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Polylithiumorganic compounds
Part 28. The reaction of allene and alkyl substituted allenes with lithium metal☆

Adalbert Maercker *, Andrea Tatai, Burkhard Grebe, Ulrich Girreser

Institut für Organische Chemie, Universität Siegen, Adolf-Reichwein-Strasse, D-57068 Siegen, Germany

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Abstract

The reaction of allene (**3a**) and alkyl substituted allenes 1,2-hexadiene (**3b**), cyclopropylallene (**3c**), and vinylidene cyclopropane (**3d**) with lithium metal was investigated in order to access 2,3-dilithioalkenes **4a**–**d**. These dilithioalkenes **4a**–**d** are very reactive in polar solvents like THF and act as strong bases, either metalation of the starting allene **3a**–**d**, the solvent, or sufficiently acidic intermediates like **8 a**–**d** is observed. The metalation products **5**–**7** show follow-up reactions like 1,3-H shift to the corresponding 1-lithio-1-alkynes **8** and subsequent metalation to the dilithioalkynes **9**. Additionally, lithium hydride elimination and ring-chain rearrangement (for **5c**) are observed. 1,2-Hexadiene (**3b**) can be brought to reaction with lithium metal in the apolar solvent pentane, here the follow-up reactions are much slower due to the insolubility of **4b**. In all cases the elucidation of the reaction pathways is hampered by the formation of complex mixtures of, amongst others, regio- and stereoisomeric products upon quenching with simple electrophiles. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Allenes; Lithium dust; Reductive metalation; Dilithiumorganic compounds; Carbanion rearrangements

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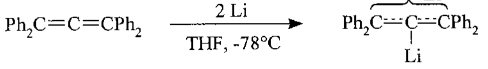
1. Introduction

The reductive metalation of unsaturated systems with lithium metal is one of the best methods to prepare polylithiumorganic compounds [2]. A most interesting organodilithium compound **2** with one σ- and one π-bonded lithium is obtained by the addition of lithium to tetraphenylallene (**1**) [3] (Scheme 1). The structure of **2** deduced by NMR spectroscopy was controversial at first [4,5]. However, the equivalence of both lithium atoms can be explained by assuming fast equilibration on the NMR time scale [6]. This is also reasonable according to ab initio calculations on the parent compound, 2,3-dilithiopropene [7]. We were interested in the preparation of this class of compounds and forwarded an investigation into the reactivity of allene and alkyl substituted allenes towards lithium metal. For butatriene, the next higher homologue of allene, a different behaviour of phenyl and alkyl substituted systems towards lithium metal has been observed, the latter showing 2,3- [8] and even 3,4-addition of lithium [9] instead of 1,4-addition with the former.



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Scheme 1. The known reaction of tetraphenylallene **1** to dilithioallene **2** with one σ-bonded and one π-bonded lithium.

2. Results and discussion

2.1. Propadiene (3a)

With the gaseous unsubstituted allene **3a** (b.p. −40 °C), only qualitative experiments have been performed. Allene does not react with lithium metal in apolar solvents like pentane, the reaction of **3a** with lithium

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* Corresponding author. Tel.: +49-271-740-4377; fax: +49-271-740-3270.

E-mail address: maercker@chemie.uni-siegen.de (A. Maercker).

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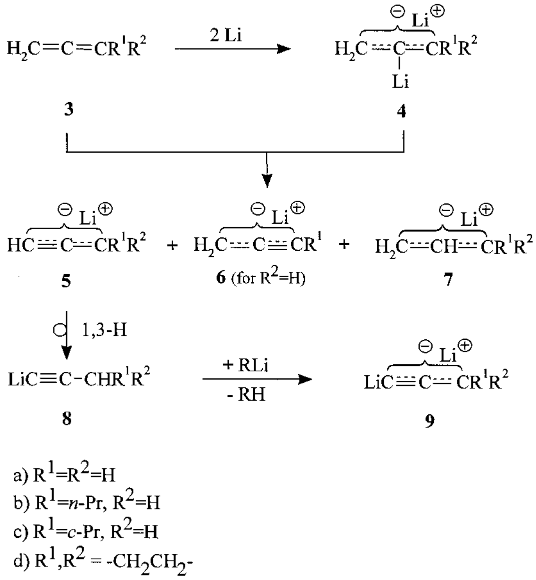


Scheme 2. Formation and all possible follow-up reactions of dilithioalkenes **4a**–**d**.

