Polylithiumorganic Compounds, 25[◇]

Controlled Rearrangement of 2,3-Dilithio-1,3-butadienes to 2,5-Dilithio-1,3-butadienes: Synthesis of 2-Isopropylidene-2,5-dihydrosilols

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Received December 4, 1997

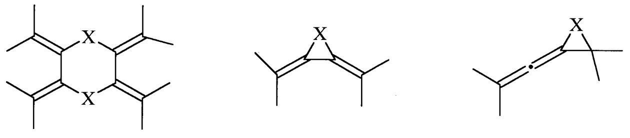
Keywords: Lithium / Polylithiumorganic compounds / Rearrangement / Cross conjugation / 2,5-Dihydrosilols

3,4-Dilithio-2,5-dimethyl-2,4-hexadiene (**4a**) rearranges to the cross-conjugated 2,5-dimethylhexadienediyl dianion **11a**. A mechanistic investigation proves the intermolecularity of this rearrangement, which is also observed when starting from **4b**. The 3-lithio-2,5-dimethylhexadienyl anion **10a** with one vinyllithium and one allyllithium group, is a true intermediate in this rearrangement, its synthetic potential is employed in the reaction with dichlorosilanes to form 2-isopropylidene-2,5-dihydrosilols **8**.

Introduction

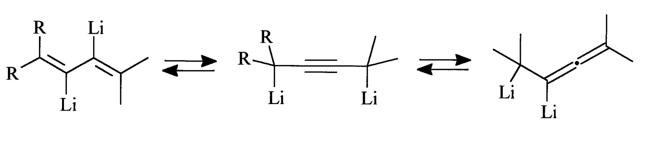
Among polylithiumorganic compounds, 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (**4a**) has proved valuable for the synthesis of hetero[6]radialenes **1**, hetero[3]radialenes **2**, or the cyclopropanes **3**, introducing either phosphorus, tin, boron, silicon, or titanium into these highly unsaturated ring systems.[2] The dilithiobutadienes **4a** and **4b**, free of lithium halide, are easily accessible by the addition of lithium metal to triene **7** in diethyl ether.[3] Alternatively, reaction of 2,5-dibromo-2,5-dimethyl-3-hexyne[4] with lithium metal affords **4a** as a solution containing lithium bromide.[5] The 2,3-dilithio-1,3-butadiene structure of **4a** in the solid state and in solution was investigated by X-ray analysis[6] and by NMR investigations in either perdeuterated diethyl ether or THF.[7]

Scheme 1



1 2 3

$X = PR', SnR'_2, BNR', SiR'_2$, Ti; R' = alkyl, aryl



4 5 6

a) R = Me b) R,R = -(CH$_2$)$_5$-

Preliminary results indicated that **4a** was not stable for prolonged periods (e.g. when stored as a solution in diethyl ether for a number of weeks at room temperature), and after quenching with water isomeric hydrocarbons were obtained.[5] One possible explanation for this isomerization would be a slow tautomerism as indicated by the structures **4** to **6**. This kind of tautomerism has been observed, in the case of a dilithiumorganic compound, in the solid-state structures of dilithium 1,2-diphenylbenzocyclobutadienediide, where the lithium atoms are at different positions in the same molecule.[8] This phenomenon has been termed "lithiotropy".[8a] More recently, thorough low-temperature NMR studies by Reich and co-workers on simple allenyl-/propargyllithium compounds, have established that for special cases, a real equilibrium exists between tautomeric intermediates in solution.[9] This equilibration has to be taken into account when analysing the product mixtures obtained upon derivatization with sufficiently reactive electrophiles, especially when the lithiumorganic compound is generated in situ by a metal-metal exchange reaction.[10]

We have, however, shown that for unsymmetrically substituted 2,3-dilithiobutadienes (which would be better named 3,4-dilithio-1,2-butadienes − with the corresponding structure **6**) the product mixtures obtained upon reaction with various electrophiles are mainly determined by the nature of the electrophile.[11] The same mesomeric dianion gives different isomeric products with either 1,2-butadiene-, 2-butyne-, or 1,3-butadiene skeleton. So far, there is no experimental evidence that a fast equilibration is responsible for the products obtained after derivatization of these dilithiobutadienes. From a preparative point of view, the mode of derivatization, i.e. either addition of the dilithiumorganic compound to the electrophile at high temperatures, or slow addition of the electrophile to the dilithiumorganic compound at low temperatures, would be the

