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Polylithiumorganic Compounds. Part 27:[1] C,C-Bond Forming Reactions of 3,4-Dilithio-2,5-dimethyl-2,4-hexadiene

Adalbert Maercker,[a,*] Joachim van de Flierdt[a] and Ulrich Girreser[b]

[a]*Institut für Organische Chemie der Universität Siegen, Adolf-Reichweinstr. 2, D-57068 Siegen, Germany*
[b]*Pharmazeutisches Institut der Christian-Albrechts-Universität, Gutenbergstr. 76, D-24118 Kiel, Germany*

Dedicated to Professor Harald Günther on the occasion of his 65th birthday

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Abstract—The reaction of the title compound 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (**4**) with various mono- and bifunctional carbon-centered electrophiles is investigated, with special emphasis on carbonyl and carbonic acid derivatives. Depending on the nature of the electrophile, mono- and disubstituted derivatives with either butadiene, allene, or alkyne skeleton are obtained. Ring forming reactions in the second derivatization step are only observed in a few cases. Electrophiles bearing halogens as leaving groups react by a different mechanism and are not suitable in C,C-bond forming reactions. The compounds obtained in this investigation are suitable and highly reactive building blocks for further modifications.

Introduction

Among dilithiumorganic compounds with both negative charges formally located at sp^2-hybridized carbon atoms, 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (**4**)[2] has a high potential for the synthesis of heterocycles, only comparable to the well investigated 1,2-dilithiobenzene (**3**) or (*Z*)-β,*o*-dilithiostyrene (**5**) and its derivatives.[3] The structure of **4** is known in solution[4] as well as in the solid state,[5] and its stability, rearrangement and decomposition products have been analyzed in different solvents.[6] **4** Allows access to fascinating compound classes, that are hetero[6]radialenes **6**, hetero[3]radialenes **7**, and allene derivatives **8**.[7] **4** is easily accessible, stabilized with lithium salt, by lithium bromine exchange starting from dibromide **1**, or free of lithium salt by addition of lithium metal to the highly reactive triene **2**, even on a molar scale.[8] Thus, a systematic investigation of the reactivity of **4** towards carbon-centered biselectrophiles and simple electrophiles was forwarded, in order to evaluate the potential of **4** in the synthesis of functionalized carbocycles and reactive disubstituted derivatives. The structure of these derivatives is mainly determined by the nature of the electrophile, i.e. its hardness according to Pearson's concept of hard and soft acids and bases, as we have already shown for the derivatization of unsymmetrically substituted 2,3-dilithiobutadienes with a variety of electrophiles (Scheme 1).[9]

Keywords: C,C-bond formation; cyclizations; polylithiumorganic compounds; synthetic methods.
* Corresponding author. Tel.: +49-271-740-4377; fax: +49-271-740-2512; e-mail: maercker@chemie.uni-siegen.de

Results and Discussion

The results obtained upon reaction of **4** with different electrophiles and biselectrophiles will be divided into the following chapters:

1. Ring closure reactions and attempted ring closure of **4** with carbon disulfide, carbon dioxide, and follow-up reactions;
2. An investigation into the reaction of **4** with diethyl carbonate, esters, and amides;
3. Reaction of **4** with various aldehydes and ketones; and
4. Reaction of **4** with miscellaneous electrophiles.

Ring closure reactions and attempted ring closure of 4 with carbon disulfide, carbon dioxide, and follow-up reactions

A solution of the dilithiobutadiene **4** in diethyl ether is brought to reaction with one equivalent of carbon disulfide. After work-up of the reaction mixture with a degassed, oxygen-free aqueous ammonium chloride solution the thiophenthione **15** is obtained in 60% yield as main product. Purification is possible by several cleaning procedures, while avoiding thermal stress that leads to decomposition. A possible reaction mechanism is outlined in Scheme 2, structure assignment is simplified by comparison of the spectroscopic data with those of thiophenthione **20**.[10] Interestingly, when a non-degassed aqueous ammonium chloride solution is used, the hydroxylated thiophenthione **16** is the major product. When hydrolysis of the reaction is completely omitted in order to access the hypothetical

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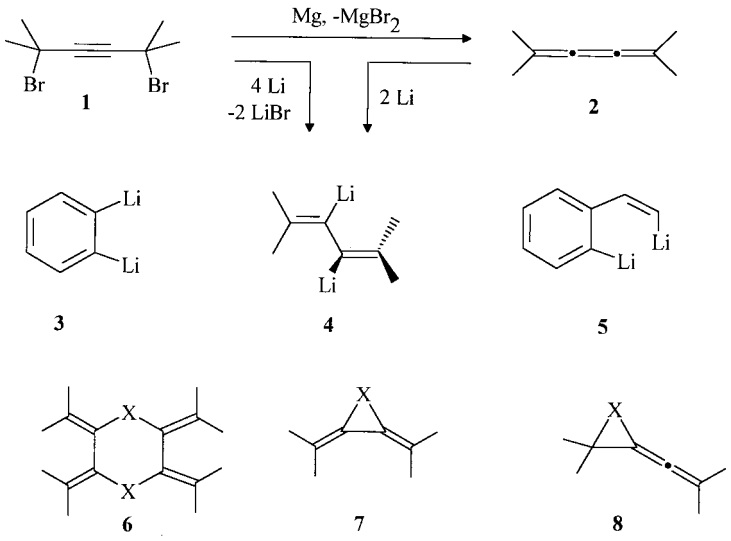
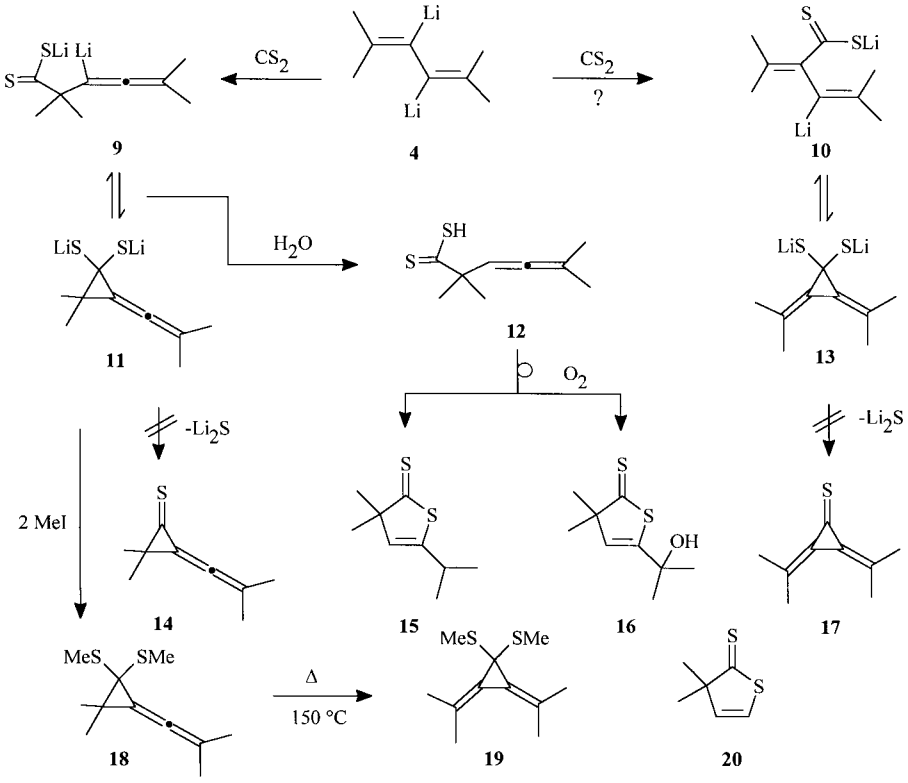


