**) *and 2,3-dideuterio-4-methyl-1,3-pentadiene* (**25a, E = D**). In the same way and on the same scale as described above the derivatization with deuterium oxide yielded 1.02 g (12 mmol, 82 %) of the isomeric hydrocarbons **24a, E = D** and **25a, E = D**. GC-MS analysis of the reaction mixture gave 8.8 % of **24a, E = D**, 73.0 % of **25a, E = D**, 1.6 % not identified, and 16.6 % non-volatile, mainly polymeric material. **MS** (70 eV) of **24a, E = D**: m/z 84 (M$^+$, 100), 82(83), 69(50), 68(92), 66(20), 65(25), 43(17), 42(53), 41(90), 39(49). **25a, E = D**: **^{1}H NMR** (80 MHz, CDCl$_3$) δ 1.79 (s, 6 H, methyl), 4.95/5.05 (2 × m, 2 H, vinyl). **MS** (70 eV): m/z 84 (M$^+$, 81), 83(31), 82(25), 81(19), 69(100), 68(57), 67(23), 43(17), 42(29), 41(27).

1,1-Pentamethylene-1,2-butadiene (**19**) *and 1,1-pentamethylene-1,3-butadiene* (**25b, E = H**). A solution of 15 mmol of **20b** in 150 ml of diethyl ether was derivatized with water as described above. Bulb-to-bulb distillation afforded 1.18 g (9.7 mmol, 65 %) of the isomeric hydrocarbons **19** and **25b, E = H**. Complete analysis of the product mixture by GC-MS coupling yielded 8.2 % of **19**, 56.4 % of **25b, E = H**, 3.2 % not identified (several compounds, a single compound not more than 1 %), 32.2 % non-volatile (mainly polymeric material). Characterization of **19**: the **^{1}H NMR** data were in accordance with reported values.[30] **^{13}C NMR** (20 MHz, acetone-d$_6$) δ 16.3, 28.0, 29.3, 33.5, 84.8, 103.3, 201.3. **MS** (70 eV): m/z 122 (M$^+$, 67), 107(42), 93(50), 91(34), 81(17), 79(100), 77(33), 67(25), 41(26), 39(21). **25b, E = H**: the **^{1}H NMR** data were in accordance with reported values.[65] **^{13}C NMR** (100 MHz, CDCl$_3$) δ 26.8, 27.7, 28.5, 29.2, 37.1, 114.2, 122.6, 132.5, 144.0. **MS** (70 eV): m/z 122 (M$^+$, 52), 107(56), 93(42), 81(76), 80(34), 79(100), 77(24), 67(48), 41(24), 39(28).

1,2-Dideuterio-4,4-pentamethylene-2,3-butadiene (**24b, E = D**) *and 2,3-dideuterio-1,1-pentamethylene-1,3-butadiene* (**25b, E = D**). The reaction of 150 ml of a 0.1 M solution of **20b** in diethyl ether was performed as described above, thereby 1.12 g (9 mmol, 60 %) of the isomeric hydrocarbons were obtained. GC analysis of the crude reaction mixture yielded 5.6 % of **24b, E = D**, 55.3 % of **25b, E = D**, 2.9 % not identified, 36.2 % non-volatile (mainly polymeric) material. Characterization of **24b, E = D**: **MS** (70 eV): m/z 124 (M$^+$, 65), 123(32), 108(86), 94(64), 81(100), 80(79), 79(50), 77(19), 67(22), 39(30). **25b, E = D**: **^{1}H NMR** (80 MHz, CDCl$_3$) δ 1.57 (br s, 6 H, ring-methylene), 2.26 (br m, 4 H, ring-allyl), 5.01 (br m, 2 H, vinyl). **MS** (70 eV): m/z 124 (M$^+$, 41), 109(31), 94(26), 82(26), 81(100), 80(48), 79(50), 68(29), 67(35), 41(24).

2,4-Dimethyl-2,3-hexadiene (**24a, E = Me**), *and 2,3,4-trimethyl-1,3-pentadiene* (**25a, E = Me**). To 30 mmol of **20a** in 400 ml of diethyl ether 15.1 g (0.12 mol) of freshly distilled dimethyl sulfate in 100 ml of diethyl ether were added dropwise at -20 °C. The reaction mixture was allowed to warm to room temperature and 200 ml of ammonia were added. This mixture was heated to reflux for 30 min. The separated organic layer was washed with 1 % hydrochloric acid and brine until neutral. The ethereal solution was dried over magnesium sulfate and the solvent evaporated. The remaining oil was purified by bulb-to-bulb distillation (0.01 Torr, 30 °C maximum bath temperature). Thereby 2.43 g (22 mmol, 73 %) of the isomeric hydrocarbons were obtained. The ratio of **24a, E = Me/25a, E = Me** was determined by GC analysis in the order of 0.5 : 99.5. Characterization of **24a, E = Me**: the **^{1}H-NMR** data were in accordance with earlier reported values.[24] **MS** (70 eV): m/z 110 (M$^+$, 100), 95(71), 81(61), 79(15), 77(14), 67(70), 55(58), 53(51), 41(69), 39(41). **IR** 1960, ν(C=C=C). **25a, E = Me**: The **^{1}H-NMR** and **^{13}C NMR** data were in accordance with earlier reported data.[66] **MS** (70eV): m/z 110 (M$^+$, 91), 95(100), 81(19), 79(14), 77(13), 67(74), 55(42), 53(31), 41(62), 39(43).