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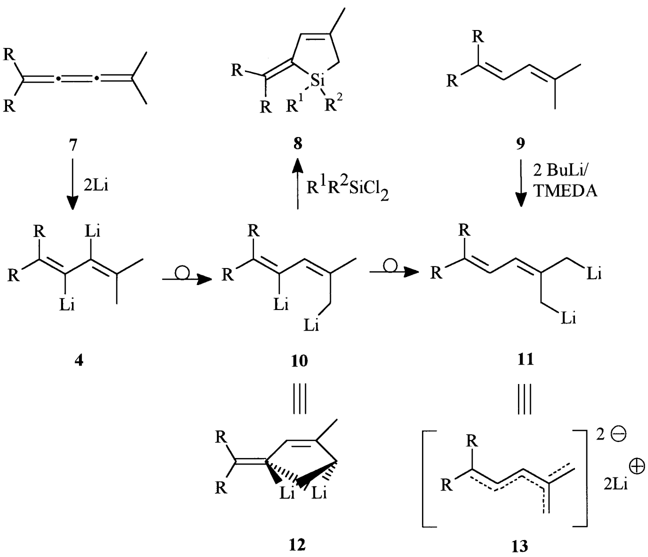
most obvious and straightforward indicator for any equilibrium influencing the product distribution. This was not the case for the unsymmetrically substituted dilithiobutadienes.[11] We therefore proceeded with an investigation of the observed slow isomerization and long-term stability of the tetraalkyl-substituted dilithiobutadienes **4a** and **4b**.

Results and Discussion

When freshly prepared solutions of **4a** are hydrolyzed, the only product isolated is 2,5-dimethyl-2,4-hexadiene (**9a**) in up to 90% yield.[3] The remainder is non-volatile material, probably formed by competing polymerization of the starting triene **7a** during the synthesis of **4a**. Upon workup with deuterium oxide, **14a** is isolated, with the deuterium atoms exclusively located in 2- and 3-position.[3] A solution of **4a**, however, containing lithium bromide, which has been stored for seven days at 20°C and subsequently derivatized with either water or deuterium oxide, gives a mixture with the 2,4-hexadiene **9a** as the main product. A small amount of the isomeric 2,5-dimethyl-1,4-hexadiene can also be identified from the mixture, after isolation by preparative gas chromatography. The corresponding products obtained upon deuterolysis provide more complex spectroscopic data: GC/MS analysis shows for the 1,4-hexadiene as well as for the 2,4-hexadiene derivative, the presence of mono-, di- and – to a small extent – trideuterated species. This is supported by the ^{13}C-NMR spectra for the 2,4-hexadiene, where deuterium is found not only at the 2- and 3-positions, but is also incorporated into the methyl groups. Therefore, besides **14a**, the presence of **15a**, which is confirmed by the integration of the ^{1}H-NMR spectrum, can also be concluded. There is evidence for structure **17a** for the dideuterated 2,5-dimethyl-1,4-hexadiene.

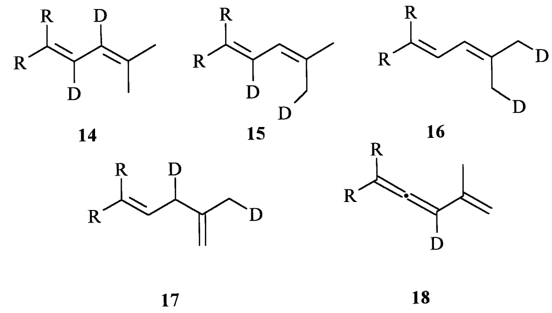
The isomerization of **4a** to **10a** can therefore be assumed, where one vinyllithium subunit isomerizes to the more stable, allyllithium subunit. In order to investigate this rearrangement in detail, solutions of **4a** were stored, with variation of crucial experimental parameters. Table 1 lists the ratio of 2,4-hexadiene to 1,4-hexadiene obtained. The yield of the mixture of isomeric hydrocarbons was not influenced by the storage conditions. Furthermore, only traces of other volatile products were formed (usually only a single compound to an extent of less than 1% according to GC/MS analysis). The amount of non-volatile material (determined be weighing after bulb-to-bulb distillation of the volatile products) was not affected by the storage conditions either. The amount of dilithiumorganic compound, determined by Gilman double titration,[12] decreases only marginally, so solvent cleavage[13] is not one of the major pathways observable.