dust in THF requires temperatures of −30 °C and is indicated by a green coloration of the solution. No dilithiopropene **4a**, however, could be detected among the reaction products (Scheme 2). The main product after a reaction time of 1 h at −20 °C was the dilithiopropyne **9a** yielding 57% of 3-heptyne (**12**) after derivatization with diethyl sulphate, which was employed instead of dimethyl sulphate in order to obtain less volatile products. The σ-bonded lithium of the primarily formed dilithium compound **4a** has metalated the starting material **3a** affording allyl lithium (**7a**), which is detected as 1-pentene (**10**). As the amount of **7a** (20%) found in the product mixture is rather small, it was assumed that propadiene (**3a**) is metalated by allyl lithium (**7a**) as well. This could be shown in an independent experiment by treating propadiene (**3a**) with allyl lithium prepared from allyl phenyl ether and lithium [10], although this time besides metalation (5–6%) mainly non-volatile products have been obtained. The primary metalation product **5a** undergoes 1,3-hydride shift—a known reaction [11]—to 1-lithiopropyne (**8a**), trapped as 2-pentyne (**11**) in a yield of 23% yield after quenching with diethyl sulphate. 1-Lithiopropyne (**8a**) is mainly metalated once more to the final propargylide **9a**—again with one σ- and one π-bonded lithium [2]-affording 3-heptyne (**12**) after quenching with diethyl sulphate. So the reaction products obtained in the reaction of propadiene **3a** with lithium metal indicate the intermediate formation of the 2,3-dilithioalkene **4a**, which is not stable under the reaction conditions but acts as a strong base, starting a cascade of metalation and rearrangement reactions.

*2.2. 1,2-Hexadiene (**3b**)*

Propylallene (**3b**) and lithium metal essentially react in the same way in THF at −40 °C as the unsubstituted allene **3a** (Scheme 2). After 2 h of reaction time and separation of unreacted lithium metal by filtration, the addition of dimethyl sulphate to the dark green solution yielded a complex mixture, consisting of the following compounds (gas chromatography, *n*-decane as internal standard, see also Table 1): 16% of (*E*,*Z*)-2-hexene (**13**) (1:2) and 2% of 1-hexene (**14**), then 10% of 3-methyl-1,2-hexadiene (**15a**) and 3% of 3-heptyne (**16a**), both originating from **6b**. Furthermore 13% of (*E*,*Z*)-3-heptene (**17a**) (1:5) and 8% of 3-methyl-1-hexene (**18a**) were found as derivatives of **7b**. The main product (31% yield) in this reaction was 2-heptyne (**19a**) originating from 1-lithio-1-hexyne (**8b**), while **9b** delivered only 4-methyl-2-heptyne (**20a**) in 10% yield. Of unknown products, 7% (less than 1% each) were also detected by gas chromatography. So in the reaction of propylallene (**3b**) with lithium metal in THF a direct derivative of the primarily formed dilithium compound **4b** could not be found (Fig. 1).

We were lucky, however, that the reaction of 1,2-hexadiene (**3b**) with lithium dust also took place in boiling pentane, a solvent in which **4b** is more stable, simply due to its insolubility. The excess of lithium metal could not be filtered off, thus after 12 h of reflux the pale green reaction mixture was quenched with dimethyl sulphate. The main reaction products this time were (*E*)- and (*Z*)-3-methyl-3-heptene (**21a**) (41% 1:1) as well as 21% of 2,3-dimethyl-1-hexene (**22a**). Other products were found in lower yield: 6% of (*E*,*Z*)-2-hexene (**13**) (1:2), 6% of (*E*,*Z*)-3-heptene (**17a**) (1:1), and 4% of 3-methyl-1-hexene (**18a**), 10% of 2-heptyne (**19a**), and 9% of 4-methyl-2-heptyne (**20a**). Only 3% of unknown compounds were found and no **14**, **15a** and **16a** could be detected, demonstrating that in pentane as the solvent deprotonation in the 3-position of 1,2-hexadiene (**3b**) to **6b** did not occur.

Another run was deuterated after 10 h of reflux in pentane. Besides starting material **3b** and dimers, 6% each, the following deuterated compounds could be detected: 62% of (*E*,*Z*)-2-hexene-1,2-d_2 (**21b**) and 16% of 1-hexene-2,3-d_2 (**22b**), both originating from **4b**. Additionally, 6% of 1-hexyne-1-d_1 (**19b**) arising from 1-lithio-1-hexyne (**8b**) was found.

When the reaction mixture of **3b** with lithium metal was quenched with trimethylsilyl chloride in boiling pentane, the dilithium compound **4b** interestingly gave only (*E*,*Z*)-1,2-bis(trimethylsilyl)-2-hexene (**21c**) (*E*/*Z* = 2.2:1) in 53% yield corresponding to **21a** and **21b**. The product corresponding to **22a** and **22b** was not obtained. In addition, 20% of *E*,*Z*-**17c** (1.5:1) deriving from **7b** (one regioisomer only!) as well as 7% of **19c** from **8b** and 13% of **20c** from **9b** could be detected. As products of hydrolysis, 4% of (*E*,*Z*)-2-hexene (**13**) (1:1) and 3% of 1-hexyne were identified. The main product in the reaction mixture *E*-**21c** was isolated by distillation in 17% yield.