3-Methyl-1,1-pentamethylene-1,2-pentadiene (**24b, E = Me**) *and 2,3-dimethyl-1,1-pentamethylene-1,3-butadiene* (**25b, E = Me**). The derivatization of **20b** with dimethyl sulfate was performed on the same scale and in the same way as described above. Thereby 3.20 g (21 mmol, 71 %) of the isomeric hydrocarbons were obtained. The ratio of **24b, E = Me/ 25b, E = Me** was determined in different experiments to be between 1 : 99 and 3 : 97. Characterization of **24b, E = Me**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.98 (t, ^3J = 7.1 Hz, 3 H, methyl), 1.56 (m, 6 H, ring-methylene), 1.67 (s, 3 H, methyl), 1.83 (q, ^3J = 7.1 Hz, 2 H, methylene), 2.08 (br m, 4 H, ring-allyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 12.4, 19.8, 26.4, 27.4, 28.0, 32.3, 98.7, 102.5, 194.9. **MS** (70 eV): m/z 150 (M$^+$, 39), 136(66), 107(100), 94(47), 93(52), 81(91), 77(39), 68(69), 67(56), 41(48). **IR** 1950, ν(C=C=C). **25b, E = Me**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.53 (br s, 6 H, ring-methylene), 1.71/1.78 (2 × s, 2 × 3 H, 2 × methyl), 2.15 (m, 4 H, ring-allyl), 4.58/4.81 (2 × m, 2 × 1 H, 2 × vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 17.2, 22.5, 27.0, 28.1, 28.8, 30.1, 31.7, 111.1, 128.6, 132.8, 148.3. **MS** (70 eV): m/z 150 (M$^+$, 80), 121(69), 107(93), 93(100), 91(48), 79(96), 77(43), 67(73), 55(56), 41(59).

1,2-Bis(methylthio)-4-methyl-2,3-pentadiene (**24a, E = SMe**) *and 2,3-bis(methylthio)-4-methyl-1,3-pentadiene* (**25a, E = SMe**). 30 mmol of **20a** in 300 ml of diethyl ether were dropped slowly at -20 °C into a solution of 8.46 (90 mmol) of dimethyl disulfide in 100 ml of diethyl ether. The reaction mixture was allowed to warm to room temperature slowly, water was added and the organic layer was washed with brine. The solvent was evaporated in vacuo (10-15 Torr) and the remainder was isolated by bulb-to-bulb distillation (0.01 Torr, 60 °C maximum bath temperature): 3.45 g (20 mmol, 66 %) of the isomeric bis(methylthio) derivatives, b.p. = 61-63 °C (0.2 Torr). The ratio of **24a, E = SMe : 25a, E = SMe** was determined to be 5 : 95 by GC analysis. **24a, E = SMe** could not be isolated in pure form due to its thermolability. Characterization of **24a, E = SMe**: **MS** (70 eV): m/z 174 (M$^+$, 71), 159(57), 127(21), 126(100), 113(79), 112(32), 111(96), 80(75), 78(64), 53(20). **IR** 1940, ν(C=C=C). **25a, E = SMe**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.83/1.94 (2 × s, 2 × 3 H, 2 × methyl), 2.14/2.23 (2 × s, 2 × SMe), 4.97/5.04 (2 × s, 2 × 1 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.9, 15.9, 21.6, 22.7, 109.9, 127.6, 135.7, 143.4. **MS** (70 eV): m/z 174 (M$^+$, 98), 159(45), 126(97), 113(57), 112(29), 111(100), 82(16), 80(49), 78(48), 53(18). **Anal.** calc. for the mixture of the two isomers of $C_8H_{14}S_2$: C, 55.12; H, 8.09; S, 36.79; found: C, 55.20; H, 7.97; S, 36.67.

2,3-Bis(trimethylstannyl)-4-methyl-1,3-pentadiene (**25a, E = $SnMe_3$**). 30 mmol of **20a** in 300 ml of diethyl ether were dropped slowly to 12.56 g (63 mmol) of trimethylstannyl chloride in 100 ml of diethyl ether at -20 ° C. The reaction mixture was allowed to reach room temperature during 4 h and then were added 50 ml of an oxygen-free saturated solution of sodium bicarbonate. This mixture was transferred under argon into a separatory funnel and washed neutral with several portions of oxygen-free water. After drying the organic layer with sodium sulfate and evaporation of the solvent the remainder was fractionated to afford 6.43 g (16 mmol, 25 %) of **25a, E = $SnMe_3$**, b.p. = 125-132 °C (0.01 Torr). Furthermore 15 % of hexamethyldistannane, 8 % of products of hydrolysis and 45 % of non-volatile, mainly polymeric material were obtained. **^{1}H NMR** (80 MHz, C_6D_6) δ 0.22/0.29 (2 × s, 2 × 9 H, $SnMe_3$), 1.75/1.80 (2 × s, 2 × 3 H, methyl), 5.35 (AB-quartet, ^2J = 3.2 Hz, 2 H, vinyl). **^{13}C NMR** (100 MHz, C_6D_6) δ -8.8, -7.6, 22.7, 26.6, 120.9, 121.0, 136.4, 160.7. **MS** (70 eV): m/z (M$^+$ not found), 325(87), 324(36), 323(65), 321(40), 175(100), 165(64), 163(48), 133(42), 119(44), 55(37).