Scheme 2



a) R = CH_3, b) R, R = -$(CH_2)_5$-
$R^1,R^2 = CH_3$, $R^1,R^2 = H$, $R^1 = H, R^2 = CH_3$

Figure 1. Products obtained upon derivatization of lithiated intermediates



The following results lead to a conclusive understanding of the mechanism of rearrangement. With prolonged storage, the amount of the 2,4-hexadiene decreases (entries 5–10). After only 21 days, the final and thermodynamically stable ratio of 66:34 is reached. The same final ratio is obtained when storing solutions of **4a** at higher temperatures (entries 1–3). Interestingly, when a sample of the "completely" rearranged **4a** is derivatized with deuterium oxide, the NMR data show a change of the positions of deuterium incorporation, which are mainly located at the methyl groups, and thus we can conclude that structure **16a** is the main product with the 2,4-hexadiene framework. The conceivable formation of the alternative 1,6-dideuterio-2,4-hexadiene, is not supported by the experimental results obtained in the analysis of the products of rearrangement of 2,3-dilithio-4-methyl-1,1-pentamethylene-1,3-pentadiene (**4b**), which are described below. For the 1,4-hexadiene derivative obtained after complete rearrangement, **17a** is still the main product.

With higher concentrations of the dilithiumorganic compound, the ratio of 2,4-hexadiene to 1,4-hexadiene also changed faster (entries 7, 11–13). This, besides the formation of mono- and trideuterated derivatives upon deuterolysis, is a second indication of the intermolecularity of this rearrangement.

In order to investigate the influence of the solvent, some experimental difficulties had to be overcome. Since **4a** is only poorly soluble in hydrocarbons like cyclopentane, and crystallizes at room temperature after being synthesized at

Table 1. Relative amounts of products with 2,4- and 1,4-hexadiene structure obtained by starting from **4a** (E = electrophile)

Entry	Storage Conditions	*t*	*T* [°C]	E	Solvent	*c* [mol/l]	**(14a–16a)/17a**[a]
1	containing LiBr	7 d	−10	H_2O	Et_2O	0.92	100:0
2	containing LiBr	7 d	20	H_2O	Et_2O	0.92	95:5[b]
3	containing LiBr	7 d	30	D_2O	Et_2O	0.92	66:34
4	free of lithium salts	7 d	20	D_2O	Et_2O	1.00	92:8[c]
5	free of lithium salts	–	20	H_2O	Et_2O	0.79	100:0
6	free of lithium salts	7 d	20	H_2O	Et_2O	0.79	94:6[d]
7	free of lithium salts	14 d	20	H_2O	Et_2O	0.79	81:19
8	free of lithium salts	21 d	20	D_2O	Et_2O	0.79	66:34[e]
9	free of lithium salts	28 d	20	D_2O	Et_2O	0.79	66:34
10	free of lithium salts	35 d	20	D_2O	Et_2O	0.79	66:34
11	free of lithium salts	14 d	20	D_2O	Et_2O	0.52	90:10
12	free of lithium salts	14 d	20	H_2O	Et_2O	1.00	73:27
13	free of lithium salts	14 d	20	H_2O	Et_2O	sat.	69:31
14	free of lithium salts	21 d	20	D_2O	C_5H_{10}	[f]	95:5
15	free of lithium salts	120 d	20	D_2O	C_5H_{10}	[f]	91:9
16	free of lithium salts, addn. of TMEDA	48 h	20	D_2O	C_5H_{10}	[f]	67:33[g]
17	free of lithium salts, addn. of TMEDA	24 h	20	D_2O	Et_2O	0.81	89:11[g]
18	containing LiBr	21 d	20	D_2O	Et_2O	0.80	77:23
19	free of lithium salts	21 d	20	D_2O	Et_2O	0.52	73:27
20	containing LiBr	21 d	20	D_2O	Et_2O	0.52	82:18
21	LiBr, deriv. within 10 h	21 d	20	D_2O	Et_2O	0.80	77:23
22	LiBr, deriv. within 15 s	21 d	20	D_2O	Et_2O	0.80	77:23
23	LiBr, deriv. within 9 h	–	20	H_2O	Et_2O	0.80	100:0
24	LiBr, deriv. within 20 s	–	20	H_2O	Et_2O	0.80	100:0
25	metalation of **9a**	48 h	20	D_2O	Et_2O	0.68	65:35[h]

