194. Regioselective Alkylation of the Polyfunctional Nucleophile 1-(Methylthio)-3-triethylsilyloxypentadienyllithium

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Dedicated to Prof. *Vladimir Prelog* on the occasion of his 75th birthday

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Summary

γ-Selective sulfenylation of the triethysilyloxypentadienyllithium **1** gave the versatile alkylthiodiene **4** which on successive deprotonation and alkylation furnished with high regioselectivity the γ-products **6**. Fluoride-promoted silylether cleavage **6**→**7** may be followed by intramolecular [4+2]-addition **7c**→**8** and sulfoxide elimination **8**→**9**. The conversions **7b**→**12** and **7a**→**17** demonstrate the feasibility of **5** to serve as an equivalent of the hypothetical β-deprotonated divinylketone **13** whose two enone units may be unmasked separately.

Introduction. – In connection with our general interest in intramolecular *Diels-Alder* reactions we have reported the electrophilic substitution of the lithiated triethylsilyloxypentadiene **1** [1] [2]. The utility of **1** as a convenient C_5-unit for both the construction and attachment of the functionalized dienes **2** and dienophile units depends on a selective γ-substitution (**1**→**2**). This is generally achieved with carbonyl electrophiles. On alkylation of the metalated diene **1**, however, the undesired α-attack **1**→**3** was unsatisfactorily competitive *(Scheme 1)*. As a solution to this problem we present here a reliable method for regioselective γ-alkylation of 3-silyloxydienes.

Preparation and Alkylation of the Methylthiosilyloxypentadienyllithium 5. – Determinative to this approach was the regioselective γ-sulfenylation of **1**: Dropwise addition of dimethyl disulfide (1 mol-equiv.) to a freshly prepared 2 M solution of **1** in THF at −78° under argon, stirring of the reaction mixture for 15 min at −78°, quenching with sat. aq. NH_4Cl-solution and distillation gave the methylthiodiene **4** as a stable colorless oil in 81% yield. Not even a trace of the α-sulfenylated isomer **3**, (E = SMe) was found in the reaction mixture. The methylthio substituent was expected not only to facilitate conveniently the deprotonation **4**→**5**, but, particularly, to direct the alkylation of **5** entirely towards the desired γ-products **6**[1]). Indeed, addition of **4** to LDA (1.1 mol-equiv.) in THF/HMPA at −78° gave a deep-red solution of

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[1]) For the electrophilic substitutions of sulfur-substituted allyl anions see reviews [3] [4], as well as [5] [6]; for the preparation of 1,1-bis(methylthio)-3-trimethylsilyloxydiene see [7]. This work has been presented by one of us *(W. O.)* at the 6th International Symposium on Synthesis in Organic Chemistry, Cambridge (England), July 1979.

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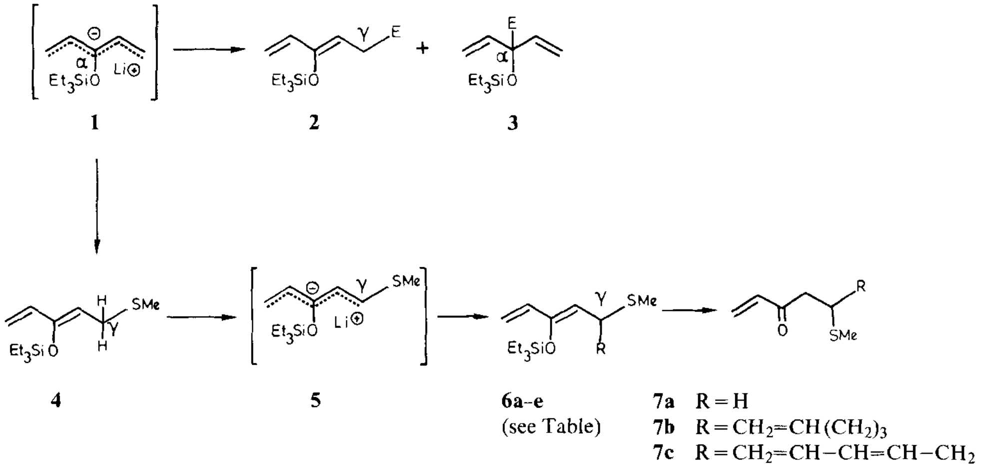
Scheme 1