4-(1-Hydroxy-1-methylethyl)-2,6,6-trimethyl-2,3-heptadiene-6-ol (**24a, E = CMe_2OH**) *and 2,3,3,7-tetramethyl-4-octyne-2,7-diol* (**26a, E = CMe_2OH**). To a solution of 0.1 mol of **20a** in 500 ml of diethyl ether were added at -80 °C 17.4 g (0.3 mol) of dry acetone in 100 ml of diethyl ether. After the addition the reaction mixture was allowed to warm to -40 °C during 30 min and hydrolyzed with water. The organic layer was washed with water until neutral and dried with sodium sulfate. The solvent was evaporated and the remainder was fractionated to afford the two isomeric diols, 11.9 g (60 mmol, 60 %), b.p. = 65-70 °C (0.02 Torr). The ratio was determined to be 1 : 4. Characterization of **24a, E = CMe$_2$OH**: **MS** (70 eV): m/z (M^+ not found), 122(19), 107(85), 91(18), 79(13), 67(16), 61(28), 59(100), 43(61), 41(35), 31(15). **IR** 1945, ν (C=C=C). **26a, E = CMe$_2$OH** : **^{1}H NMR** (80 MHz, DMSO-d$_6$) δ 1.16/1.18/1.23 (3 × s, 3 × 6 H, methyl), 4.12/4.40 (2 × s, 2 × 1 H, OH). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 24.8, 24.9, 28.6, 34.3, 41.0, 70.0, 74.0, 78.6, 89.0. **MS** (70 eV): m/z (M^+ not found), 122(21), 107(76), 91(17), 81(8), 79(13), 67(17), 59(100), 43(45), 41(18), 31(16). **IR** 2240, ν(C≡C). **Anal.** calc. for the mixture of the two isomers of $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; found: C, 72.86; H, 10.99.

4-(Hydroxymethyl)-2-methyl-2,3-heptadiene-7-ol (**24a, E = CH$_2$OH**) *and 2,2-dimethyl-3-hexyne-1,6-diol* (**26a, E = CH$_2$OH**). A solution of 0.1 mol of **20a** in 500 ml of diethyl ether was cooled to -40 °C. Into this solution was introduced a stream of formaldehyde (obtained by thermically depolymerizing paraformaldehyde) through a wide-bore tubing, until the red solution turned completely colorless. The work-up of the reaction mixture was performed as described above to afford 5.96 g (42 mmol, 42 %) of a mixture of the two isomeric diols in a ratio of 2 : 3. Characterization of **24a, E = CH$_2$OH**: **MS** (70 eV): m/z (M^+ not found), 124(56), 109(49), 94(64), 93(74), 92(77), 91(54), 79(100), 77(92), 53(54), 43(97), 39(67). **IR** 1945, ν(C=C=C). **26a, E = CH$_2$OH**: **MS** (70 eV): m/z (M^+ not found), 124(7), 112(35), 111(37), 81(44), 79(55), 77(45), 55(31), 53(45), 43(67), 41(100), 31(35). **IR** 2240, ν(C≡C). **Anal.** calc. for the mixture of the two isomers of $C_8H_{14}O_2$: C, 67.57; H, 9.92; found: C, 67.88; H, 9.98.

*Reaction of **20a** with dimethyl sulfate in the presence of TMEDA.* To 30 mmol of **20a** in 300 ml of diethyl ether were dropped at -40 °C 13.9 g (0.12 mol) of TMEDA, thereby a yellow precipitate was formed. The reaction mixture was then derivatized as described for 3-methyl-1,1-pentamethylene-1,2-pentadiene (**24a, E = Me**) and 2,3-dimethyl-1,1-pentamethylene-1,3-butadiene (**25a, E = Me**) with 15.1 g (0.12 mol) of dimethyl sulfate to afford 2.11 g (19 mmol) of the isomeric hydrocarbons **24a, E = Me** (27 %), **25a, E = Me** (70 %), **26a, E = Me** (2 %), and **27a, E = Me** (1 %), with b.p. = 95-102 °C. The characterization of **24a, E = Me** and **25a, E = Me** is given above. 3,4,4-Trimethyl-1,2-pentadiene (**27a, E = Me**): **^{1}H NMR** (80 MHz, CDCl$_3$) δ 1.02 (s, 9 H, methyl), 1.67 (t, ^5J = 3.2 Hz, 3 H, allyl), 4.57 (q, ^5J = 3.2 Hz, 2 H, vinyl). Due to a discrepancy with reported ^{1}H NMR data[67] **27a, E = Me** was prepared independently[68] to confirm the values given above. **^{13}C NMR** (20 MHz, acetone-d$_6$) δ 14.6, 28.6, 32.7, 74.7, 107.2, 204.3. **MS** (70 eV): m/z 110 (M^+, 31), 95(25), 67(18), 57(100), 56(12), 55(18), 44(11), 41(39), 39(17), 29(23). **IR** 1950, ν(C=C=C). Characterization of 2,2-trimethyl-3-hexyne **26a, E = Me: MS** (70 eV): m/z 110 (M^+, 41), 95(100), 93(13), 81(16), 77(16), 67(63), 55(56), 53(26), 41(55), 39(21). The identy with an authentic sample[69] was proved by GC-MS analysis.