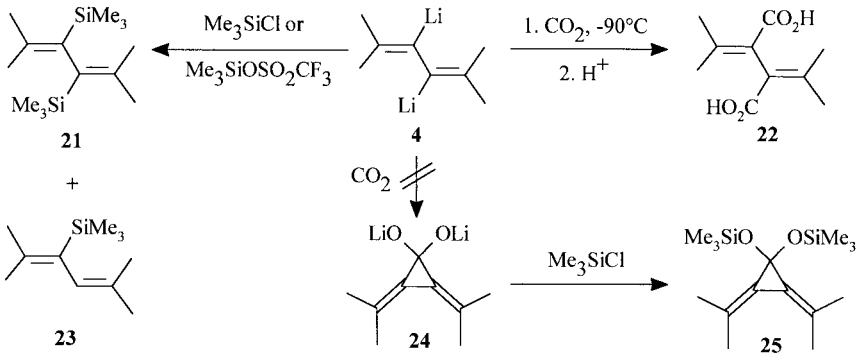
Scheme 1. X=SiR_2, SnR_2, Ti, BNR; R=aryl, alkyl.

thioketones **14** and **17**, exclusive formation of an orange–red tar is observed, giving no evidence for the wanted three-membered rings. The formation of tarry products upon reaction of metallorganic compounds with carbon disulfide is well known.[11] Similarly, when quenching **4** with either two equivalents of carbon disulfide or diethyl trithiocarbonate, complex mixtures are formed, consisting mainly of polymeric material. There is no sufficient spectroscopic evidence for the formation of **17** or the formation of a 1,4-dithioketo[6]-radialene as is shown by GC/MS analysis of the volatile compounds.

However, when a non-aqueous workup of the reaction mixture of **4** with 1 equiv. of carbon disulfide is performed by addition of methyl iodide, the three-membered ring **18**, the bismethylthio derivative of **11** is isolated in over 50% yield. Structure assignment of the allene is straightforward when looking at the ^{13}C NMR data with the sp-hybridized carbon atom at about 186 ppm and the allenic stretching vibration at 2000 cm^{-1} in the IR spectrum and the corresponding Raman resonance at 2000 cm^{-1} for the asymmetric stretching vibration.[12] Furthermore a chemical proof is given by the fact that **18** does not react readily with PTAD (3,5-dihydro-4-phenyl-4*H*-1,2,4-triazole-3,5-



Scheme 2.



Scheme 3.

dione), one of the strongest dienophiles,[13] in contrast to the [3]- and [6]radialenes investigated so far.[14] The allene **18** rearranges quantitatively to the 1,3-diene **19** upon heating to 150°C, this rearrangement requires as much as 360°C for the corresponding hydrocarbon without sulfur atoms.[15] Obviously, lithium sulfide elimination of either **11** or **13** is not the favored reaction, instead polymerization or rearrangement of their hydrolysis products to **12** is observed (Scheme 2).

The reaction of **4** with carbon dioxide leads to 2,3-diisopropylidene-succinic acid (**22**) in over 80% yield.[2] The diacid is the only product isolated, either upon addition of **4** to a suspension of carbon dioxide in diethyl ether at −120°C or by slowly blowing carbon dioxide gas into a solution of **4** at room temperature. Even the optimized reaction conditions employed by Bickelhaupt et al. to cyclize 1,3-di(bromomagnesio)propane with carbon dioxide to cyclobutane by using a carbon dioxide/argon mixture[16] do not afford any cyclization product with **4**. Attempts to trap the hypothetical cyclic intermediate **24** are performed in the presence of trimethylsilyl (TMS) chloride. This derivatization reagent reacts rather slowly with **4** affording **21** in 40% yield and a remarkable amount of **23** as well as 2,5-dimethyl-2,4-hexadiene. Yields are better when using a better leaving group like the triflate anion (see Experimental) (Scheme 3).

So TMS chloride is a suitable reagent for the trapping of **24**. However, 1,1-bis(trimethylsilyloxy)cyclopropane **25** cannot be detected when performing the simultaneous addition of carbon dioxide and TMS chloride to **4** at temperatures between −90°C and room temperature or by quenching **4** with carbon dioxide in the presence of TMS chloride. Triggering the reactivity of **4** by addition of freshly prepared magnesium bromide has no effect on the outcome of the reaction with carbon dioxide either.

Despite the reasonably assumed formation of **11** or **13** in the reaction of **4** with carbon disulfide, the formation of **24** cannot be concluded. Probably steric constraints and not the reactivity of the intermediate monosubstituted vinyllithium compound determine the ring closure.

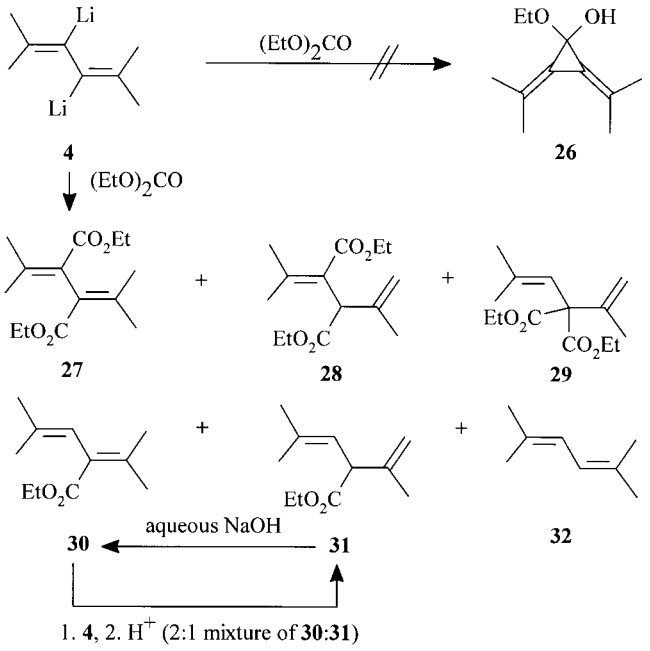
An investigation into the reaction of 4 with diethyl carbonate, esters, and amides

The reaction of **4** with diethyl carbonate affords a complex product mixture (see Table 1 for the identified compounds), the possible cyclization product **26** is not found. Instead, two monosubstituted and three disubstituted ester derivatives can be identified, besides minor amounts of the butadiene **32**, arising from double hydrolysis. The structure of these compounds can be determined by NMR spectroscopy after fractional distillation and further separation by preparative gas chromatography, the structure assignment of diester **29** is only tentative. Formation of the isomeric monoesters can be explained by the high acidity of diethyl carbonate, responsible for the partial hydrolysis of the dilithiobutadiene **4**. The 1,4-dienes **29** and **31** are generated via an intermolecular metallation of monosubstituted **30** by **4**, as the acidity of the methyl groups is increased through the already present ester function. Quenching of the stable allyl anion **33** then leads—kinetically controlled—to **31** or to the thermodynamically more stable 1,3-diene **30**, respectively. The same is true for the interconversion between **27**

Table 1. Products obtained upon reaction of **4** affording esters and diesters **27** to **32**

Entry	Reaction conditions	Yield of compound (%)[a]					
		27	**28**	**29**	**30**	**31**	**32**
1	Addition of 1 equiv. of $(EtO)_2CO$ at −40°C to **4**	15	6	3	44	15	1
2	Addition of **4** to 1 equiv. of $(EtO)_2CO$ at −30°C	6	0	11	42	23	nd[b]
3	Addition of **4** to 2 eq. of $(EtO)_2CO$ at −30°C	22	3	3	64	0	nd[b]
4	Addition of **4** to 4 eq. of $(EtO)_2CO$ at −30°C	35	2	2	58	0	nd[b]
5	Addition of **4** to 8 equiv. of $(EtO)_2CO$ at −30°C	50	0	0	50	0	nd[b]
6	Addition of $C(OEt)_4$ and BF_3 at −80°C to **4**	15	6	3	40	3	12[c]
7	Addition of 1 equiv. of $(EtO)_2CO$ and then Et_2SO_4 to **4** at −30°C	3	0	**34**:62	13	0	5

[a] Remainder consisting of a complex mixture of various by-products, a single compound to a small extent only.
[b] Not determined.
[c] Besides 4% of **2** and 5% of $(EtO)_2CO$.