In order to obtain an NMR spectrum of the primarily formed dilithiumorganic compound **4b**, the white precipitate of **4b** in pentane was filtered off and dissolved in THF. Unfortunately, again decomposition took place with the formation of 1-lithio-1-hexyne (**8b**), although 1,2-hexadiene (**3b**) this time was absent and metalation therefore could not represent the origin of **8b** according to Scheme 2 (see also Table 1). A simple explanation is the assumption that in the absence of the acidic starting material **3b** the dilithiohexene **4b** splits off lithium hydride leading to the same lithioallene **5b**, which is formed by metalation of 1,2-hexadiene (**3b**). The other possible product **6b**, deprotonated in 3-position, is not formed, probably due to the influence of the alkyl substituent. The reaction corresponds to the formation of vinyl lithium from ethylene and lithium via 1,2-dilithioethane, whereby again lithium hydride is lost [12–16].

Deuteration of the THF solution of **4b** with D_2O after 1 h yielded 68% of **19b** from **8b** as well as 27% of *E*,*Z*-**21b** and 5% of **22b**. In diethyl ether as the solvent the decomposition of **4b** also takes place, although more slowly. Deuteration after 1 h yielded only 24% of **19b** besides 67% of *E*,*Z*-**21b** and 9% of **22b**.

Upon addition of 1,2-hexadiene (**3b**) to lithium dust in diethyl ether at room temperature the solution turns warm and deuterolysis after half an hour yielded only one deuterated product, namely again 1-hexyne-1-d_1 (**19b**) (28%) besides 16% of (*E*,*Z*)-2-hexene (**13**), 28% of 1-hexene (**14**) and 9% of 2-hexyne. The same was true for the reaction in dimethoxyethane (DME) as solvent, yielding 42% of **19b**, 26% of *E*,*Z*-**13**, 6% of **14** and 8% of 2-hexyne. The latter is the product of isomerization of the starting material **3b** formed via **6b**. In both solvents dimeric products ($M = 166$ g mol^{-1}) could be detected as well, in 19 and 18% yield, respectively. It was not excluded experimentally that some of the rearrangements observed upon deuterolysis of the reaction mixtures take place during the work-up under basic conditions, however, they are in accordance with the

Table 1
Relative amount in % of compounds obtained in the reaction of **3b** with lithium metal

Entry	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Reaction conditions and derivatization reagent	THF, −40 °C Me_2SO_4	THF, 22 °C Me_2SO_4	C_5H_{10}, 40 °C Me_2SO_4	C_5H_{10}, 40 °C D_2O	C_5H_{10}, 40 °C Me_3SiCl	C_5H_{10}, 40 °C precipitate dissolved in THF, D_2O	C_5H_{10}, 40 °C precipitate dissolved in Et_2O, D_2O	Et_2O, r.t. D_2O	DME, r.t. D_2O
E/*Z*-**13**	16 (1:2)	20 (1:1.5)	6 (1:2)	–	4 (1:1)	–	–	16	26
14	2	3	–	–	–	–	–	28	6
15a	10	8	–	–	–	–	–	–	–
16a	3	3	–	–	–	–	–	–	–
E/*Z*-**17a**	13 (1:5)	–	6 (1:1)	–	–	–	–	–	–
18a	8	4	4	–	–	–	–	–	–
19a	31	57	10	–	–	–	–	–	–
20a	10	–	9	–	–	–	–	–	–
E/*Z*-**21a**	–	–	41 (1:1)	–	–	–	–	–	–
22a	–	–	21	–	–	–	–	–	–
E/*Z*-**21b**	–	–	–	62	–	27	67	–	–
22b	–	–	–	16	–	5	9	–	–
19b	–	–	–	6	–	68	24	28	42
E/*Z*-**21c**	–	–	–	–	53 (2.2:1)	–	–	–	–
E/*Z*-**17c**	–	–	–	–	20 (1.5:1)	–	–	–	–
19c	–	–	–	–	7	–	–	–	–
20c	–	–	–	–	13	–	–	–	–
Dimeric products	–	–	–	6	–	–	–	19	18
Other	7 [a]	4 [a]	3 [a]	6 [b]	3 [c]	–	–	9 [d]	8 [d]

[a] Sum of unidentified products, less than 1% each.

[b] Educt **3b**.

[c] 1-Hexyne.

[d] 2-Hexyne.