*Reaction of **20b** with dimethyl sulfate in the presence of TMEDA.* The addition of TMEDA and the work-up with dimethyl sulfate was performed on the same scale as described above for **20a** to afford 2.85 g (19 mmol, 62 %) of the isomeric hydrocarbons **24b, E = Me** (31 %), **25b, E = Me** (67 %), **26b, E = Me** (1.5 %), and **27b, E = Me** (0.5 %), with b.p. = 59-64 °C (15 Torr). Characterization of 1-(2-methyl-3,4-butadienyl)-1-methylcyclohexane (**27b, E = Me**): **MS** (70 eV): m/z 150 (M^+, 69), 135(98), 93(100), 91(74), 89(42), 79(52), 67(46), 53(37), 41(63), 39(32). 1-Methyl-1-(3-pentynyl)cyclohexane (**27b, E = Me**): **MS** (70 eV): m/z 150 (M^+, 45), 135(82), 107(89), 93(100), 91(74), 81(35), 79(63), 53(35), 41(68), 39(40). **Anal.** calc. for the mixture of the four isomers of $C_{11}H_{18}$: C, 87.93; H, 12.07; found: C, 87.98; H, 11.97.

*Compounds obtained in the reaction of **12c** with lithium metal, derivatization with water and deuterium oxide.*
1-(3-Methyl-1,2-butadienyl)-2,2,3,3-tetramethylcyclopropane. The spectroscopic data of **24c, E = H** (= **16b**) are given above.
1-(4-Methyl-1,3-pentadienylidene)-2,2,3,3-tetramethylcyclopropane (**25c, E = H**). **MS** (70 eV): m/z 164 (M^+, 20), 149(100), 134(24), 133(18), 121(31), 107(42), 105(33), 93(17), 91(31).

(3-Methyl-1-butynyl)-2,2,3,3-tetramethylcyclopropane (**26c, E = H**). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.81 (d, ^5J = 1.9 Hz, 1 H, cyclopropyl-methine), 1.06/1.09 (2 × s, 2 × 6 H, cyclopropyl-methyl), 1.15 (d, ^3J = 6.9 Hz, 6 H, methyl), 2.57 (sept of d, ^3J = 6.9 Hz, ^5J = 1.9 Hz, 1 H, methine). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.2, 20.8, 22.4, 23.7, 24.7, 24.9, 78.2, 86.6 **MS** (70 eV): m/z 164 (M^+, 93), 149(86), 121(79), 107(100), 105(54), 91(62), 69(38), 55(52), 43(45), 41(66). **IR** 2250, ν(C≡C).

2,6,6,7-Tetramethyl-2-octen-4-yne (**32, E = H**). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.98 (d, ^3J = 6.5 Hz, 6 H, methyl), 1.19 (s and m, 7 H, methyl and isopropyl-methine), 1.79 (d, ^4J = 1.2 Hz, 3 H, allyl), 1.89 (d, ^4J = 0.6 Hz, 3 H, allyl), 5.27 (m, 1 H, vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.3, 23.8, 24.5, 27.2, 35.4, 37.6, 78.7, 99.0, 105.9, 146.3. **MS** (70 eV): m/z 164 (M^+, 40), 122(24), 121(100), 107(10), 106(10), 105(29), 91(27), 79(18), 77(21), 41(18). **IR** 2265, ν(C≡C), 1665, ν(C=C). **Anal.** calc. for the mixture of the four isomers of $C_{12}H_{20}$: C, 87.73; H, 12.27; found: C, 87.90; H, 12.13.

4,4-Bis(1-(4-methyl-2-pentyne)-2,2,3,3-tetramethylcyclopropane) (**29, E = H**). After bulb-to-bulb distillation of the volatile compounds the remainder was triturated with a boiling mixture of diethyl ether and ethanol (3:1) to afford **29, E = H** as colorless crystals, m.p. = 120-121 °C. **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.81 (s, 2 H, cyclopropyl-methine), 1.03/1.06 (2 × s, 2 × 12 H, cyclopropyl-methyl), 1.26 (s, 12 H, methyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 18.5, 22.5, 25.0, 25.4, 26.6, 38.7, 80.5, 86.3. **MS** (70 eV): m/z 326 (M^+, 1), 163(100), 135(20), 121(79), 107(32), 105(19), 69(21), 57(40), 55(17), 43(30), 41(31). **Anal.** calc. for $C_{24}H_{38}$: C, 88.27; H, 11.73; found: C, 87.88; H, 12.02.

1-(1-Deuterio-3-methyl-1,2-butadienyl)-1-deuterio-2,2,3,3-tetramethylcyclopropane (**24c, E = D**). **MS** (70 eV): m/z 166 (M^+, 15), 151(100), 150(56), 109(57), 108(53), 98(43), 57(67), 56(50), 55(92), 43(32), 41(58).

1-(2,3-Dideuterio-4-methyl-1,3-pentadienylidene)-2,2,3,3-tetramethylcyclopropane (**25c, E = D**). **MS** (70 eV): m/z 166 (M^+, 19), 151(100), 150(26), 109(25), 108(23), 107(23), 106(24), 93(22), 92(21), 41(29).

(1-Deuterio-3-methyl-1-butynyl)-1-deuterio-2,2,3,3-tetramethylcyclopropane (**26c, E = D**). **MS** (70 eV): m/z 166 (M^+, 55), 165(56), 151(54), 150(57), 122(71), 108(100), 106(53), 92(53), 43(64), 41(70).

3-Deuterio-2,6,6,7-tetramethyl-2-octen-4-yne (**32, E = D**). **MS** (70 eV): m/z 165 (M^+, 14), 123(17), 122(100), 121(13), 106(14), 92(12), 91(10), 80(11), 79(10), 41(11).