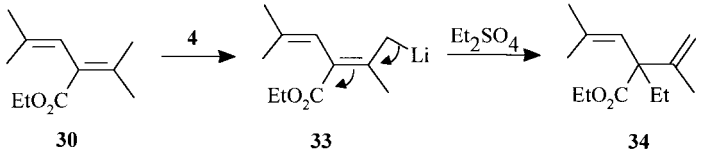
Scheme 4.

and **28**. The 1,4-diene **31** can easily be rearranged to **30** by using a 5% aqueous solution of sodium hydroxide (Scheme 4). There is further evidence for the complex reaction mechanism: when quenching **4** stepwise with 1 equiv. of diethyl carbonate and 1 equiv. of diethyl sulfate, the 1,4-diene **34** is obtained in 62% yield (Scheme 5).

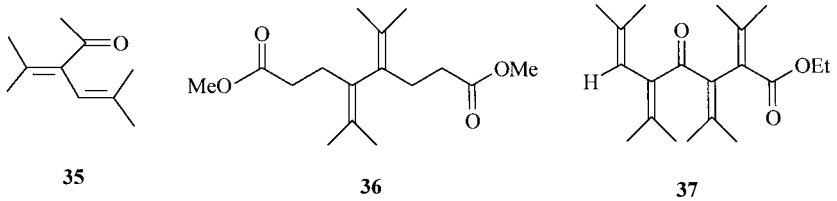
So the formation of **27** and **30** is partly occurring during the work-up. This type of intermolecular rearrangement has been investigated and proved previously by us for dilithiobutadienes.[9] Here the metallation occurs with the monosubstituted compound **33** and is favored by the polar solvent system, consisting of the solvent, unchanged diethyl carbonate, and the already formed lithium ethoxide. When the reacting mixture of **4** and diethyl carbonate is quenched with deuterium oxide, no noticeable deuterium incorporation into the products of hydrolysis is observed. Upon reacting **30** with 1 equiv. of **4** and subsequent hydrolysis a 2:1 mixture of **30** and **31** is found, demonstrating the postulated acidity of the methyl groups and the kinetically controlled quenching of the allyl anion **33** (Scheme 5).

Furthermore, quenching **4** with ethyl chloroformiate affords a 1:1 mixture of **30** and **31**, probably as the true product distribution of kinetic controlled reaction, as the lithium chloride formed during the reaction is of course not a strong base.

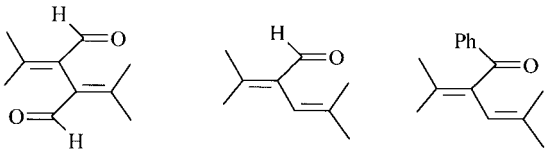
The outcome of the reaction of **4** with ethyl acetate is predictable, as the protons of this ester are even more acidic than those of diethyl carbonate, monosubstituted butadiene **35** is isolated in 53% yield. With methyl acrylate, besides many other products, the diester **36** is formed as the main component arising by a double Michael-type addition. When attempting to cyclize **4** with 1 equiv. of the diester **27** under high dilution conditions polycondensation occurs, a hydrolysis product of the first polymerization step, namely **37**, is isolated in about 5% yield, demonstrating the nature of the polycondensate (Scheme 6).



Scheme 5.



Scheme 6.



38 **39** **40**

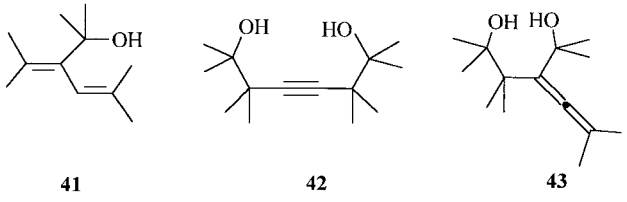
Scheme 7.

spectrometry after purification by preparative gas chromatography. The reaction is analyzed in detail in the temperature range of −100 to 35°C in intervals of 20°C in diethyl ether, the results thereby obtained are summarized in Table 2 (Scheme 8).

Three different products of disubstitution can be formed in principle, arising from the three different mesomeric forms **4a**–**4c**, as shown below (Scheme 9). Structure **4c** has the

Table 2. Product distribution in the reaction of **4** with acetone

Entry	Reaction conditions	Yield of compound (%)			
		41	**42**	**43**	**32**
1	Addition of acetone to **4** between −100 and −60°C	29	34	15	6
2	Addition of acetone to **4** between −60 and 35°C	31	23	3	9
3	Addition of acetone to a mixture of **4** and 2 equiv. HMPA at −80°C	28	34	33	5
4	Addition of **4** to a tenfold excess of acetone at −40°C	70	20	0	10



41 **42** **43**

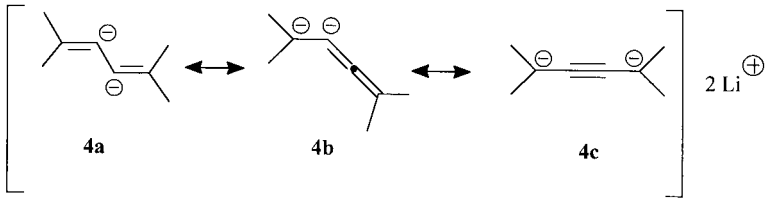
Scheme 8.

With *N*,*N*-dimethylformamide a mixture of products of di- and monosubstitution (**38**: 48%, **39**: 27%) is obtained upon reaction with **4**; with *N*,*N*-dimethylbenzamide the exclusive formation of the monosubstituted compound **40** (85%) is observed (Scheme 7).

Reaction of 4 with various aldehydes and ketones

The reaction with acetone is quite remarkable and delivers three different alcohols, **41**, **42**, and **43**, the structure of these products is unequivocally assigned by NMR and mass

two anionic centers located at sp^3 hybridized carbon atoms with the higher polarizability, thus being the softer base according to Pearsons's concept of hard and soft acids and bases,[17] when compared to **4a**. Esters, amides, and carbon dioxide can be considered as hard acids, so the formation of derivatives with a 1,3-butadiene skeleton is preferred. As was observed for unsymmetrically substituted dilithiobutadienes before,[9] the preferential formation of the 1,4-substituted 2-butynes is observed upon reaction with aldehydes and ketones. Quite interestingly, the allenic structure **43** is obtained as well, arising from structure **4b** with intermediate basicity. Upon addition of complexing additives like hexamethyl phosphoric acid (HMPA) or DMPU or TMEDA the amount of allene increases, here the charge distribution is changed in the complex in favoring the formation of **43**. When adding **4** to an excess of acetone partial hydrolysis is the main reaction observed. The rearrangement of allene **43** to butyne **42** is not possible, stirring of **43** with an excess of *n*-butyllithium at room temperature for several days does not afford any **42** after the usual work-up (Scheme 8).