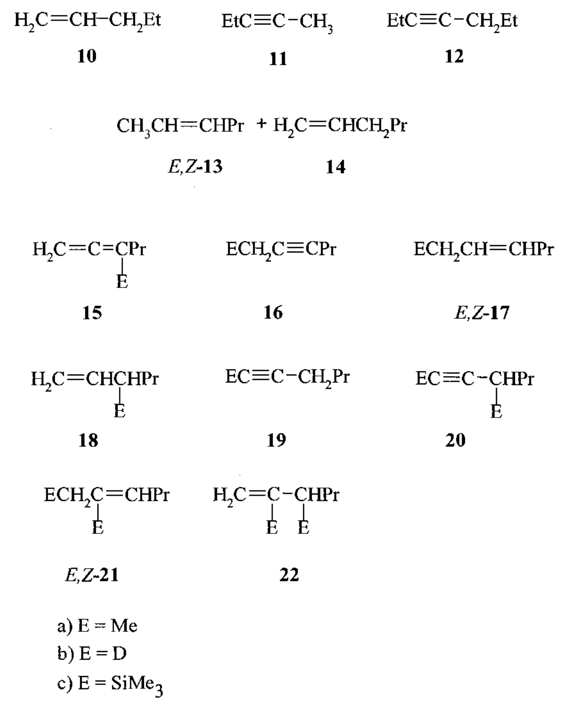
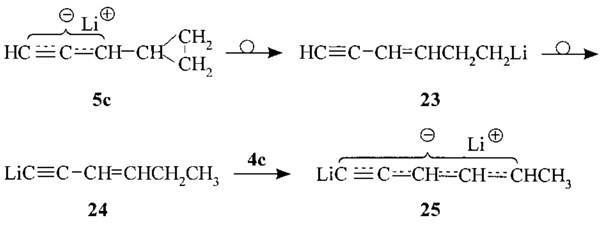


Fig. 1. Products obtained after derivatization of reaction mixtures of propadiene (**3a**) and 1,2-hexadiene (**3b**) with lithium metal.



Scheme 3. Rearrangements observed in the reaction of cyclopropylallene **3c** with lithium metal.

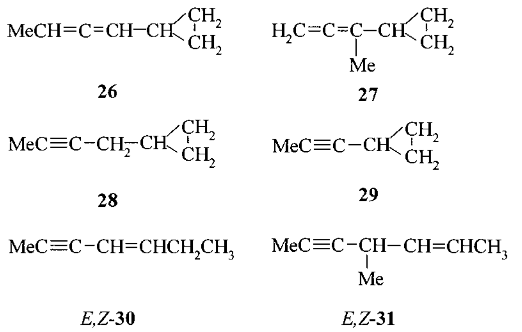


Fig. 2. Products obtained upon derivatization with dimethyl sulphate of the reaction mixture of cyclopropylallene (**3c**) with lithium metal.

results obtained in the quenching reactions with dimethyl sulphate where such reactions are impossible. Thus, in the apolar solvent pentane, direct proof for the formation of the dilithioalkene **4b** is obtained. When performing the synthesis of **4b** in an ethereal solvent or when dissolving the dilithioalkene **4b** in either diethyl ether or THF, the same follow-up reactions which were observed for **3a** are found. Interestingly a smaller number of derivatives are obtained when quenching **4b** with the less reactive trimethylsilyl chloride; due to steric as well as electronic reasons the reaction occurs preferentially at the terminal end of **4b** and **7b**.

2.3. *Cyclopropylallene (3c)*

In order to trap the primarily formed labile dilithiumorganic compound by an *intra*molecular ring-chain rearrangement we replaced the *n*-propyl group of the allene **3b** with a cyclopropyl group. This method [17] was already successful, not only with cyclopropyl alkene [18] and alkyne derivatives [19], but also with methylenecyclopropane [20] and numerous derivatives thereof [21,22].

Unfortunately, cyclopropylallene (**3c**) did not react with lithium dust in boiling pentane as the solvent, even on using ultrasonic irradiation. In THF as the solvent the reaction took place in a similar way as with propylallene (**3b**), although showing some significant differences (Scheme 2). Cyclopropylallene (**3c**) is less reactive than propylallene (**3b**) and did not react below −10 °C; the solution after starting of the reaction turned green, and later orange–brown. The starting material metalated in the endposition **5c** is fairly stable below 0 °C and can be trapped in high yield with dimethyl sulphate as **26**. The allene structure in **26** is retained as expected [23]. The primarily formed dilithiumorganic compound **4c** does not undergo ring-chain rearrangement as was anticipated, and no allyl lithium derivative corresponding to **7b** could be detected. Presumably **5c** is formed by lithium hydride elimination, which could not be isolated from the reaction mixture. It has to be mentioned, however, that the total yield of volatile products determined by gas chromatography using *n*-decane as internal standard was only 32% as a maximum and some intermediates are lost by polymerization. Deprotonation of the allenic proton α to the cyclopropylmethyl group occurs to a high extent as well, yielding **6c**, which is detected as **27** after quenching with dimethyl sulphate. Isomerization of the starting material **3c** with formation of **29** also takes place via **6c**. The acetylide **8c** formed by 1,3-hydride shift from **5c** this time is not metalated a second time to a propargylide corresponding to **9a** and **9b**. This propargylide could be prepared independently from **8c** and butyl lithium and no ring-opening takes place. Compound **5c**, however, undergoes ring-chain rearrangement to **24** presumably via **23**, even below 0 °C (Scheme 3). At even higher reaction temperatures, above 0 °C, **24** is also metalated to the resonance stabilized pentadienyl dianion **25**. Dianion **25** yields only *E*,*Z*-**31** upon the reaction with dimethyl sulphate, while **24** yields *E*,*Z*-**30** as expected (Fig. 2).