[a] H instead of D for E = H_2O. – [b] 0.89 mol/l after storage, total yield 78%, not identified 3%, non-volatile 19%. – [c] 1.00 mol/l after storage, total yield 84%, not identified 3%, non-volatile 13%; **16**: 35% [D_1], 55% [D_2], 3% [D_3]; **17**: 33% [D_1], 60% [D_2], 2% [D_3]. – [d] 0.79 mol/l after storage, total yield 87%, not identified 3%, non-volatile 10%. – [e] A sample prepared in [D_{10}]Et_2O stored for 21 d at 20°C, was derivatized with water, the products obtained showed no deuterium incorporation, solvent decomposition was not detected. – [f] Concentration too low to be determinable by Gilman titration. – [g] In the presence of TMEDA up to 2% of 3-deuterio-2,5-dimethyl-1,3,4-hexatriene was found, which was independently prepared from the triene **7a** with 1 equivalent of BuLi and TMEDA (20°C, 48 h) in 55% yield. – [h] Total yield 98%.

reflux conditions, it was impossible to separate **4a** from the excess lithium metal necessarily employed in the synthesis. The solutions of **4a** were therefore stored together with this excess of lithium, and prior to derivatization, the solvent was evaporated in vacuo, and the residue dissolved in diethyl ether and filtered. Another difficulty which we had to overcome was that **4a** in cyclopentane is only accessible by addition of lithium to the triene **7a**. Since **7** has to be synthesized in an ethereal solvent, the diethyl ether was removed completely by evaporation, followed by addition of a small amount of cyclopentane and evaporation of the solvent again. This procedure was repeated twice.

As can be seen from Table 1 (entries 14–18) the rate of rearrangement increases in the more polar solvent systems. Acceleration of the isomerization is especially dramatic with the addition of TMEDA. Upon addition of TMEDA, the amount of monodeuterated products isolated after work-up with deuterium oxide also increases. Secondly, up to 2% of 3-deuterio-2,5-dimethyl-1,3,4-hexatriene (**18a**) are found when TMEDA is added. The most reasonable explanation for the origin of **18** is the metalation of minor amounts of the triene **7a**. This can be shown by independent metalation of the cumulene with one equivalent of *n*-butyllithium and equimolar amounts of TMEDA, which after subsequent deuterolysis affords, besides polymeric material, 55% of **18**.

Lithium bromide has a stabilizing effect on the 2,3-dilithio-1,3-butadiene (**4a**) (compare entries 8, and 18–20), and the rate of isomerization decreases when two equivalents of lithium salt are present. As discussed in the introduction, the speed of derivatization is important in evaluating fast isomerizations. However, no effect (entries 21–24) can be detected on the composition of the product mixture when either quenching within a few seconds (that is as fast as possible at reflux conditions) or by allowing solutions of the dilithiobutadiene to warm to room temperature very slowly in the presence of the electrophile. In this case, the slow decoloration of the deeply red solutions of **4a** at about −5°C allows the observation of the slow rate of derivatization. Additionally, it should be mentioned that no difference can be observed when storing solutions of **4a** either in daylight or in the dark (data not given in the table).

The final product from the rearrangement, **11a**, has been obtained independently by metalation of 2,5-dimethyl-2,4-hexadiene (**9a**).[14] A comparison of the reported ^{1}H-NMR data with those obtained for **11a**, shows that indeed the same compound is present. The products obtained by deuterolysis of metalated **9a** (entry 25) afford the same products, and in the same ratio as is observed when starting from **4a**. The degree of deuteration, however, is smaller, and the extent of monodeuterated products is higher in the former case.

Similar results are obtained when starting from 2,3-dilithio-4-methyl-1,1-pentamethylene-1,3-pentadiene (**4b**)[3a][5] (see Table 2). Prolonged storage leads to an increase of the 1,4-pentadiene derivative compared to the 1,3-pentadiene (entries 3–6), as does storage at higher temperatures (entries 1, 7, and 8). The final ratio of 1,3-diene to 1,4-diene deviates only a few percent from the ratio observed for **11a**. After deuterolysis, the main products found are **16b** and **17b**, and no deuterium is detectable incorporated into the allylic positions of the cyclohexane ring. Solutions of the dilithiobutadiene **4b** containing lithium iodide rearrange slower (compare entries 1 and 2), and in less polar solvents, the isomerization is also slower (entries 9 and 10). Metalation of the parent hydrocarbon **9b** gives approximately the same ratio, and the same products as are observed for the fully rearranged **11b** (entry 11).