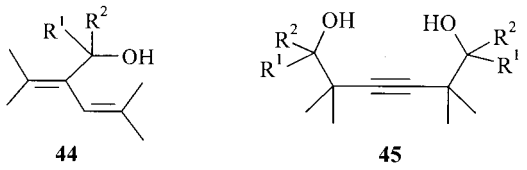
4a **4b** **4c**

Scheme 9.

Table 3. Alcohols obtained upon reaction of **4** with aldehydes and ketones

Entry	Reaction conditions	Compound, R^1, R^2	Yield (%)[a]		
			44	**45**	**32**
1	Introducing formaldehyde gas into a solution of **4** at −50°C	**a**: R^1=R^2=H	0	83 (68)	0
2	Addition of acetaldehyde at −60°C	**b**: R^1=H, R^2=Me	33	47	20
3	Addition of benzaldehyde at −30°C	**c**: R^1=H, R^2=Ph	0	65 (52)	0
4	Addition of acetophenone at −60°C	**d**: R^1=Me, R^2=Ph	10	70	20
5	Addition of benzophenone at −30°C	**e**: R^1=R^2=Ph	0	78 (65)	0

[a] Isolated yield of crude product after distillation, number in brackets isolated compound after recrystallization, **45b**–**d** as mixture of diastereomers.



44 45

Scheme 10.

4 is brought to reaction with a number of aldehydes and ketones, the results are summarized in Table 3. The formation of allenic derivatives cannot be strictly excluded, however, under the reaction conditions the amount is too small to allow structure assignment. The formation of 1,4-disubstituted 2-butyne derivatives **45** is observed throughout. The monosubstituted derivatives **44** are formed after hydrolysis of one carbanionic center and have a 1,3-butadiene skeleton (Scheme 10).

Reaction of 4 with miscellaneous electrophiles

Using a nitrogen analogue of carbon disulfide, for example dicyclohexyl carbodiimide, affords the expected disubstituted butadiene **46**. Electrophiles with one nitrogen and one sulfur at the electrophilic carbon atom, that is ethyl and phenyl thiocarbamate work well too, when the primarily formed addition product is trapped with methyl iodide, allowing the isolation of **47** and the hydrolysis product **48** (Scheme 11).

Reaction of **4** with electrophiles bearing halogens as the leaving groups does not afford any products of substitution. Either quantitative lithium halogen exchange occurs, which leads to the formation of triene **2**, or the product mixtures are of such a complexity—usually together with a large amount of polymeric material—that no main compounds can be isolated or identified. Among the electrophiles, which were tested are tetrachloromethane, dichloromethane, 2,2-dichloro-1,1-diphenylethene, phenylisonitrile dichloride, phthalic acid dichloride, epichlorohydrin, *t*-butyl chloride, or phosgene (employed as triphosgene). Among the carbonyl compounds that were tested are diethyl phthalate, phthalic acid anhydride, and maleic acid anhydride, for example. Carbonyl diimidazolide does not afford any monomeric cyclopropanone derivative either, but instead quantitative polymerization occurs.

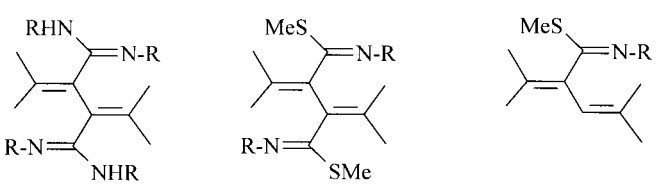
Conclusions

4 is a suitable reagent for C,C-bond forming reactions when employing proper electrophiles, however, ring closure reactions are only observed in a few cases. The reason for this is the high steric requirements of this ring closure reaction, the carbon–carbon bond to be formed is short (154 pm) compared to the carbon, heteroatom bonds which are formed upon reaction of **4** with heteroatom electrophiles (for example C–B 157 pm, C–P 184 pm, C–Si 189 pm, C–Sn 216 pm). Furthermore the ring closure of **4** is successful with dichloromethylsilane, but not with dichlorodimethylsilane, demonstrating the steric requirements of the ring closure. Secondly, only those intermediates can cyclize easily, which exhibit a 1,3-butadiene skeleton, the ring closure is nearly impossible if the monosubstituted derivative has preferentially an allenic or alkynic skeleton. Thirdly, the heteroatoms mentioned above probably react via ate complexes, which is not possible for carbon centered electrophiles.

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. Mass spectra were obtained on a Varian MAT 112 (OV 101 capillary); *m/z* values are reported followed by the relative intensity in parantheses. The ten strongest peaks and, if not enclosed, the intensity of the molecular ion is given. The molecular ion is given as M^+, but of course radical cations are formed. High resolution mass spectra were recorded on a Varian MAT 311 A. Nuclear Magnetic Resonance (^1H, 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). The following stationary phases were employed: 10% DEGS on Chromosorb W 47/60 mesh, 15% DEGS on Chromosorb W 60/80 mesh, 20% CW 1000 42/60 mesh, 10% SE 30. 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.



R = *c*-C_6H_{11} **a**: R = Et, **b**: R = Ph

46 47 48

Scheme 11.

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).

General procedure for the derivatization of 4 with electrophiles

Salt free solutions of **4** were prepared in a concentration of about 1 M as described elsewhere,[8] the content of lithium-organic compound was determined by titration of diphenylacetic acid.[18] The solutions were stored at −40°C to avoid rearrangement.[6] A solution of **4** in diethyl ether was cooled to −40°C if not stated otherwise, and a solution of the electrophile in diethyl ether was added dropwise at this temperature. The reaction mixture was allowed to warm to room temperature, then a saturated solution of ammonium chloride was added. The organic layer was washed with a solution of saturated sodium bicarbonate and dried over magnesium sulfate. After evaporation of the solvent with a rotary evaporator the crude product was usually purified by fractional distillation and analytical samples, when necessary, were further purified by preparative gas chromatography.

3,3-Dimethyl-5-(1-hydroxy-1-methylethyl)-3H-thiophen-2-thione (16). The reaction of 100 mmol of **4** in 100 ml of diethyl ether with 6.0 ml (100 mmol) of carbon disulfide afforded after distillation 14.0 g of crude product, consisting of **16** and **15**, bp 34–39°C (0.01 Torr). Bulb-to-bulb distillation delivered 9.0 g (44 mmol, 44%) of **16** and 3.2 g (17 mmol, 17%) of **15**. Further purification by preparative gas chromatography (SE 30) was necessary. Characterization of **16**: ^{1}H NMR (80 MHz, $CDCl_3$) 1.31 (s, 6H, 2×Me), 1.52 (s, 6H, $C(OH)Me_2$), 6.05 (s, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 29.8, 68.5, 70.5, 132.0, 146.7, 250.6. MS (70 eV): *m/z* 202 (M^+, 17), 186(17), 171(33), 145(33), 111(25), 110(75), 92(33), 77(33), 55(92), 43(100).