Compounds obtained in the reaction of 12c with lithium metal, derivatization with trimethylsilyl chloride.

2,6,6,7-Tetramethyl-3-trimethylsilyl-2-octen-4-yne (**32, E = SiMe$_3$**). This compound was obtained by bulb-to-bulb distillation of the reaction mixture with b.p. = 55-57 °C (0.05 Torr). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.21 (s, 9 H, $SiMe_3$), 1.03 (d, ^3J = 8.0 Hz, 6 H, methyl), 1.20 (s, 6 H, methyl), 1.89/2.03 (2 × s, 2 × 3 H, allyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 0.3, 18.5, 23.8, 25.2, 27.5, 36.1, 37.9, 82.7, 102.4, 117.9, 154.6. **MS** (70 eV): m/z 236 (M^+, 14), 194(12), 193(62), 167(7), 123(5), 97(16), 74(7), 73(100), 59(10), 45(8). **HRMS** calc. for $C_{15}H_{28}Si$: 236.1960; found, 236.1957.

1,6-Bis(1-trimethylsilyl-2,2,3,3-tetramethylcyclopropyl-3,3,4,4-tetramethyl)-1,5-hexadiyne (**29, E = SiMe$_3$**). F.p. = 183-184 °C (from diethyl ether/ethanol). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.18 (s, 18 H, $SiMe_3$), 1.16 (s, 24 H, cyclopropyl-methyl), 1.30 (s, 12 H, methyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 1.4, 20.6, 21.0, 27.0, 30.1, 38.9, 85.1, 85.2. **MS** (70 eV): m/z (M^+ not found), 335(68), 306(7), 302(4), 162(9), 161(47), 97(26), 75(8), 74(14), 73(100), 57(15). **Anal.** calc. for $C_{30}H_{54}Si_2$: C, 76.52; H, 11.56; found: C, 76.28; H, 11.64.

1,2-Bis(trimethylsilyl)-4,4-pentamethylene-1,3-butadiene (**33**). 1,2-Bis(trimethylsilyl)-4,4-pentamethylene-2,3-butadiene (**24b, E = SiMe$_3$**) was stored for several days in chloroform-d_1 and characterized as follows. **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.05/0.07 (2 × s, 2 × 9 H, $SiMe_3$), 154 (m, 6 H, ring-methylene), 2.07 (m, 4 H, ring-allyl), 5.73 (m, 1 H, vinyl), 6.10 (d, ^4J = 2.0 Hz, 1 H, terminal-vinyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ -1.3, -0.2, 26.9, 27.5, 28.5, 30.3, 36.9, 125.0, 137.8, 143.1, 163.4. **MS** (70 eV): m/z 266 (M^+, 6), 178(8), 177(6), 163(8), 119(6), 118(19), 74(7), 73(100), 59(13), 45(11). **Anal.** calc. for $C_{15}H_{30}Si_2$: C, 67.59; H, 11.34; found: C, 67.62; H, 11.27.

4,11-Bis(trimethylsilyl)-2,3,3,7,7,8,8,12,12,13-decamethyl-tetradeca-1,4,5,9,10,13-hexaene (**34**).
The rearrangement was performed as described above. **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.12 (s, 18 H, $SiMe_3$), 1.07 (s, 12 H, methyl), 1.24/1.27 (2 × s, 2 × 6 H, methyl), 1.73 (br s, 6 H, allyl-methyl), 4.75/4.82 (2 × m, 2 × 2 H, vinyl), 5.18 (s, 2 H, allenyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 1.1, 20.6, 23.8/24.1, 24.5/24.6, 28.7, 29.0,

40.7, 43.4, 95.8, 106.47/106.53, 109.4, 152.4, 204.4 (only for three signals a splitting is observed due to the presence of *meso* and *d,l* form).

Metalation of the allenes ***16a****,* ***16b*** *and* ***19****.*
1-Deuterio-1-cyclopropyl-3-methyl-1,2-butadiene (**35a, E = D**) *and 3-deuterio-1-cyclopropyl-3-methyl-1-butyne* (**36a, E = D**).[70] 1.56 g (14.4 mmol) of **16a** were brought to reaction with 90 ml (0.14 mol) of a 1.6 M solution of butyllithium in hexane and 33.4 g (0.29 mol) of TMEDA at room temperature. The reaction mixture was dropped into an excess of 50 ml of deuterium oxide and the work-up and the isolation performed in the same procedure as described above to afford 1.38 g (12.7 mmol, 88 %) of the isomeric hydrocarbons in a ratio of 91:9. Characterization of **35a, E = D**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.31/0.65 (2 × m, 2 × 2 H, cyclopropyl-methylene), 1.17 (m, 1 H, cyclopropyl-methine), 1.69 (m, 6 H, methyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 6.8, 10.0, 20.9, 92.9 (t, $^1J_{C\text{-}D}$ = 24.4 Hz), 96.8, 200.8. **MS** (70 eV): m/z 109 (M^+, 21), 95(58), 94(100), 92(69), 78(86), 77(45), 42(48), 41(53), 39(66). Characterization of **36a, E = D**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.35/0.68 (2 × m, 2 × 2 H, cyclopropyl-methylene), 1.12 (m, 1 H, cyclopropyl-methine), 1.02 (br s, 6 H, methyl), 2.41 (m, 0.1 H (remainder of the undeuterated compound), methine). **MS** (70 eV): m/z 109 (M^+, 35), 94(100), 92(83), 80(29), 78(91), 77(39), 67(31), 42(61), 41(55), 39(35).