Table 2
Products of the reaction of cyclopropylallene (**3c**) with lithium dust in THF after derivatization with dimethyl sulphate in (%)

Conditions	**26**	**27**	**28**	**29**	*E*,*Z*-**30**	*E*,*Z*-**31**	Total yield
1 h, −10 °C–0 °C	55	22	–	3	7	–	23
1 h, 10 °C–20 °C	13	7	9	8	20	6	32
18 h, room temperature	–	6	60	19	2	2	13

Three runs of the reaction of cyclopropylallene (**3c**) with lithium dust in THF have been performed at three different temperatures and the results can be taken from Table 2.

2.4. Vinylidenecyclopropane (**3d**)

At last vinylidenecyclopropane (**3d**), the next higher homologue of methylenecyclopropane [20], was reacted with lithium dust, whereby again only THF worked as the solvent, although the reaction took place already at −40 °C. The results are quite similar to those with the unsubstituted allene **3a**; interestingly no open-chain products could be obtained. After 1 h at −40 °C, the excess of lithium was filtered off and dimethyl sulphate was added as usual. Gas chromatography using *n*-decane as internal standard showed only two reaction products in 76% yield: 1-cyclopropyl-1-propyne (**29**) and ethylidenecyclopropane (**32**) in a ratio of about 2:1 (Scheme 4). Only on using *n*-butyl lithium instead of lithium, about one half of the acetylide **8d** was metalated once more to the propargylide **9d** yielding **29** and **33** (1:1) upon the addition of dimethyl sulphate. Even on the level of the dianion the cyclopropane ring did not open up.

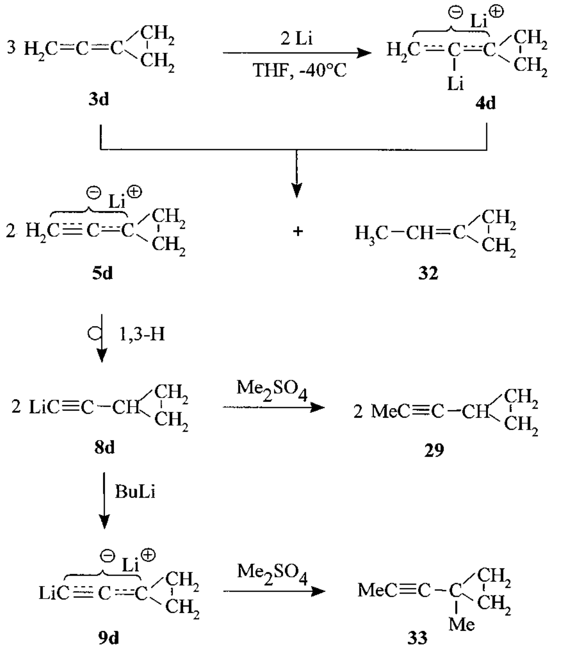
3. Conclusions

The highly activated tetraphenylallene **1** reacts smoothly even at very low temperatures with lithium metal to the stabilized dilithioallene **2** [2]. When switching to alkyl substituents, two general effects can be observed. Firstly, the reaction of the allenes **3a**–**d** with lithium metal requires higher temperatures, even when using highly reactive lithium dust containing 2% of sodium. This might be one reason for the observed follow-up reactions, especially for **3b** in pentane. Secondly, a polar solvent like THF or diethyl ether is required to bring about the reaction of **3a**,**c** and **3d** with lithium metal, in these polar solvents the dilithioalkenes **4a**–**d** then simply act as strong bases. So the use of the least polar solvent is recommended for the investigation of dilithioalkenes **4**. From a synthetic point of view, the formation of mixtures in quenching the dilithioalkene **4b** is the major problem, also in the evaluation of the follow-up reactions shown in Scheme 2. The results in the quenching experiments of **4b** presented here, however, show some selectivity when using less reactive electrophiles, like trimethylsilyl chloride. In this respect the use of other electrophiles would be interesting, and an investigation on triggering the reactivity of the dilithioalkene **4** by transmetalation would be worthwhile.