3,3-Dimethyl-5-isopropyl-3H-thiophen-2-thione (15). The reaction was performed on the same scale as described above, during the work-up degassed solutions of ammonium chloride and sodium bicarbonate were used to afford 15 g of a red oil as crude product, which was purified by distillation, bp=30–35°C (0.01 Torr), yield 2.0 g (11 mmol, 11%). The remaining compound formed a tar during distillation. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.19 (d, *J*=7.2 Hz, 6H, $CHMe_2$), 1.30 (s, 6H, 2×Me), 2.69 (septet of d, *J*=7.2, 1.6 Hz, 1H, CH), 5.90 (d, *J*=1.6 Hz, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 29.1, 30.0, 68.2, 131.9, 145.3, 251.3. MS (70 eV): *m/z* 186 (M^+, 83), 171(44), 153(30), 144(100), 127(35), 111(39), 95(43), 67(30), 59(22), 41(30).

2,2-Bis(methylthio)-3,3-dimethyl-1-(2-methyl-1-propenylidene)cyclopropane (18). The reaction was performed on the same scale as above. After addition of the solution of carbon disulfide the reaction mixture was kept at −40°C for 1 h, then a solution of 12.5 g (200 mmol) of methyl iodide in 80 ml of diethyl ether was added dropwise. After the usual work-up 23 g of crude product was obtained, which afforded, after fractional distillation, 5.0 g (23 mmol, 23%) of **18**, bp 55°C (0.01 Torr). Further purification of an analytical sample was possible by preparative gas chromatography (DEGS). ^{1}H NMR (80 MHz, $CDCl_3$) 1.55 (s, 6H, 2×Me), 1.78 (s, 6H, 2×Me), 2.22 (s, 6H, 2×SMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 21.5, 23.1, 36.7, 47.9, 94.6, 101.0, 187.7. MS (70 eV): *m/z* 214 (M^+, 26), 199(100), 152(44), 151(53), 137(18), 111(48), 105(24), 91(40), 77(24), 41(21). IR (KBr pellet): 2000 cm^{-1}, s, (C=C=C). Anal. calcd for $C_{11}H_{18}S_2$: C, 61.63; H, 8.46; S, 29.91; found: C, 61.62; H, 8.50; S, 29.09.

1,1-Bis(methylthio)-2,3-diisopropylidenecyclopropane (19). 0.5 ml of **18** were heated slowly to 150°C, when reaching this temperature the rearrangement was completed according to the spectroscopic data: ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.98 (s, 6H, 2×Me), 2.00 (s, 6H, 2×Me), 2.30 (s, 6H, 2×SMe). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 23.2, 23.6, 35.1, 119.8, 122.7.

3,4-Bis(trimethylsilyl)-2,5-dimethyl-2,4-hexadiene (21) and 2,5-dimethyl-3-trimethylsilyl-2,5-hexadiene (23). To a solution of 55 mmol of **4** in 70 ml of diethyl ether were added 20.0 ml (110 mmol) of trimethylsilyl trifluoromethanesulfonate in 60 ml of diethyl ether at −20°C. The reaction mixture was then stirred for 24 h at room temperature. After the work-up the crude product (13.0 g) was distilled to afford 5.0 g (20 mmol, 37%) of **21**, bp 65–67°C (0.01 Torr). ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.12 (s, 18 H, $SiMe_3$), 1.56/1.86 (2×s, 2×6H, Me). MS (70 eV): *m/z* 254 (M^+, 33), 180(17), 166(17), 155(17), 151(17), 124(15), 99(13), 84(23), 73(100), 45(17). Anal. calcd for $C_{14}H_{30}Si_2$: C, 66.06; H, 11.88; found: C, 66.16; H, 11.76. As by-product, **23** was found: MS (70 eV): *m/z* 182 (M^+, 9), 167(6), 113(15), 93(7), 74(13), 73(100), 59(15), 45(22), 43(9), 41(7).

Reaction with diethyl carbonate

To a solution of 50 mmol of **4** in 50 ml of diethyl ether were added 12.0 ml (100 mmol) of diethyl carbonate. After work-up the crude product (15.0 g) was purified by distillation, the main fractions with bp 63–65°C (0.005 Torr). The mono-substituted esters **30** and **31** could be further enriched by preparative gas chromatography on DEGS, the diesters on a SE 30 column. Yields are given in Table 1, the esters were characterized as follows.

Ethyl 2-isopropylidene-4-methyl-3-pentenoate (30). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.29 (t, *J*=7.3 Hz, 3H, OCH_2CH_3), 1.55 (d, *J*=2 Hz, 3H, Me), 1.75 (d, *J*=1 Hz, 3H, Me), 1.81 (d, *J*=1 Hz, 3H, Me), 2.00 (d, *J*=2 Hz, 3H, Me), 4.19 (q, *J*=7.3 Hz, 2H, OCH_2CH_3), 5.78 (br. septet, *J*=2 Hz, 1H, =CH). ^{13}C NMR {off-resonance decoupling} (100 MHz, $CDCl_3$) δ 14.3(q), 19.3(q), 22.1(q), 22.5(q), 25.6(q), 60.2(t), 120.8(d), 126.7(s), 136.3(s), 142.8(s), 169.4(s). MS (70 eV): *m/z* 182 (M^+, 100), 139(28), 137(39), 109(61), 93(61), 87(39), 67(50), 59(56), 43(44), 41(39). Anal. calcd for $C_{11}H_{18}O_2$ (containing isomer **31**): C, 72.49; H, 9.95; found: C, 72.53; H, 10.00.

Ethyl 2-(1-methylethenyl)-4-methyl-3-pentenoate (31). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.27 (t, *J*=7.3 Hz, 3H, OCH_2CH_3), 1.58 (d, *J*=2 Hz, 3H, Me), 1.66 (d, *J*=1 Hz, 3H, Me), 1.77 (m, 3H, Me), 3.90 (d of m, *J*=8 Hz, 1H,

CH), 4.14 (q, J=7.3 Hz, 2H, OCH_2CH_3), 4.88 (m, 2H, $=CH_2$), 5.42 (d of m, J=8 Hz, 1H, =CH). ^{13}C NMR {off-resonance decoupling} (100 MHz, $CDCl_3$) δ 14.2(q), 18.0(q), 20.9(q), 25.9(q), 52.3(d), 60.7(t), 112.7(t), 121.2(d), 135.3(s), 142.9(s), 172.9(s). MS (70 eV): m/z 182 (M^+, 20), 111(12), 109(100), 108(8), 81(14), 79(8), 67(52), 55(14), 43(18), 41(14).

Diethyl 2,3-diisopropylidene-succinate (27). ^1H NMR (80 MHz, $CDCl_3$) δ 1.23 (t, J=7.2 Hz, 6H, OCH_2CH_3), 1.72/2.17 (2×s, 2×6H, Me), 4.14 (q, J=7.2 Hz, 4H, OCH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.1, 23.6, 59.9, 125.8, 149.0, 167.3. MS (70 eV): m/z 254 (M^+, 15), 209(30), 208(48), 167(11), 163(11), 162(100), 135(15), 134(37), 107(30), 43(15). Anal. calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72; found: C, 66.34; H, 8.64.