Table 2. Relative amounts of products with 1,3- and 1,4-pentadiene structure obtained by starting from **4b** (E = electrophile)

Entry	Storage Conditions	t	T [°C]	E	Solvent	c [mol/l]	(**14b**−**16b**)/ **17b**[a]
1	free of lithium salts	7 d	20	D_2O	Et_2O	0.82	95:5[b]
2	containing LiI	7 d	20	D_2O	Et_2O	0.89	96:4[c]
3	free of lithium salts	–	20	H_2O	Et_2O	0.82	100:0
4	free of lithium salts	21 d	20	D_2O	Et_2O	0.82	87:13
5	free of lithium salts	35 d	20	D_2O	Et_2O	0.82	70:30
6	free of lithium salts	42 d	20	D_2O	Et_2O	0.82	70:30
7	free of lithium salts	7 d	−10	H_2O	Et_2O	0.82	100:0
8	free of lithium salts	7 d	30	H_2O	Et_2O	0.82	73:27
9	free of lithium salts	7 d	20	D_2O	C_5H_{10}	[d]	98:2
10	free of lithium salts	7 d	50	D_2O	C_5H_{10}	[d]	94:6
11	metalation of **9b**	48 h	20	D_2O	Et_2O	0.68	72:28[e]

[a] H instead of D for E = H_2O. – [b] 0.80 mol/l after storage, total yield 85%, not identified 2%, non-volatile 13%. – [c] 0.89 mol/l after storage, total yield 83%, not identified 3%, non-volatile 14%. – [d] Concentration too low to be determinable by Gilman titration. – [e] Total yield 85%.

For the preferential formation of the cross-conjugated dianions, compared to the linear butadienyl dianions, the concept of "Y-aromaticity" has been forwarded. This concept, which has been the subject of controversial discussion,[15] and is primarily used to explain the higher stability of branched bis-allylic dianions with $4n+2$ π-electrons, has also been under discussion for systems with 4 and 8 π-electrons.[14] However, ab-initio calculations show that "Y-aromaticity" in general does not exist. Refined calculations on the dianions in the gas phase result in a higher stability for the linear system.[16] The interactions of the counter ions, and the solvation by the solvent, therefore have to be considered to explain the experimental findings. Double bridged structures, which are a ubiquitous feature of 1,2-, 1,3-, and 1,4-dilithio compounds,[17] as indicated in structure **12** for **10a**, are most probably responsible for the observed stabilities.

The postulated, partly rearranged 1,4-dilithiobutadiene **10**, is indeed a stable intermediate in the rearrangement of **4** to **11**. However, the rearrangement of **4** can not be controlled when using diethyl ether as solvent. The metastable **10** is successfully trapped by a solvent mixture consisting of 5% of diethyl ether and 95% of pentane. This solvent mixture is still sufficiently polar to allow slow isomerization. Due to its greater polarity, **10** is very insoluble, and so precipitates from this solvent mixture, and the second rearrangement step does not occur. Therefore, by storing solutions of **4a** in this solvent mixture a dark coloured solid is formed. This solid, consisting mainly of **10a**, can be dissolved by adding a 1:1 mixture of diethyl ether/pentane. Thus, separation form the fully rearranged and even more polar **11a**, is achieved. This solution of **10a**, when cooled down to low temperatures and quenched immediately as described below, can be used in a synthetic manner:

The substituted silols **8** are accessible by addition of a solution of **10a** to a solution of a bifunctional silane (i.e. dichlorodimethylsilane, dichloromethylsilane, or dichlorosilane). Silols **8** can be isolated, when the work-up is performed with strict exclusion of air, water, and traces of acid. Separation from the additionally formed silanoles and siloxanes is otherwise nearly impossible. Traces of **8** (R^1 = R^2 = Me) have previously been obtained by quenching a stored solution of **4a** with dimethylbis(trifluorosulfonyloxy)silane.[18] The silols are obtained in yields of up to 26%, with only **8** (R^1 = R^2 = H) being formed in a smaller amount of 12% due to the lower reaction temperature applied for the low-boiling electrophile. When the dianion **11a** is treated with the same electrophiles, only polymeric material is formed, and the conceivable formation of a silacyclobutane derivative is not observed.

We would like to thank the *Volkswagen-Stiftung* and the *Fonds der Chemischen Industrie* for the support given.

Experimental Section

General: For general notes on preparative techniques for air- and water-sensitive compounds and instrumental equipment as well as the purification of solvents see ref.[11]. The mixtures of hydrocarbons were separated by preparative gas chromatography using a HUPE-BUSCH 1075c Prep GC (Hewlett Packard). A 2-m SE 30 column with nitrogen as carrier gas was employed. For the determination of the product composition analytical gas chromatography was used.