4. Experimental

4.1. General

All reactions with air sensitive compounds were carried out under an atmosphere of dried Ar (99.996%). Ethereal solvents were purified by adsorptive filtration over basic aluminium oxide (activity I) and freshly distilled under Ar from sodium–benzophenone ketyl. Dimethyl sulphate and diethyl sulphate were distilled in vacuo and stored over molecular sieve (3 Å). Mass spectra were obtained using GC–MS coupling on a HP 5988A mass spectrometer (hp5 capillary); *m*/*z* values



Scheme 4. Reaction of vinylidenecyclopropane **4d** with lithium metal and products obtained after quenching with dimethyl sulphate.

are reported followed by the relative intensity in parentheses. The ten strongest peaks and, if not enclosed, the intensity of the molecular ion is given. Nuclear magnetic resonance (^{1}H and ^{13}C) spectra were recorded on the Bruker instruments AC 200 and WH 80. 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 HP 5890 with a SE30 column (25 m) and FID was used.

4.2. Starting materials and reference compounds

Propadiene (**3a**) was obtained by reaction of 2,3-dichloro-1-propene with zinc powder [24]. The gas was condensed at − 100 °C and immediately used for further reactions. 1,2-Hexadiene (**3b**) was obtained from 1-hexyne according to Meisters and Swan [25]. Cyclopropylallene (**3c**) was synthesized by addition of dibromocarbene to vinylcyclopropane and subsequent reaction with methyl lithium [26]. Vinylcyclopropane itself was obtained by reaction of the *p*-tosylhydrazone of cyclopropyl methyl ketone with sodium amide [27]. Vinylidenecyclopropane (**3d**) was synthesized by addition of dibromocarbene to methylenecyclopropane [28] and reaction of the 1,1-dibromospiropentane with methyl lithium [29]. However, contrary to the reported method [29], it proved advisable to perform the addition of methyl lithium at − 100 °C and to keep the reaction mixture below − 40 °C throughout, in order to achieve acceptable yields. Furthermore, the yield decreased remarkably if the scale of the reaction was higher than 30 mmol.

1- and 2-pentene, 1-, 2-, and 3-hexenes and the corresponding pentynes and hexynes and the various heptenes are commercially available. 2-Heptyne (**19a**) was obtained by base-catalyzed rearrangement of 1-heptyne [30]. (*E*,*Z*)-3-Methyl-3-heptene (**21a**) was obtained by Wittig reaction of *s*-butyl triphenylphosphonium bromide [31] with *n*-butanal [32]. 2,3-Dimethyl-1-hexene (**22a**) was made available by subsequent alkylation of ethyl acetoacetate, first with propyl bromide and then with methyl iodide, base-catalyzed cleavage and Wittig reaction with methyl triphenylphosphonium bromide.

*4.3. General procedure for the reaction of allenes **3a–d** with lithium and subsequent derivatization*

If not stated otherwise, the allenes were added slowly as diluted solutions to a suspension of lithium dust [33] in the solvent given, with magnetic stirring. A small amount of the allene was added at a temperature slightly higher than the stated reaction temperature until the reaction starts, which was usually noticeable by a coloration of the reaction mixture. After quenching of the reaction mixture by addition of a solution of the dialkyl sulphate or the electrophile as a solution in the solvent employed, the reaction mixture was allowed to warm to room temperature (r.t.). In order to destroy the excess of dialkyl sulphate, a concentrated solution of ammonia was added and the mixture stirred at r.t. overnight. The aqueous layer was extracted with Et_2O, dried over sodium sulphate, and the solvents were evaporated using a rotary evaporator. Then the collected solvent was checked by gas chromatography for the presence of low boiling hydrocarbons deriving from the allenes.

*4.4. Reactions of propadiene (**3a**)*

*4.4.1. Reaction of propadiene (**3a**) with lithium*

To 0.36 g (52 mmol) of lithium dust in 25 ml of THF was introduced **3a**, generated from 6.02 g (55 mmol) of 2,3-dichloro-1-propene, at − 100 °C. The reaction mixture was allowed to warm to − 20 °C and kept at this temperature for 1 h. Then unreacted lithium was filtered off and the filtrate was quenched with 6.7 ml of diethyl sulphate. After the usual work-up the following products were identified using GC–MS coupling and commercially available reference compounds: 20% of 1-pentene (**10**), 23% of 2-pentyne (**11**), and 57% of 3-heptyne (**12**) [34–36].

*4.4.2. Reaction of propadiene (**3a**) with allyl lithium*

Allyl lithium was prepared by addition of freshly distilled allyl phenyl ether to lithium chunks in THF at − 15 °C with a catalytic amount of biphenyl [10]. After 2 h the solution was filtered off from the formed lithium phenolate and added dropwise to **3a** in an Et_2O–THF mixture at − 85 °C. This mixture was warmed to − 40 °C within 90 min, then derivatization was performed with diethyl sulphate. After the usual work-up bulb-to-bulb condensation afforded 5% of 1,2-pentadiene [37] and 1% of 2-pentyne (**11**) [38]. The remainder was of polymeric nature.