Diethyl 2-(1-methylethenyl)-3-isopropylidene-succinate (28). ^1H NMR (80 MHz, $CDCl_3$) δ 1.22/1.25 (2×t, J=7 Hz, 2×3H, $2\times OCH_2CH_3$), 1.79/2.09 (2×s, 2×3H, Me), 1.82 (m, 3H, $C(=CH_2)CH_3$), 4.12/4.15 (2×q, J=7 Hz, 2×2H, $2\times OCH_2CH_3$), 4.13 (m, 1H, CH), 4.85/4.95 (2×m, 2×1H, $C(=CH_2)CH_3$). MS (70 eV): m/z 254 (M^+, 20), 209(50), 208(70), 181(20), 162(75), 135(60), 134(40), 108(25), 107(100), 91(25). Tentatively assigned **29:** MS (70 eV): m/z 254 (M^+, 9), 209(42), 208(83), 162(67), 151(50), 135(42), 134(83), 107(100), 93(42), 43(50).

Ethyl 2-ethyl-2-(1-methylethenyl)-4-methyl-3-pentenoate (34). To 100 ml of a 1 M solution of **4** in diethyl ether (100 mmol) was added slowly a solution of 12.0 ml (100 mmol) of diethyl carbonate at −30°C and stirred for another hour without cooling, the reaction mixture warmed to 10°C. This mixture was cooled to −30°C again, then a solution of 13.0 ml (100 mmol) of diethyl sulfate in 30 ml of ether was added dropwise and, as the reaction mixture turned highly viscous, another aliquot of 100 ml of ether. After the work-up the crude product (18.0 g) afforded after distillation 13.0 g (62 mmol, 62%) of **34**, bp 110–112°C (12 Torr). An analytical sample was purified by preparative gas chromatography (SE 30). ^1H NMR (80 MHz, $CDCl_3$) δ 0.82 (t, J=8.0 Hz, 3H, CH_2CH_3), 1.25 (t, J=7.2 Hz, OCH_2CH_3), 1.58/1.77 (2×d, J=1.5 Hz, 2×3H, 2×Me), 1.71 (t, J=1.5 Hz, 3H, $C(=CH_2)CH_3$), 1.89/2.03 (AB part of ABX_3 system, 2×pseudoquartet, J=8.0, 11.2 Hz, CH_2CH_3), 4.16 (q, J=7.2 Hz, 2H, OCH_2CH_3), 5.03 (m, 2H, $=CH_2$), 5.62 (septet, J=1.5 Hz, 1H, =CH). ^{13}C NMR {off-resonance decoupling} (100 MHz, $CDCl_3$) δ 9.4(q), 14.2(q), 20.8(q), 27.4(q), 28.9(t), 57.2(s), 60.7(t), 112.9(t), 124.3(d), 134.7(s), 145.2(s), 174.8(s), one signal overlaid. MS (70 eV): m/z 210 (M^+, 54), 195(15), 181(27), 138(15), 137(100), 109(19), 107(31), 95(81), 81(39), 41(19). Anal. calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54; found: C, 73.96; H, 10.80.

3-Isopropylidene-5-methyl-4-hexen-2-one (35). To 100 ml of a 1 M solution of **4** in diethyl ether was added at −30°C a solution of 9.5 ml (100 mmol) of ethyl acetate in 100 ml of ether. Fractional distillation of the crude product (10.3 g) afforded 8.0 g (53 mmol, 53%) of **35**, bp 80°C (0.01 Torr). ^1H NMR (80 MHz, $CDCl_3$) δ 1.53 (d, J=1.6 Hz, 3H, Me), 1.70 (d, J=1.4 Hz, 3H, Me), 1.82 (d, J=0.9 Hz, 3H, Me), 1.92 (d, J=1.2 Hz, 3H, Me), 2.14 (s, 3H, COMe), 5.82 (m, 1H, =CH).

Dimethyl 3,4-diisopropylidene-1,6-hexanedicarboxylate (36). From 100 ml of a 1 M solution of **4** in diethyl ether (100 mmol) and 9.5 ml (100 mmol) of methyl acrylate. After the usual work-up the material was further purified by bulb to bulb-distillation. Yield not determined. ^1H NMR (80 MHz, $CDCl_3$) δ 1.48/1.72 (2×s, 2×6H, $=CMe_2$), 2.28 (m, 8H, CH_2CH_2), 3.64 (s, 6H, OMe). MS (70 eV): m/z 282 (M^+, 55), 222(38), 218(50), 135(100), 133(50), 121(55), 119(50), 107(38), 105(38), 55(50).

Ethyl 4-keto-7-methyl-2,3,5-triisopropylidene-6-octenoate (37). To a solution of 5.0 g (20 mmol) of **28** in 350 ml of diethyl ether was added dropwise a solution of **4** (20 mmol) in 150 ml of diethyl ether over a period of 90 min. at −70°C. After the usual work-up a polycondensate was isolated, furthermore 300 mg (1.0 mmol, 5%) of **37**, bp 115–120°C (0.01 Torr). ^1H NMR (80 MHz, $CDCl_3$) δ 1.17 (t, J=7.1 Hz, 3H, OCH_2CH_3), 1.44/1.56 (2×d, J<1 Hz, 2×3H, $CH=C(CH_3)_2$), 1.61/1.64/1.66/1.69/2.05/2.07 (6×s, 6×3H, 6×Me), 4.02 (q, J=7.1 Hz, 2H, OCH_2CH_3), 5.48 (septet, J<1 Hz, 1H, =CH). MS (70 eV): m/z 318 (M^+, 50), 303(40), 257(41), 229(43), 109(100), 107(65), 55(42), 53(24), 43(70), 41(64).

2,3-Diisopropylidene-succinaldehyde (38) and 2-isopropylidene-4-methyl-3-pentenal (39). To 100 ml (100 mmol) of a 1 M solution of **4** in diethyl ether were added dropwise at −50°C 19.0 ml (250 mmol) of *N*,*N*-dimethylformamide in 150 ml of diethyl ether. After warming to room temperature the reaction mixture was poured into an ice-cold solution of 20 ml of hydrochloric acid in 150 ml of water. The aqueous layer was extracted several times with diethyl ether. After washing and drying of the combined organic layers, the remainder (15.0 g) was distilled to afford 8.0 g (48 mmol, 48%) of **38** and 3.8 g (27 mmol, 27%) of **39**. Characterization of **38**: Bp 75–80°C (0.05 Torr), the liquid solidified upon standing to a brownish solid. ^1H NMR (80 MHz, $CDCl_3$) δ 1.76/2.31 (2×s, 2×6H, Me), 10.09 (s, 2H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 24.2, 133.2, 158.8, 188.9. MS (70 eV): m/z 166 (M^+, 56), 151(50), 123(51), 95(59), 77(41), 67(73), 55(50), 43(100), 41(94), 39(56). HRMS calcd for $C_{10}H_{14}O_2$: 166.09938; found 166.09937. Anal. calcd for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49; found: C, 71.81; H, 8.55.

Characterization of 39. Bp 47–50°C (0.05 Torr), the liquid solidified upon storing at −30°C to a red-brownish material. ^1H NMR (80 MHz, $CDCl_3$) δ 1.44 (d, J=1.1 Hz, 3H, Me), 1.82 (d, J=1.4 Hz, 3H, Me), 1.85 (d, J=0.5 Hz, 3H, Me), 2.21 (d, J=1.5 Hz, 3H, Me), 5.60 (m, 1H, =CH), 10.10 (s, 1H, CHO). ^{13}C NMR {off-resonance decoupling} (100 MHz, $CDCl_3$) δ 19.0(q), 19.4(q), 24.2(q), 25.0(q), 118.4(d), 134.7(s), 137.5(s), 155.7(s), 190.1(d). MS (70 eV): m/z 123 (M^+-Me, 51), 105(34), 95(59), 67(75), 55(56), 53(46), 51(41), 43(51), 41(100), 39(82). HRMS calcd for $C_9H_{14}O$: 138.10447; found 138.10450.