Synthesis of the Dilithiobutadienes **4a** *and* **4b**: The synthesis of **4a**, free of any lithium salt, is described in ref.[3b]. Dilithiobutadiene **4b** was synthesized by the addition of lithium metal to triene **7b**, which is available from 2,3-diiodo-4-methyl-1,1-pentamethylene-1,3-pentadiene.[19]

Storage of the Dilithiobutadienes **4a** *and* **4b**: Solutions were stored in conventional glass equipment or – when stored for prolonged periods above 21 d – in fused-glass tubes equipped with a magnetic stirring bar. For storage times of less than 21 d no difference could be detected using either mode. For each entry the sample amount was in the range of 0.05 to 0.1 mol.

2,5-Dimethyl-1,4-hexadiene (**17a**; H instead of D): ^{1}H-NMR data are in accordance with literature data.[20] − ^{13}C NMR (100 MHz, CDCl$_3$, $^1J_{\mathrm{CH}}$ coupling in Hz in parentheses): δ = 17.62 (125.3), 22.52 (125.2), 25.75 (125.3), 36.60 (125.1), 109.66 (151.8), 121.94 (152.0), 132.88, 145.48. − MS; *m/z* (%): 110 (35) [M$^+$], 95 (100), 93 (9), 69 (9), 68 (9), 67 (65), 35 (47), 53 (24), 41 (62), 39 (32).

2,5-Dimethyl-2,4-hexadiene (**9a**): The identity was confirmed by comparison with commercially available material (Aldrich) and the spectroscopic data in ref.[20].

2,5-Dimethyl-1,4-hexadiene-3,1'-[D$_2$] (**17a**): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.64 (s, 2.5 H, CH$_2$D) 1.74 (s, 6 H, CH$_3$), 2.69 (m, 1 H, CHD), 4.70 (m, 2 H, =CH$_2$), 5.19 (m, 1 H, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 17.58, 22.26 (t, $^1J_{\mathrm{CD}}$ = 19.3 Hz), 22.45, 25.75, 36.25 (t, $^1J_{\mathrm{CD}}$ = 19.2 Hz), 109.67, 121.94, 132.88, 145.34. − MS; *m/z* (%): 112 (39) [M$^+$], 111 (39) [M$^+$], 97 (69), 96 (100), 69 (23), 68 (43), 50 (26), 42 (31), 41 (28).

Mixture of 2,5-Dimethyl-2,4-hexadiene-1,4-[D$_2$] (**15a**) *and 2,5-Dimethyl-2,4-hexadiene-1,1'-[D$_2$]* (**16a**): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.75 (s, 6 H, CH$_3$, CH$_2$D), 1.80 (s, 7 H, CH$_3$, CH$_2$D), 6.00 (s, 1 H, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 17.72 (t, $^1J_{\mathrm{CD}}$ = 19.1 Hz), 18.01, 25.91 (t, $^1J_{\mathrm{CD}}$ = 19.3 Hz), 26.20, 120.97 (t, $^1J_{\mathrm{CD}}$ = 23.3 Hz), 121.31, 132.0. − MS; *m/z* (%): 112 (70) [M$^+$], 111 (60) [M$^+$], 97 (67), 96 (100), 95 (43), 68 (53), 67 (33), 56 (27), 55 (23).

Mixture of 2,5-Dimethyl-2,4-hexadiene-1,1'-[D$_2$] (**16a**) *and 2,5-Dimethyl-2,4-hexadiene-1-[D$_1$]:* ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.76 (s, 2.5 H, s, CH$_2$D), 1.81 (s, 3 H, CH$_3$), 6.00 (s, 1 H, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 17.73 (t, $^1J_{\mathrm{CD}}$ = 19.1 Hz), 18.00, 25.92 (t, $^1J_{\mathrm{CD}}$ = 19.2 Hz), 26.20, 121.31, 132.05. − MS; *m/z* (%): 113 (29) [M$^+$], 112 (89) [M$^+$], 111 (46) [M$^+$], 97 (96), 96 (100), 95 (29), 69 (28), 68 (54), 67 (32), 56 (36).

2,5-Dimethyl-2,3,5-hexatriene (**18a**; H instead of D): The ^{1}H-NMR data are in accordance with literature data.[21] − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 19.49, 20.36, 95.75, 97.68, 112.99, 140.52, 203.67. − MS; *m/z* (%): 108 (100) [M$^+$], 93 (48), 91 (75), 77 (70), 67 (13), 65 (15), 57 (10), 41 (18), 39 (23).