*4.5. Reactions of hexadiene (**3b**)*

*4.5.1. Reaction of 1,2-hexadiene (**3b**) with lithium*

To a suspension of 0.18 g (26 mmol) of lithium dust in 10 ml of *n*-pentane was added slowly a solution of 1.01 g (12 mmol) of **3b** in 3.5 ml of *n*-pentane. The reaction mixture was brought to reflux; after 30 min it turned brownish and a green solid was formed. After refluxing overnight the mixture was transferred into a separation funnel and the lithiumorganic compound was drawn off. The excess lithium stuck to the wall of the separation funnel. After derivatization with dimethyl sulphate and the usual work-up the reaction mixture was purified by bulb-to-bulb condensation and analyzed by GC–MS coupling after addition of *n*-decane as standard. Total yield of hydrocarbons was in the order of 65%. The reaction of **3b** in ethereal solvents was performed on the same scale as described above at the temperatures given in Table 1, the reaction mixture was separated from unreacted lithium by filtration. Total yield of hydrocarbons was in the range of 75%. Characterization of the products obtained upon derivatization with either dimethyl sulphate or D_2O was performed employing reference compounds (see above) with identical retention times (gas chromatography) and mass spectra (GC–MS coupling).

4.5.2. Derivatization with trimethylsilyl chloride on a preparative scale

Starting from 1.50 g (0.22 mol) of lithium metal, 8.21 g (0.10 mol) of **3b** in 150 ml of pentane the reaction was performed as described above with reflux for 10 h. Then 24.4 g (0.23 mol) of trimethylsilyl chloride were added dropwise and the mixture was heated to reflux for another 12 h. After the usual work-up, GC–MS coupling yielded the composition of the product mixture as given in Table 1. After two consecutive distillations, the products were characterized as follows. 1-Hexynyltrimethylsilane (**19c**): b.p. 47–58 °C (10 Torr), mass spectrum [39] and ^{1}H-NMR spectrum [40] were in accordance with reference data. 2-Hexenyltrimethylsilane (**17c**): ^{1}H- and ^{13}C-NMR spectrum in accordance with reference data [41]; MS (70 eV): *m*/*z* 156 [M$^+$, 7], 113(3), 99(2), 75(4), 74(9), 73(100), 59(8), 45(6), 43(4), 41(2). 1,3-Bis(trimethylsilyl)-1-hexyne (**20c**): MS (70 eV): *m*/*z* 226 [M$^+$, 9], 155(13), 139(6), 138(36), 110(5), 109(30), 74(9), 73(100), 59(5), 45(8). As main product *E*- and *Z*-1,2-bis(trimethylsilyl)-2-hexene (**21c**) were obtained, the *E*-isomer was isolated: 3.39 g (17 mmol, 17%) with b.p. 87–89 °C (10 Torr). ^{1}H-NMR (80 MHz, $CDCl_3$): δ 0.0 (s, 9H, $\mathrm{CH_2Si(C\underline{H}_3)_3}$), 0.05 (s, 9H, $\mathrm{{=}CSi(C\underline{H}_3)_3}$), 0.9 (t, 3H, CH_3), 1.4 (m, 2H, $\mathrm{C\underline{H}_2CH_3}$), 1.7 (d, 2H, $\mathrm{C\underline{H}_2Si(CH_3)_3}$), 2.0 (q, 2H, $\mathrm{{=}CC\underline{H}_2}$), 5.6 (tt, 1H, $\mathrm{{=}C\underline{H}}$). ^{13}C-NMR (20 MHz, $CDCl_3$): δ −1.1, −0.2, 14.0, 20.2, 22.6, 31.6, 137.5, 137.8. MS (70 eV): *m*/*z* 228 [M$^+$, 6], 140(17), 125(20), 112(6), 111(5), 75(4), 74(9), 73(100), 59(10), 45(10).