3-Benzoyl-2,5-dimethyl-2,4-hexadiene (40). To 100 ml of a 1 M solution of **4** in diethyl ether were added 13.4 g (90 mmol) of *N*,*N*-dimethylbenzamide in 150 ml of diethyl

ether at 0°C. Using an excess of this reagent led to problems during isolation of the product. The work-up was performed as described for **38** to afford 17.5 g of crude product, 16.4 g (77 mmol, 85%) after distillation, bp 140–145°C (0.05 Torr) of a yellow oil, which solidifies at −25°C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.54 (d, J=1.0 Hz, 3H, Me), 1.71 (s, 6H, 2×Me), 1.82 (s, 3H, Me), 5.87 (m, 1H, =CH), 7.40–7.90 (m, 5H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 20.6, 21.3, 25.5, 120.7, 127.8, 128.7, 132.2, 133.7, 135.7, 136.2, 137.0, 198.5. MS (70 eV): m/z 214 (M^+, 37), 213(23), 109(23), 105(100), 77(72), 67(44), 55(26), 43(29), 41(45). HRMS calcd for $C_{15}H_{18}O$: 214.13577; found 214.13566. Anal. calcd for $C_{15}H_{18}O$: C, 84.06; H, 8.47; found: C, 83.61; H, 8.42.

Reaction of 4 with acetone

To 100 ml of a 1 M solution of **4** were added 14.7 ml (200 mmol) of acetone in 150 ml of diethyl ether with varying reaction temperatures (see Table 2). The usual work-up afforded the three alcohols **41**–**43** (for the yield see Table 2). These products were characterized as follows.

3-Isopropylidene-2,5-dimethyl-4-hexen-2-ol (41). Bp 75–78°C (0.4 Torr), mp 74–75°C (pentane/methanol). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.35 (s, 6H, C(OH)(CH_3)$_2$), 1.49 (d, J=1.0 Hz, 3H, Me), 1.57 (d, J=1.1 Hz, 3H, Me), 1.65 (s, 1H OH), 1.75 (d, J=1.2 Hz, 3H, Me), 1.95 (d, J=1.7 Hz, 3H, Me), 5.64 (m, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 21.4, 24.0, 25.6, 29.4, 30.9, 73.9, 124.3, 129.3, 134.2, 136.9. The two signals at 29.4 and 30.9 ppm show one broad signal at room temperature, at −50°C two signals are observed for the methyl groups. MS (70 eV): m/z 150 ($M^+-Me_2CO-H_2O$, 36), 135(100), 119(32), 107(27), 93(29), 91(37), 81(22), 79(42), 77(26), 41(41). HRMS calcd for $C_{11}H_{20}O-H_2O$: 150.14085; found 150.14085. Anal. calcd for $C_{11}H_{20}O$: C, 78.50; H, 11.99; found: C, 78.39; H, 11.82.

2,3,3,6,6,7-Hexamethyl-4-octyn-2,7-diol (42). Bp 98–103°C (0.2 Torr), mp 80–82°C (pentane/methanol). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.19 (s, 12H, Me), 1.24 (s, 12H, Me), 1.87 (s, 2H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 24.9, 40.6, 74.0, 87.9. MS (70 eV): m/z 150 ($M^+-Me_2CO-H_2O$, 18), 135(61), 125(32), 118(14), 110(25), 85(46), 67(18), 59(100), 43(46), 41(29). Anal. calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58; found: C, 74.57; H, 11.58.

3-(2-Methyl-1-propenylidene)-2,4,4,5-tetramethylhexan-2,5-diol (43). Bp 117–120°C (0.2 Torr), mp 136–138°C (pentane/methanol). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.16 (s, 6H, Me), 1.20 (s, 6H, Me), 1.37 (s, 6H, Me), 1.63 (s, 6H, =CMe_2), 3.78/4.24 (2×br. s, 2H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 25.9, 27.0, 34.1, 46.1, 73.0, 76.0, 95.7, 115.9, 201.5. MS (70 eV): m/z 193 (M^+-Me-H_2O, 81), 168(11), 150(38), 135(100), 125(27), 110(16), 95(27), 59(89), 43(35), 41(19). Anal. calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58; found: C, 74.30; H, 11.59.

2,2,5,5-Tetramethyl-3-hexyn-1,6-diol (45a). Gaseous formaldehyde, obtained by depolymerization of paraformaldehyde, was introduced into a solution of **4** (100 mmol) in 300 ml of diethyl ether at −50°C, until the red solution turned slightly yellow. After warming to room temperature and the usual work-up, the crude product (14.0 g) was purified by fractional distillation, to afford 11.5 g (68 mmol, 68%) of **45a**, bp 120°C (3 Torr), mp 90–92°C (pentane/methanol). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.11 (s, 12H, Me), 2.98 (s, 4H, CH_2), 3.30 (s, 2H, OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 34.0, 71.7, 86.7. MS (70 eV): m/z 140 (M^+-CH_2O, 10), 120(31), 110(54), 108(46), 90(38), 80(54), 68(62), 55(62), 43(100), 41(62). HRMS calcd for $C_{10}H_{18}O_2-CH_2O$: 140.12012; found 140.12010. Anal. calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66; found: C, 70.39; H, 11.30.

5-Methyl-3-isopropylidene-4-hexen-2-ol (44b) and 3,3,6,6-tetramethyl-4-octyn-2,7-diol (45b). To 100 ml of a 1 M solution of **4** (100 mmol) was added at −60°C a solution of 11.3 ml (200 mmol) of acetaldeyde in 100 ml of diethyl ether. After the usual work-up the two alcohols were isolated by fractional distillation from the crude product (18.0 g). For the yields see Table 3. **44b**: Bp 90°C (0.01 Torr). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.19 (d, J=6.5 Hz, 3H, CHCH_3), 1.52 (d, J<1 Hz, 3H, Me), 1.57 (d, J<1 Hz, 3H, Me), 1.74 (d, J<1 Hz, 3H, Me), 1.74 (d, J<1 Hz, 3H, Me), 4.50 (q, J=6.5 Hz, 1H, CHCH$_3$), 5.70 (m, 1H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 19.5, 22.0, 23.3, 25.2, 67.0, 120.1, 128.1, 134.2, 137.2. MS (70 eV): m/z 121 (M^+-H_2O–Me, 100), 105(53), 93(40), 91(42), 79(22), 77(34), 67(26), 55(26), 41(50), 39(29). HRMS calcd for $C_{10}H_{18}O$: 154.13576; found 154.13576; calcd for $C_{10}H_{18}O-H_2O$: 136.12520; found 136.12519. **45b**: Bp 160°C (0.01 Torr). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.15 (s, 6H, Me), 1.21 (d, J=6.2 Hz, 6H, CHCH_3), 1.22 (s, 6H, Me), 1.87 (s, 2H, OH), 3.50 (q, J=6.2 Hz, 2H, CHCH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 24.8, 25.9, 37.5, 74.2, 87.0. MS (70 eV): m/z 121 ($M^+-MeCHO-H_2O$–Me, 54), 111(100), 95(32), 93(31), 91(29), 67(73), 55(36), 45(43), 43(73), 41(42). HRMS calcd for $C_{10}H_{18}O-H_2O$–Me: 165.12795; found 165.12792.