2,5-Dimethyl-2,3,5-hexatriene-4-[D] (**18a**): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.74 (s, 9 H, 3 × CH$_3$), 5.83 (m, 2 H, =CH$_2$). − MS; *m/z* (%): 109 (100) [M$^+$], 94 (50), 92 (75), 91 (19), 79 (18) 78 (48), 77 (35), 66 (10), 41 (15), 39 (21).

4-Methyl-1,1-pentamethylene-1,4-pentadiene (**17b**; H instead of D): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.41−1.80 (m, 6 H, ring CH$_2$), 1.72 (s, 3 H, CH$_3$), 2.12 (br. m, 4 H, allylic ring CH$_2$), 2.69 (d, 2 H, ^3J = 7.4 Hz, CH$_2$), 4.71 (m, 2 H, =CH$_2$), 5.12 (t, 1 H, ^3J = 7.4 Hz, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 22.48, 26.99, 27.83, 28.69, 28.76, 35.63, 37.27, 109.71, 118.55, 141.07, 145.55. − MS; *m/z* (%): 150 (63) [M$^+$], 135 (94), 107 (50), 94 (25), 93 (50), 68 (43), 67 (100), 52 (26), 51 (44), 49 (88). − C$_{11}$H$_{18}$ (150.3): calcd. C 87.93, H 12.07; found C 87.90, H 12.04

4-Methyl-1,1-pentamethylene-1,3-pentadiene (**9b**): ^{1}H-NMR data were in accordance with those in ref.[5], ^{13}C-NMR data with those in ref.[22]. − MS; *m/z* (%): 150 (93) [M$^+$], 135 (75), 102 (58), 93 (67), 92 (45), 82 (57), 81 (45), 79 (100), 67 (72), 41 (50).

4-Methyl-1,1-pentamethylene-1,4-pentadiene-3,4'-[D$_2$] (**17b**): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.40−1.59 (br. m, 6 H, ring CH$_2$), 1.72 (m, 2 H, CH$_2$D), 2.12 (br. m, 4 H, allylic ring CH$_2$), 2.69 (d, 1 H, ^3J = 7.4 Hz, CHD), 4.71 (m, 2 H, =CH$_2$), 5.13 (d, 1 H, ^3J = 7.4 Hz, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 22.18 (t, $^1J_{\mathrm{CD}}$ = 19.3 Hz), 26.98, 27.83, 28.69, 28.76, 35.33 (t, $^1J_{\mathrm{CD}}$ = 19.3 Hz), 37.27,109.72, 118.55, 141.07, 145.55. − MS; *m/z* (%): 152 (83) [M$^+$], 137 (65), 136 (67), 95 (57), 94 (57), 81 (58), 80 (70), 79 (73), 70 (75), 67 (100).

Mixture of 4-Methyl-1,1-pentamethylene-1,3-pentadiene-2,3-[D$_2$] (**14b**), *4-Methyl-1,1-pentamethylene-1,3-pentadiene-2,5-[D$_2$]* (**15b**), *and 4-Methyl-1,1-pentamethylene-1,3-pentadiene-5,4'-[D$_2$]* (**16b**): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.56 (m, 6 H, ring CH$_2$), 1.77−1.80 (2 × s, ca. 6 H, CH$_2$D), 2.21 (m, 4 H, allylic ring CH$_2$), 6.00 (m, 0.5 H, =CH). − MS; *m/z* (%): 152 (83) [M$^+$], 136 (75), 108 (33), 107 (42), 94 (100), 94 (58), 83 (42), 80 (38), 79 (92), 68 (37).

4-Methyl-1,1-pentamethylene-1,3-pentadiene-5,4'-[D$_2$] (**16b**): ^{1}H NMR (80 MHz, CDCl$_3$) δ = 1.55 (m, 6 H, ring CH$_2$), 1.80 (m, 4 H, CH$_2$D), 2.20 (m, 4 H, allylic ring CH$_2$), 5.98 (m, 2 H, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 17.73 (t, $^1J_{\mathrm{CD}}$ = 19.3 Hz), 26.93 (t, $^1J_{\mathrm{CD}}$ = 19.3 Hz), 27.78, 28.73, 28.98, 37.62, 118.05, 120.42, 132.50, 140.53.