4.6. Reactions of cyclopropylallene (3c)

4.6.1. Reaction of cyclopropylallene (3c) with lithium

The reactions were performed as described in the general procedure. To 0.42 g (60 mmol) of lithium dust in 25 ml of THF were added 1.50 g (19 mmol) of **3c** and the internal standard in 5 ml of THF. The reaction mixture was kept for 1 h at the temperature given in Table 2. After filtration, derivatization with dimethyl sulphate, work-up, and bulb-to-bulb condensation, the products were isolated by preparative gas chromatography and characterized as follows. 1-Cyclopropyl-1-propyne (**29**): ^{1}H- and ^{13}C-NMR spectra were in accordance with reference data [42,43]; MS (70 eV): *m*/*z* 80 [M$^+$, 90], 79(100), 77(72), 65(17), 53(16), 52(26), 51(31), 50(22), 39(29), 28(24). 3-Cyclopropyl-1,2-butadiene (**27**): The mass spectrum as well as the ^{1}H- and ^{13}C-NMR spectrum was in accordance with reference data [44]. 1-Cyclopropyl-1,2-butadiene (**26**): The ^{1}H-NMR spectrum was in accordance with reference data [45]; MS (70 eV): *m*/*z* 94 [M$^+$, 17], 91(25), 79(100), 78(11), 77(83), 65(18), 53(20), 51(16), 39(39), 27(18). 1-Cyclopropyl-2-butyne (**28**): ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.2/0.45 (2 × m, 2 × 2H, cyclopropyl-CH_2), 0.9 (m, 1H, cyclopropyl–CH), 1.8 (t, $J = 2.5$ Hz, 3H, CH_3), 2.15 (dq, $J = 5.9/2.5$ Hz, 2H, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 3.5, 3.8, 9.8, 23.1, 75.6, 77.6. (*E*,*Z*)-4-Hepten-2-yne (**30**): The ^{1}H-NMR spectrum was in accordance with reported values [46], the mass spectra of the two isomers were nearly identical. MS (70 eV): *m*/*z* 94 [M$^+$, 73], 91(23), 79(80), 78(14), 77(100), 66(11), 65(15), 53(17), 51(17), 39(23). (*E*,*Z*)-4-Methyl-2-hepten-5-yne (**31**): The ^{1}H-NMR spectrum was in accordance with reported values [47], the mass spectra of the two isomers were nearly identical. MS (70 eV): *m*/*z* 108 [M$^+$, 47], 93(68), 91(79), 79(15), 78(16), 77(100), 65(26), 51(13), 41(18), 39(28).

4.6.2. Reaction of cyclopropylallene (3c) with *n*-butyl lithium

To 1.50 g (19 mmol) of **3c** in 5 ml of Et_2O were added 10 ml of a 2 M solution of *n*-butyl lithium in pentane at −30 °C. Then the solution was allowed to warm to −10 °C within 40 min and was quenched with dimethyl sulphate. After the usual work-up, which afforded a total yield of 90%, the following product composition was obtained: 9% of cyclopropylallene (**3c**), 28% of 3-cyclopropyl-1,2-butadiene (**27**), 11% of 1-cyclopropyl-2-butyne (**28**), 11% of 1-cyclopropyl-1-butyne, 22% of 4-cyclopropyl-2-pentyne, 22% not identified. Characterization of 1-cyclopropyl-1-butyne: The ^{1}H-NMR spectrum was in accordance with reported values [48]; MS (70 eV): *m*/*z* 94 [M$^+$, 27], 91(21), 79(100), 77(94), 66(35), 65(26), 53(25), 50(19), 39(38), 27(15). Characterization of 4-cyclopropyl-2-pentyne: MS (70 eV): *m*/*z* 108 [M$^+$, 2], 93(96), 91(45), 80(100), 79(84), 77(71), 67(26), 65(35), 41(39), 39(45). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.1–0.5 (m, 4 H, cyclopropyl–CH_2), 0.7–0.9 (m, 1 H, cyclopropyl–CH), 1.2 (d, $J = 6.9$ Hz, 3H, $\mathrm{CH{-}C\underline{H}_3}$), 1.8 (d, $J = 2.5$ Hz, 3H, $\mathrm{{=}CCH_3}$), 2.1 (m, 1H, $\mathrm{C\underline{H}{-}CH_3}$).

*4.7. Reactions of vinylidenecyclopropane (**3d**)*

*4.7.1. Reaction of vinylidenecyclopropane (**3d**) with lithium*

To 0.26 g (34 mmol) of lithium dust in 15 ml of THF were added 1.06 g (16 mmol) of **3d** in 15 ml of Et_2O at −40 °C. After quenching with dimethyl sulphate and the usual work-up the total yield of hydrocarbons was 76%, consisting of 39% of ethylidenecyclopropane (**32**) and 61% 1-cyclopropyl-1-propyne (**29**). The mass spectrum of **32** was in accordance with a reference spectrum [49].

*4.7.2. Reaction of vinylidenecyclopropane (**3d**) with n-butyl lithium*

To a solution of 0.76 g (11 mmol) of **3d** in 7 ml of Et_2O and 4 ml of THF were added at −60 °C 5.5 ml of a 2 M solution of *n*-butyl lithium in pentane (11 mmol). The reaction mixture was allowed to warm to −30 °C within 90 min and was then quenched with dimethyl sulphate. After the usual work-up 0.36 g (5.5 mmol, 50%) of a 1:1 mixture of 1-cyclopropyl-1-propyne (**29**) and 1-methyl-1-propynyl-cyclopropane (**33**) was obtained. The ^{1}H-NMR spectrum of **33** was in accordance with reported values [50]. MS (70 eV): *m*/*z* 94 (M^+, 100), 91(29), 79(88), 77(92), 65(24), 63(9), 53(14), 51(11), 40(9), 39(20).

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