1-(1-Deuterio-3-methyl-1,2-butadienyl)-2,2,3,3-tetramethylcyclopropane (**35c, E = D**) *and 1-(3-deuterio-3-methyl-1-butynyl)-2,2,3,3-tetramethylcyclopropane* (**36c, E = D**). In the same way as described above starting from 2.36 g (14.4 mmol) of **16b** and 90 ml (0.14 mol) of a 1.6 M solution of butyllithium in hexane and 33.4 g (0.29 mol) of TMEDA 1.92 g (11.7 mmol, 81 %) of the isomeric hydrocarbons were obtained in a ratio of 95:5. Characterization of **35c, E = D**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.79 (br s, 1 H, cyclopropyl-methine), 0.99/1.11 (2 × s, 2 × 6 H, cyclopropyl-methyl), 1.68 (s, 6 H, methyl). **MS** (70 eV): m/z 165 (M^+, 8), 150(87), 121(29), 108(86), 97(56), 91(30), 57(58), 55(100), 43(53), 41(84). Characterization of **36c, E = D**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.81 (br s, 1 H, cyclopropyl-methine), 1.06/1.09 (2 × s, 2 × 6 H, cyclopropyl-methyl), 1.15 (br s, 6 H, methyl). **MS** (70 eV): m/z 165 (M^+, 60), 150(50), 107(100), 106(51), 91(56), 56(50), 43(60), 42(95), 41(62).

2-Cyclopropyl-3-methyl-2,3-pentadiene (**35a, E = Me**). The reaction mixture from 1.56 g (14.4 mmol) of **16a**, 90 ml (0.14 mol) of a 1.6 M solution of butyllithium in hexane and 16.7 g (0.14 mol) of TMEDA was poured into an excess of dimethyl sulfate and afforded 1.49 g (12.2 mmol, 85 %) of **35a, E = Me. ^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.32/0.61 ((2 × m, 2 × 2 H, cyclopropyl-methylene), 1.10 (br m, 1 H, cyclopropyl-methine), 1.65 (s, 6 H, methyl), 1.69 (s, 3 H, methyl). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 6.1, 14.1, 18.5, 21.1, 95.4, 99.9, 197.7. **MS** (70 eV): m/z 122 (M^+, 31), 107(100), 91(98), 79(61), 77(39), 70(39), 56(27), 43(64), 41(67), 39(57).

4,4-Pentamethylene-2-trimethylsilyl-2,3-butadiene (**35a, E = $SiMe_3$**). The reaction of 1.757 g (12.4 mmol) of **19** with 90 ml (0.14 mol) of a 1.6 M solution of butyllithium in hexane and 16.7 g (0.14 mol) of TMEDA afforded after subsequent derivatization with trimethylsilyl chloride as described above 2.095 g (10.8 mmol, 75 %) of **35a, E = $SiMe_3$** with b.p. = 72-74 °C (1.5 Torr) and 0.851 g (3.2 mmol, 22 %) of **24b, E = $SiMe_3$**. Characterization of **35a, E = $SiMe_3$**: **^{1}H NMR** (80 MHz, $CDCl_3$) δ 0.30 (s, 9 H, $SiMe_3$), 1.58 (m, 6 H, methylene), 1.87 (s, 3 H, methyl), 2.25 (m, 4 H, allyl). **^{13}C NMR** (100 MHz, C_6D_6) δ -1.4, 16.3, 26.7, 28.1, 31.7, 89.6, 96.0, 202.0. **MS** (70 eV): m/z 194 (M^+, 14), 179(4), 120(31), 105(8), 97(26), 74(7), 73(100), 59(6), 45(14), 43(6).

Metalation of ***19*** *and derivatization with dimethyl sulfate.* 1.757 g (14.4 mmol) of **19** and 90 ml (0.14 mol) of a 1.6 M solution of butyllithium in hexane and 16.7 g (0.14 mol) of TMEDA were brought to reaction and were derivatized with 72.58 g (0.576 mol) of dimethyl sulfate. After the usual work-up 0.541 g (3.6 mmol, 25 %) of the isomeric hydrocarbons **24b, E = Me**, **25b, E = Me**, **26b, E = Me**, and **27b, E = Me** were isolated, besides products of monometalation which were not analyzed in detail. The ratio of the compounds was determined to be 28 : 70 : 1 : 1.