1.4-Dilithio-2,5-dimethyl-2,4-hexadiene (**10a**): A suspension of 2,3-dilithio-2,5-dimethyl-2,4-hexadiene (**4a**) is prepared as described in ref.[3], starting from 6.90 g (1.00 mol) of commercially available lithium powder (Metallgesellschaft) and 37.8 g (0.35 mol) of the triene **7a** in 340 ml of *n*-pentane. To this green suspension, 10 ml of diethyl ether was added, and the mixture was stored for 5 weeks at 20°C. During this period, the suspension turned pale red and the solid turned darker. Then, 340 ml of diethyl ether was added, and the mixture was stirred vigorously and then filtered quickly. From this dark red solution, a solid precipitated, for best results this solution was used immediately after filtration.

2-Isopropylidene-1,1,4-trimethyl-1,5-dihydrosilole (**8**; R^1 = R^2 = CH$_3$): To a solution of 64.55 g (0.50 mol) of dichlorodimethylsilane (Merck) in 500 ml of diethyl ether, was added, dropwise at 35°C, a solution of **10a** (0.35 mol in 340 ml of solvent), the preparation of which is described above. After complete addition, the mixture was stirred for another hour at room temperature. After filtration under inert gas, the solvent was evaporated in vacuo. The remainder was purified by bulb-to-bulb distillation at 0.01 Torr and a bath temperature of 30°C. The crude product was fractionated at 12−15 Torr by distillation. Further purification by preparative gas chromatography afforded 12.28 g (0.074 mol, 21%) of **8** (R^1 = R^2 = CH$_3$) − ^{1}H NMR (80 MHz, CDCl$_3$) δ = 0.26 [s, 6 H, Si(CH$_3$)$_2$], 1.32 (s, 2 H, SiCH$_2$), 1.82−1.87 (m, 9 H, 3 × CH$_3$), 6.27 (s, 1 H, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = −1.5, 20.7, 23.2, 23.3, 25.6, 131.2, 135.8, 137.3, 141.8. − MS; *m/z* (%): 166 (100) [M$^+$], 151 (64), 123 (15), 109 (21), 107 (5), 97 (18), 83 (8), 73 (45), 59 (55), 43 (12). − C$_{10}$H$_{18}$Si (166.3): calcd. C 72.21, H 10.91; found C 72.26, H 10.96.

1,4-Dimethyl-2-isopropylidene-1,5-dihydrosilole (**8**; R^1 = H, R^2 = CH$_3$): The reaction was performed on the same scale as described above, starting from 57.55 g (0.50 mol) of dichloromethylsilane (Merck). The solution of **10a** was added dropwise in such a way to keep the temperature of the reaction mixture between 20 and 25°C to afford 13.86 g (0.091 mol, 26%) of **8** (R^1 = H, R^2 = CH$_3$). − ^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.26 (d, 3 H, J = 3.6 Hz, SiCH$_3$), 1.44 (m, 2 H, SiCH$_2$), 1.79/1.84/1.85 (3 × s, 9 H, 3 × CH$_3$), 4.45 (m, 1 H, SiH), 6.27 (s, 1 H, =CH). − ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = −4.4, 20.1, 20.7, 23.3, 26.7, 131.2, 134.9, 137.1, 142.7. − MS; *m/z* (%): 152 (100) [M$^+$], 137 (81), 110 (41), 109 (82), 97 (38), 95 (59), 83 (29), 73 (76), 59 (79), 43 (37). − C$_9$H$_{16}$Si (152.3): calcd. C 70.97, H 10.59; found C 71.03, H 10.67.

2-Isopropylidene-4-methyl-1,5-dihydrosilole (**8**; R^1 = R^2 = H): The reaction was performed on the same scale as described above with 50.55 g (0.50 mol) of dichlorosilane (Messer-Griesheim), keeping the temperature of the reaction mixture between 5 and 10°C to afford the extremely acid-sensitive **8** ($R^1 = R^2 = H$). − ^{1}H NMR (400 MHz, C_6D_6) $\delta = 1.54$ (s, 2 H, $SiCH_2$), 1.85/1.89/1.95 (3 × s, 9 H, 3 × CH_3), 4.64 (s, 2 H, SiH_2), 6.52 (s, 1 H, =CH). − $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): $\delta = 16.22$, 20.69, 23.13, 27.84, 131.44, 132.34, 138.01, 143.11. − MS; *m/z* (%): 138 (58) [M^+], 123 (60), 96 (95), 95 (91), 81 (51), 69 (53), 67 (69), 59 (58), 55 (78), 43 (100). − HRMS for $C_8H_{14}Si$: calcd. 138.0862; found 138.0865.

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