1 **2** **3**

4 **5** **6a–e** (see Table)

7a R = H
7b R = $CH_2{=}CH(CH_2)_3$
7c R = $CH_2{=}CH{-}CH{=}CH{-}CH_2$

Table. *Alkylation products of the methylthiosilyloxypentadienyllithium* **5** *by halides R-X. and corresponding yields*

X	R in **6**	Solvent	Yield of **6** (%)[a]
I	**a** CH_3	THF/HMPA 5:1	91
I	**b** C_2H_5	THF	78
Br	**c** $CH_2{=}CH(CH_2)_2$	THF/HMPA 10:1	87
Br	**d** $CH_2{=}CH(CH_2)_3$	THF/HMPA 5:1	89
Br	**e** $CH_2{=}CH{-}CH{=}CH{-}CH_2$	THF	82

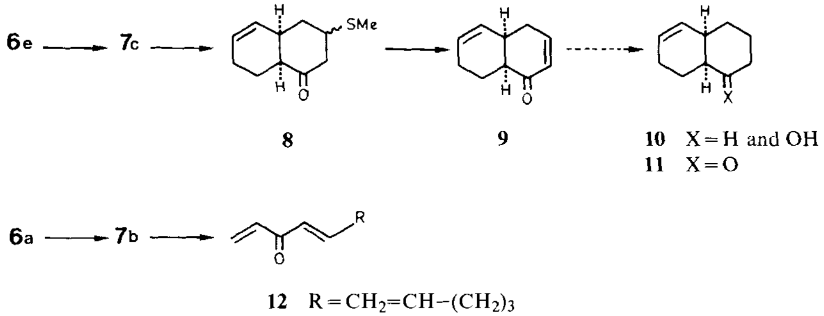
[a] Yields are based on the diene **4**.

5 which was treated with a series of alkyl or alkenyl halides (1.2 to 2.0 mol-equiv.) at –78°. Quenching of the decolorized reaction mixtures with sat. aq. NH_4Cl-solution and work-up furnished the single γ-products **6a–e** in high yields as indicated in the *Table*. Deprotonation of **4** and subsequent alkylation may be also carried out in THF without HMPA as demonstrated by the conversions **4**→**6b** and **4**→**6e**.

Further reactions of the substituted dienes 4 and 6. - This easy access to **6** containing olefinic substituents R permits their efficient use in intramolecular *Diels-Alder* reactions. For example, silyl ether cleavage of the tetraene **6e** with KF/MeOH at –10 to 0° for 1 h, subsequent aq. work-up and chromatography furnished directly the *cis*-fused bicyclodecenones **8** (C(3)-epimer-mixture) in 63% yield *(Scheme 2)*.

Hence the initially formed enone **7** undergoes a rapid *endo*-controlled intramolecular [4+2]-addition to the diene moiety. After cycloaddition, the methylthio group could be in principle reductively removed [8] or, exploited for further functionalization. Thus, oxidation of the epimers **8** with $NaIO_4$ in aq. MeOH-solution at –25° followed by sulfoxide elimination [9] in boiling CCl_4 gave the dienone **9** in 62% yield. The depicted *cis*-fusion of **9** (and of **8**), indicated by ^{1}H-NMR.-evidence ($J_{A,B}=9$ Hz), was confirmed by correlation with the previously

Scheme 2



8 **9** **10** X = H and OH **11** X = O

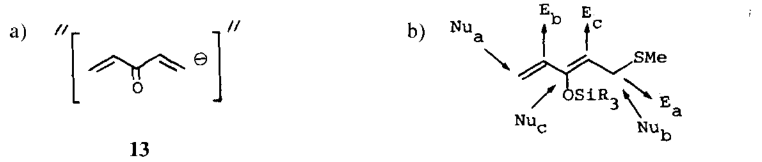
12 R = CH_2=CH–$(CH_2)_3$

described bicyclic enone **11** [2]: Reduction of **9** with $NaBH_4$ in EtOH furnished the alcohol **10** which on oxidation with PCC [10] (1.6 mol-equiv.)/NaOAc/CH_2Cl_2 gave **11** which proved to be identical with an authentic sample.