2,2,5,5-Tetramethyl-1,6-diphenyl-3-hexyn-1,6-diol (45c). From 100 ml of a 1 M solution of **4** (100 mmol) and 20.0 ml (200 mmol) of benzaldehyde at −30°C. After the usual work-up the crude product (21.0 g) was distilled to afford 16.5 g (52 mmol, 52%) of **45c**, bp 160°C (0.01 Torr), mp 108°C (pentane/methanol). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.06/1.26 (2×s, 2×6H, Me), 2.58 (d, J=4.4 Hz, 2H, CH), 4.48 (d, J=4.4 Hz, 2H, OH), 7.31 (m, 10H, phenyl). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 26.5, 37.8, 80.6, 87.6, 127.5, 127.6, 127.7, 140.3. The signals between 20 and 90 ppm show a splitting due to the presence of two diastereoisomers. MS (70 eV): m/z 216 ($M^+-PhCHO$, 23), 198(55), 184(100), 156(23), 142(36), 140(41), 81(55), 79(46), 77(41), 66(36). HRMS calcd for $C_{22}H_{26}O_2-H_2O$: 304.18272; found 304.18267. Anal. calcd for $C_{22}H_{26}O_2$: C, 81.94; H, 8.13; found: C, 82.27; H, 8.30.

3,3,6,6-Tetramethyl-2,7-diphenyl-4-octyn-2,7-diol (45d). From 100 ml of a 1 M solution of **4** and 23.0 ml (200 mmol) of acetophenone in 100 ml of diethyl ether at −60°C. The crude product proved extremely difficult to purify and was characterized as such and by using GC–MS coupling. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.14/1.18/1.70 (3×s, 3×6H, Me),

2.30 (s, 2H, OH), 7.40 (m, 10H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 25.6, 41.1, 44.3, 81.0, 88.1, 126.6, 127.0, 127.8, 143.6. MS (70 eV): *m/z* 223 (13), 197(11), 169(12), 121(34), 106(9), 105(100), 91(17), 77(50), 51(12), 43(46). HRMS calcd for $C_{24}H_{30}O_2-H_2O$: 332.21402; found 332.2140. Furthermore, there is spectroscopic evidence for **44d**, as obtained by GC/MS coupling: MS (70 eV): *m/z* 212 (M^+-H_2O–Me, 72), 197(100), 156(54), 155(55), 143(39), 141(38), 121(35), 91(46), 77(42), 41(42).

2,2,5,5-Tetramethyl-1,1,6,6-tetraphenyl-3-hexyn-1,6-diol (45e). To a solution of 50 mmol of **4** in 100 ml of diethyl ether was added a solution of 18.2 g (100 mmol) of benzophenone in 150 ml of diethyl ether. After work-up and evaporation of the solvent the remainder (18.5 g) was treated in an ultrasonic bath with pentane, thus a white powder was isolated, which was recrystallized from pentane and a small amount of methanol, mp 147–149°C, 15.4 g (33 mmol, 65%). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.32 (s, 12H, Me), 2.37 (s, 2H, OH), 7.00–7.80 (m, 20H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 39.9, 81.1, 91.2, 126.7, 127.1, 128.5, 145.1. MS (70 eV): *m/z* 275 (M^+-Ph_2CO–OH, 11), 274(5), 184(11), 183(73), 182(7), 110(6), 108(8), 106(8), 105(100), 77(40). HRMS calcd for $C_{34}H_{34}O_2-Ph_2CO$: 292.18272; found 292.18272; calcd for $C_{34}H_{34}O_2-Ph_2CO-H_2O$: 274.17216, found 274.17224. Anal. calcd for $C_{34}H_{34}O_2$: C, 86.03; H, 7.22; found: C, 86.03; H, 7.10.

***N,N′,N″,N‴*-Tetracyclohexyl-2,3-diisopropylidene-succinamidine (46).** The reaction of 100 mmol of **4** in 100 ml of diethyl ether with 20.6 g (100 mmol) of *N,N′*-dicyclohexylcarbodiimide in 100 ml of diethyl ether afforded, after the usual work-up, 18.0 g of **46**, which was recrystallized twice from diethyl ether: 14.0 g (27 mmol, 54%), mp 119–121°C. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.10–1.60 (br. m, 40H, cyclohexyl–CH_2), 1.68/1.71 (2×s, 2×6H, Me), 2.05 (br. s, 4H, cyclohexyl–CH), 3.05/3.50 (2×br. s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.9, 22.2, 24.6, 25.8, 26.1, 32.8, 35.2, 48.9, 58.0, 131.0, 133.0, 154.5. Anal. calcd for $C_{34}H_{58}N_4$: C, 78.10; H, 11.18; found: C, 78.20; H, 11.10.

Methyl *N*-ethyl-2-isopropylidene-4-methyl-3-pentenimidothioate (48a) and dimethyl *N,N′*-diethyl-2,3-diisopropylidene-succinimidothioate (47a). To 100 ml of a 1 M solution of **4** was added slowly a solution of 9.0 ml (100 mmol) of ethyl isothiocyanate in 100 ml of diethyl ether at −60°C. The reaction mixture was kept at this temperature for half an hour, then at −40°C a solution of 12.0 ml (200 mmol) of methyl iodide in 50 ml of diethyl ether was added dropwise. After the usual work-up the crude product (23.0 g) was distilled to afford 3.8 g (18 mmol, 18%) of **48a**, bp 70–75°C (0.01 Torr). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.15 (t, J=7.1 Hz, 3H, CH_2CH_3), 1.60/1.67/1.68/1.78 (4×d, J<1 Hz, 4×3H, Me), 2.28 (s, 3H, SMe), 3.30 (q, J=7.1 Hz, 2H, CH_2CH_3), 5.60 (m, 1 H, =CH). Furthermore 12.5 g (40 mmol, 40%) of **47a**, bp 100–110°C (0.01 Torr) were obtained. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.13 (t, J=7.0 Hz, 6H, CH_2CH_3), 1.67/1.75 (2×s, 2×6H, Me), 2.26 (s, 6H, SMe), 3.38 (q, J=7.0 Hz, 4H, CH_2CH_3).

Methyl *N*-phenyl-2-isopropylidene-4-methyl-3-pentenimidothioate (48b) and dimethyl *N,N′*-diphenyl-2,3-diisopropylidene-succinimidothioate (47b). The reaction of 100 mmol of **4** in 100 ml of diethyl ether with 19.0 ml (100 mmol) of phenyl isothiocyanate was performed as described above. After the usual work-up by distillation a fraction containing 15.0 g (58 mmol, 58%) of **48b** was obtained, bp 145°C (0.05 Torr). ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.37/1.58/1.79/1.84 (4×s, 4×3H, Me), 2.50 (s, 3H, SMe), 5.58 (br s, 1H, =CH), 7.10 (m, 5H, phenyl-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 19.5, 20.2, 22.4, 25.7, 120.2, 121.1, 123.0, 128.3, 128.7, 134.1, 136.6, 150.7, 170.0. MS (70 eV): *m/z* 259 (M^+–Me, 41), 227(59), 226(49), 123(100), 93(23), 91(26), 81(90), 77(44), 67(26), 41(62). The disubstituted butadiene **47b** decomposed upon distillation and could not be obtained in pure form: MS (70 eV): *m/z* 375 (M^+–SH, 100), 361(18), 360(71), 253(35), 252(16), 179(26), 171(18), 150(26), 91(26), 77(45).

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