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References and Notes

1. Part 22: Maercker, A.; Gross, A. *Angew. Chem.*, in print.
2. Taken in part from the M.Sc. and Ph.D. thesis of H. Wunderlich, University of Siegen, **1987** and **1990**.
3. For recent reviews on reductive lithiations of unsaturated compounds, see: a) Maercker, A. in Hanack, M. (Ed.), *Methoden der Organischen Chemie (Houben-Weyl)* Vol. E19d, Thieme, Stuttgart, **1993**, 448-556; b) Maercker, A. in Schleyer, P.v.R.; Sapse, A.-M. (Ed.), *Lithium Chemistry: A Theoretical and Experimental Overview,* Wiley, New York, **1995**, 477-577.
4. Zweig, A.; Hoffmann, A.K. *J. Am. Chem. Soc.* **1962**, *84*, 3278-3284.
5. Nahon, R.; Day, A.R. *J. Org. Chem.* **1965**, *30*, 1973-1976.
6. Edinger, J.M.; Day, A.R. *ibid* **1971**, *36*, 240-242.
7. Edinger, J.M.; Sisenwine, S.F.; Day, A.R. *ibid* **1971**, 36, 3614-3619.
8. The term 'quenching a lithium- or polylithiumorganic compound' implies that a snapshot of the species present (in solution) is taken, which is of course **not** the case. The X-ray analysis of 1,4-dilithio-1,4-diphenyl-2-butyne shows unambiguously the 1,4-dilithio-2-butyne structure: Setzer, W.N.; Schleyer, P.v.R. *Adv. Organomet. Chem.* **1985**, *24*, 353-451.
9. Maercker, A.; Dujardin, R. *Organomet. Synth.* **1986**, *3*, 356-357.
10. Maercker, A.; Dujardin, R. *Angew. Chem.* **1985**, *97*, 612-613; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 571-572; Maercker, A.; Dujardin, R.; Brauers, F. *Organomet. Synth.* **1988**, *4*, 362-365.
11. Maercker, A.; Dujardin, R.; Engelen, B.; Buchmeier, W.; Jung, M., unpublished results.
12. Günther, H.; Moskau, D.; Dujardin, R.; Maercker, A. *Tetrahedron Lett.* **1986**, *27*, 2251-2254.
13. Moskau, D.; Brauers, F.; Günther, H.; Maercker, A. *J. Am. Chem. Soc.* **1987**, *109*, 5532-5534.
14. Köbrich, G.; Wagner, E. *Angew. Chem.* **1970**, *82*, 548, *Chem. Ber.* **1970**, *103*, 2515-2525.
15. Köbrich, G; Merkel, D. *Liebigs Ann. Chem.* **1972**, *761*, 50-66.
16. Bauer, D; Köbrich, G. *Chem. Ber.* **1976**, **109**, 2185-2196.
17. Maercker, A.; Wunderlich, H. unpublished results.
18. a) Reich, H.J.; Yelm, K.E.; Reich, I.L. *J. Org. Chem.* **1984**, *49*, 3438-3440; b) Reich, H.J.; Reich, I.L.; Yelm, K.E.; Holladay, J.E.; Gschneidner, D. *J. Am. Chem. Soc.* **1993**, *115*, 6625-6635.
19. 1,2-, 1,3-, and 1,4-doubly bridged structures are characteristic for dilithiumorganic compounds, the lithium atoms are situated between the anionic centers: Maercker, A.; Theis, M. *Top. Curr. Chem.* **1987**, *138*, 1-61.
20. Schleyer, P.v.R. *Pure Appl. Chem.* **1983**, *55*, 355-362.
21. Schleyer, P.v.R. *Pure Appl. Chem.* **1984**, *56*, 151-162.
22. Macomber, R.S.; Hemling, T.C. *Isr. J. Chem.* **1985**, *26*, 136-139.
23. Maercker, A. *Angew. Chem.* **1987**, *99*, 1002-19; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 972-990.
24. Jacobs, T.L.; Prempree, P. *J. Am. Chem. Soc.* **1967**, *89*, 6177-6182.
25. Schaap, A.; Brandsma, L.; Arens, J.F. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1200-1202.

26. Hoff, S.; Brandsma, L.; Arens, J.F. *ibid.* **1968**, *87*, 916-924.
27. Mantione, R.; Alves, A. *Tetrahedron Lett.* **1969**, 2483-2484.
28. Klein, J.; Brenner, S. *Tetrahedron* **1970**, *26*, 2345-2352; Ref. 14 and Ref. 24.
29. Minter, D.E. Ph.D. thesis, University of Austin, **1974**.
30. Roumestant, M.L.; Gore, J. *Bull. Soc. Chim. Fr.* **1972**, 591-598; 598-605; Rona, P.; Crabbé, P. *J. Am. Chem. Soc.* **1969**, *91*, 3289-3292.
31. Maercker, A.; Theis, M. *Organomet. Synth.* **1986**, *2*, 378-380.
32. Gilman, H.; Haubein, A.H. *J. Am. Chem. Soc.* **1944**, *66*, 1515-1516.
33. Maercker, A.; Brieden, W. *Chem. Ber.* **1991**, *124*, 933-938.
34. Van de Flierdt, J.; Maercker, A. unpublished results; J. van de Flierdt, Ph. D. thesis, University of Siegen, **1990**.
35. Pearson, R.G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827-1836; Ho, T.L. *Chem. Rev.* **1975**, *75*, 1-20; Parr, R.G.; Pearson, R.G. *J. Am. Chem. Soc.* **1983**, 105, 7512-7522.
36. The importance of simple models in nucleophilic substitution, which relay on only two parameters is critically discussed by Anh, N.T. *Top. Curr. Chem.* **1980**, *88*, 145-162.
37. Giese, B. Kopping, B, Chatgilialoglu, C. *Tetrahedron Lett.* **1989**, *30*, 681-684. Giese, B. *Angew. Chem.* **1985**, *97*, 555-567; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 553-566; Giese, B. *Angew. Chem.* **1989**, *101*, 993-1004; *Angew. Chem. Int. Ed. Engl.* **1989**, **28**, 969-980.
38. Dimethyl disulfide does not fit into Pearson's concept: Creary, X. *J. Am. Chem. Soc.* **1977**, *99*, 7632-7639.
39. The gradual differences between the classical S_N2 mechanism and electron transfer mechanism are reviewed, especially the reaction of aromatic radical anions with electrophiles: Lund, H.; Daasbjerg, K.; Lund, T.; Pedersen, S.U. *Acc. Chem. Res.* **1995**, *28*, 313-319.
40. Yamatuka, H.; Kamafuji, K.; Nagareda, K.; Miyano, T.; Hanafusa, T. *J. Org. Chem.* **1989**, *54*, 4706-4708; in the reaction of Grignard reagents with benzophenone: Holm, T.; Crossland, I. *Acta Chem. Scand.* **1971**, *25*, 59-69.
41. Maercker, A. *Liebigs Ann. Chem.* **1970**, *732*, 151-164.
42. Maercker, A.; Klein, K.D. *Angew. Chem.* **1989**, *101*, 63-64; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 83-84.
43. Maercker, A.; Girreser, U. *Angew. Chem.* **1990**, *102*, 718-720; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 667-669.
44. Ichi Negishi, E. *Organometallics in Organic Synthesis*, Wiley, New York, **1980**, p. 53.
45. Huntsman, W.D. in Patai, S. (Ed.) *The chemistry of ketenes, allenes and related compounds*, Wiley, New York, **1980**, p. 561.
46. Crowley, P.J.; Leach, M.R.; Meth-Cohn, O.; Wakefield, B.J. *Tetrahedron Lett.* **1986**, *27*, 2909-2912; Zarges, W.; Marsh, M.; Harms, K.; Boche, G. *Angew. Chem.* **1989**, 101, 1424-1425; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1392-1393; the differentiation between a QUADAC and a dilithiumorganic compound by chemical means is possible: Maercker, A.; Bös, B. *Main Group Metal Chemistry* **1991**, *14*, 67-71.
47. Eberly, K.C.; Adams, H.E. *J. Organomet. Chem.* **1965**, *3*, 165-168.
48. Knorr, R. *Tetrahedron* **1981**, *37*, 929-938; Ref 42.
49. Bates, R.B.; Beavers, W.A.; Greene, M.G.; Klein, J.H. *J. Am. Chem. Soc.* **1974**, *96*, 5640-5642.