The enones **7** may also serve as precursors to the cross-conjugated dienones **12**. This is illustrated by the conversion **7b** → **12** *via* the oxidation/sulfoxide-elimination sequence (66% yield) *(Scheme 2)*. Thus introduction of the sulfur moiety into **1** has further increased the functionality of this C_5-unit so that **5** is a practical equivalent of the hypothetical β-deprotonated divinyl ketone **13** *(Scheme 3a)*[2].

A further adventage is that both latent enone functions can be liberated separately, thus permitting the regioselective polysubstitution of **4** by a range of different electrophiles and nucleophiles *(Scheme 3b)*. For example this stepwise functionalization of **4** was demonstrated by its conversion to the bicyclodecenone **17** *(Scheme 4)*. The enone **7a**, prepared by fluoride-promoted cleavage of **4**, underwent a *Michael* reaction with the enamine **14** to give, after aq. acidic work-up, the diketone **15**. Subsequent unmaking of the second enone by oxidation/sulfoxide elimination furnished **16** in 60% yield. Treatment of **16** with lithium dimethylcuprate and aq. HCl-solution gave directly the annelated product **17** in 88% yield (which arises from conjugate addition and trapping of the enolate by an intramolecular aldolisation)[3]. Thus, among the possibilities indicated in *Scheme 3* the conversion **7a** → **17** illustrates the formation of three C,C-bonds by successive attack of the nucleophiles Nu_a, Nu_b and the electrophile E_c.

Scheme 3



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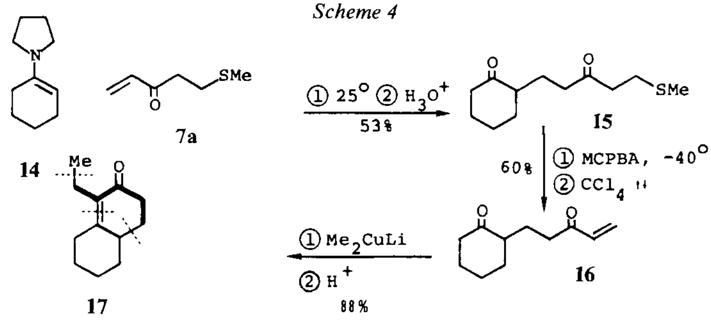
[2] For an alternative equivalent of **13** see [11].

[3] For a combination of conjugate addition with subsequent intramolecular aldolisation see [12].

Scheme 4



Accordingly, the versatile and selective reactivity of the C_5-building block **4** may prove of value in the synthesis of natural products.

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Experimental Part

General. - See [2].

Preparation and Alkylation of the Methylthiosilyloxypentadienyllithium (5) *(Scheme 1)* (→ **6a-e**). - *Preparation of (3Z)-5-(methylthio)-3-triethylsilyloxy-1,3-pentadiene* (**4**). A solution of *sec*-BuLi in cyclohexane (3 mmol) was added dropwise to a stirred solution of 3-triethylsilyloxy-1,3-pentadiene (396 mg, 2 mmol) in dry THF (6 ml) at −78° under Ar. After 30 min at −78° dimethyldisulfide (freshly distilled, 310 mg, 3.3 mmol) was added dropwise to the stirred solution of the anion **1**. After 15 min at −78° the decolorized reaction mixture was poured into sat. aq. NH_4Cl-solution. Extraction with pentane, work-up and distillation gave the thioether **4** (oil, 590 mg, 81%), b.p. 134°/12 Torr or 108-109°/1.5 Torr. Rf (hexane) 0.14, GC. (160°): 16.17. - UV.: 239 (4.22). - IR.: 2950, 2905, 2870, 1642, 1605, 1362, 1050, 910. - ^1H-NMR.: 0.5-1.2 (15 H): 2.07 (*s*, 3 H); 3,24 (*d*, $J=8$, 2 H); 4,90 (*t*, $J=8$, 1 H); 5.06 (*d*×*d*, $J=10$ and 2, 1 H); 5.38 (*d*×*d*, $J=17$ and 2, 1 H); 6.22 (*d*×*d*, $J=17$ and 10, 1 H). - MS.: 244 (4, $C_{12}H_{24}OSSi^+$), 197 (100), 169 (7), 133 (7), 115 (70), 87 (78).

Preparation of (3Z)-5-(methylthio)-3-triethylsilyloxy-1,3-hexadiene (**6a**). A solution of *n*-BuLi in hexane (0.55 mmol) was added dropwise to a stirred solution of diisopropylamine (60.5 mg, 0.6 mmol) in THF (3 ml) at −78° under Ar. After 10 min at −78° a solution of **4** (122 mg, 0.5 mmol) in THF (1 ml) was added slowly to give a clear yellow solution. After a further 20 min at −78° addition of HMPA (0.6 ml) changed the color of the mixture to deep-red. Then methyl iodide (142 mg, 1 mmol) was added to the mixture which then decolorized within 1 h at −78°. Pouring the reaction mixture into cold water,extraction with ether, work-up, chromatography (benzene) and distillation at 120-130° (bath)/1 Torr furnished **6a** (oil, 142 mg 91%), Rf (toluene) 0.67. - UV.: 240 (4.33). - IR.: 2960, 2880, 1601, 1365, 1055. - ^1H-NMR.: 0.5-1.2 (15 H); 1.3. (*d*, $J=7$, 3 H); 2.04 (*s*, 3 H); 3.80 (*m*; irradiation at 1.31 → *d*, $J=10.5$, 1 H); 4.70 (*d*, $J=10.5$, 1 H); 5.06 (*d*×*d*, $J=10$ and 2, 1 H); 5.37 (*d*×*d*, $J=17$ and 2, 1 H); 6.21 (*d*×*d*, $J=17$ and 10, 1 H). - MS.: 258 (6, $C_{13}H_{26}OSSi^+$), 211 (100), 115 (75), 105 (8), 103 (5), 87 (82).

Preparation of (3Z)-5-methylthio-3-triethylsilyloxy-1,3-heptadiene (**6b**). A solution of **4** (122 mg, 0.5 mmol) in THF (1 ml) was added dropwise to a stirred solution of lithium diisopropylamide (LDA, prepared as describe above) in THF (1.5 ml) at −78° under Ar. After 10 min at −78° ethyl iodide (156 mg, 1 mmol) was added slowly (no addition of HMPA) and the reaction mixture was left at −78° for a further 10 min. The reaction mixture changed its color from orange to pale-yellow. Pouring the mixture into cold water, extraction with ether, work-up, chromatography (hexane/toluene 1:4) and distillation at 120-130° (bath)/1 Torr furnished **6b** (oil, 105 mg, 78°), Rf (toluene) 0.69. - IR.: 2960, 2880, 1602, 1368, 1058. - ^1H-

NMR.: 0.5–1.2 (18 H); 1.63 (*m*, 2 H); 2.03 (*s*, 3 H); 3.65 (*d*×*t*, *J* = 10.5 and 7, 1 H); 4.72 (*d*, *J* = 10.5, 1 H); 5.07 (*d*×*d*, *J* = 10 and 2, 1 H); 5.38 (*d*×*d*, *J* = 17 and 2, 1 H); 6.24 (*d*×*d*, *J* = 17 and 10, 1 H). - MS.: (M^+ not observed), 121 (52), 119 (85), 117 (88), 103 (92), 87 (54), 75 (100).

(3Z)-5-(Methylthio)-3-triethylsilyloxy-1,3,8-nonatriene (**6c**). A solution of **4** (488 mg, 2 mmol) in THF (2 ml) was added slowly to a stirred solution of LDA (2.2 mmol) in THF (10 ml) at −78° under Ar. After 20 min at −78° HMPA (1 ml) was added followed by the addition of 4-bromo-1-butene (338 mg, 2.5 mmol). After further 30 min at −78° the decolorized reaction mixture was poured into cold water and extracted with ether. Work-up, chromatography (hexane/toluene 1:9) and distillation at 130–145° (bath)/1 Torr gave the triene **6c** (oil, 519 mg, 87%), Rf (toluene) 0.70. - IR.: 2960, 2880, 1644, 1605, 1365, 1057, 915. - ^{1}H-NMR.: 0.5–1.2 (15 H); 1.70 (*m*, 2 H); 2.03 (*s*, 3 H); 2.17 (*m*, 2 H); 3.71 (*d*×*t*, *J* = 10.5 and 7, 1 H); 4.71 (*d*, *J* = 10.5, 1 H); 4.9–5.2 (3 H); 5.37 (*d*×*d*, *J* = 17 and 2, 1 H); 5.84 (*m*, 1 H); 6.22 (*d*×*d*, *J* = 17 and 10, 1 H). - MS.: (M^+ not observed), 251 (66), 197 (24), 121 (55), 115 (100), 103 (76), 87 (73).