50. West, R.; Jones, P.C. *J. Am. Chem. Soc.* **1969**, *91*, 6156-6161.
51. a) Boche, G.; Etzrodt, H.; Marsch, M.; Thiel, W. *Angew. Chem.* **1982**, *94*, 141-142; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 132-133; *Angew. Chem. Suppl.* **1982**, 345-354; 355-360; Boche, G.; Etzrodt, H.; Massa, W.; Baum, G. *Angew. Chem.* **1985**, *97*, 858-859; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 863-864; Boche, G. *Top. Curr. Chem.* **1988**, *146*, 1-56.

    b) Engelhardt, L.M.; Papasergio, R.I.; Raston, C.L.; White, A.H. *J. Chem. Soc., Dalton Trans.* **1984**, 311-320.
52. a) Reich, H.J.; Holladay, J.E. *J. Am. Chem. Soc.* **1995**, *117*, 8470-8471; Reich, H.J.; Mason, J.D.; Holladay, J.E. *J. Chem. Soc., Chem. Commun.* **1993**, 1481-1483.

    b) Schade C.; Schleyer, P.v.R.; Geißler, M.; Weiss, E. *Angew. Chem.* **1986**, *98*, 922-924; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 902-904.
53. Ball, W.J.; Landor, S.R.; Punja, N. *J. Chem. Soc. (C)* **1967**, 194-197.
54. Brandsma, L.; Verkruijsse, H.D. *Synthesis of Acetylenes, Allenes and Cumulenes*, Elsevier, Amsterdam, **1976**, p. 219.
55. Bezaguet, A.; Bertrand, M. *Compt. Rend.* **1965**, *261*, 1695-1698.
56. Ref. 54, p. 192.
57. Crandall, J.K.; Paulson, D.R. *J. Org. Chem.* **1968**, *33*, 991-998.
58. Schmidbaur, H.; Schier, A.; Schubert, U. *Chem. Ber.* **1983**, *116*, 1938-1946.
59. Hennion, G.F.; Sheehan, J.J.; Maloney, D.E. *J. Am. Chem. Soc.* **1950**, *72*, 3542-3545.
60. Seyferth, D.; Yamazaki, H.; Alleston, D.A. *J. Org. Chem.* **1963**, *28*, 703-707.
61. Fantazier, R.M.; Poutsma, M.L. *J. Am. Chem. Soc.* **1968**, *90*, 5490-5498.
62. Crandall, J.K.; Sojka, S.A. *J. Am. Chem. Soc.* **1972**, *94*, 5084-5086.
63. Bly, R.S.; Swindell, R.T. *J. Org. Chem.* **1965**, *30*, 10-22.
64. Gibson, D.H., Ong, T.-S. *J. Organomet. Chem.* **1978**, *155*, 221-228.
65. Claesson, A.; Bogentoft, C. *Acta Chem. Scand.* **1972**, *26*, 2540-2542.
66. Warner, P.M.; Le, D. *Synth. Commun.* **1984**, *14*, 1341-1347.
67. Newman, M.S.; Lee, V. *J. Org. Chem.* **1973**, *38*, 2435-2438.
68. Brown, D.W.; Hendrick, M.E.; Jones, M. *Tetrahedron Lett.* **1973**, 3951-3954.
69. Compound **47** in Maercker, A.; Girreser, U. *Tetrahedron* **1994**, *50*, 8019-8034.
70. For the undeuterated compound see Ref. 15.

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