5-(Methylthio)-3-triethylsilyloxy-1,3,9-decatriene (**6d**). A solution of **4** (784 mg, 3.21 mmol) in THF (1 ml) was added slowly to a solution of LDA (3.8 mmol) in THF (8 ml) at −78° under Ar. After 20 min at −78° HMPA (1.5 ml), followed by 5-bromo-1-pentene (600 mg, 4 mmol) was added. After 1 h at −78° the reaction mixture was poured into cold water. Extraction with ether, work-up and distillation *i.v.* gave the triene **6d** (oil, 890 mg, 89%), b.p. 132–134°/0.7 Torr, Rf (toluene) 0.71. - IR.: 2955, 1642, 1601, 1368, 1055, 915. - ^{1}H-NMR.: 0.5–1.2 (15 H); 1.2–1.8 (4 H); 2.04 (*s*, 3 H); 2.07 (*m*, 2 H); 3.71 (*m*, irradiation at 1.57 → *d*, *J* = 10.5, 1 H); 4.70 (*d*, *J* = 10.5, 1 H); 4.9–5.2 (3 H); 5.37 (*d*×*d*, *J* = 17 and 2, 1 H); 5.83 (*m*, 1 H); 6.22 (*d*×*d*, *J* = 17 and 10, 1 H). - MS.: 312 (4, $C_{17}H_{32}OSSi^+$), 265 (100), 180 (6), 121 (23), 115 (44), 87 (58).

5-(Methylthio)-3-triethylsilyloxy-1,3,7,9-decatetraene (**6e**). A solution of **4** (488 mg, 2 mmol) in THF (1 ml) was added dropwise to a stirred solution of LDA (2.2 mmol) in THF (3 ml) at −78° under Ar. After 15 min at −78° a solution of 5-bromo-1,3-pentadiene [14] (323 mg, 2.2 mmol) in THF (1 ml) was added (no addition of HMPA). The instantaneously decolorized reaction mixture was poured into cold water. Extraction with ether, work-up, chromatography (hexane/toluene 1:4) and distillation at 150–160° (bath)/1 Torr gave the tetraene **6e** (oil, 508 mg, 82%), Rf (hexane) 0.23. - IR. (film): 2960, 2915, 2875, 1600, 1420, 1365, 1245, 1050, 1005, 750. - ^{1}H-NMR.: 0.5–1.2 (15 H); 2.02 (*s*, 3 H); 2.39 (*m*, 2 H); 3.77 (*d*×*t*, *J* = 10.5 and 7; irradiation at 2.39 → *d*, *J* = 10.5, 1 H); 4.71 (*d*, *J* = 10.5, 1 H); 4.8–5.4 (2 H); 5.16 (*d*×*d*, *J* = 10 and 2, 1 H); 5.37 (*d*×*d*, *J* = 17 and 2, 1 H); 5.71 (*m*, irradiation at 2.39 → *d*, *J* = 15, 1 H); 5.9–6.6 (3 H). - MS.: (M^+ not observed), 263 (5), 251 (6), 197 (45), 133 (8), 115 (100), 105 (14), 103 (10), 97 (95), 79 (36).

Reactions of the Methylthiosilyloxydienes 4 and 6 (*Schemes 2* and *4*). - cis-*4-(Methylthio)bicyclo[4.4.0]dec-7-en-2-one* (**8**). KF (174 mg, 3 mmol) was added during 5 min to a stirred solution of crude **6e** (733 mg, 2.36 mmol) in methanol (25 ml) at −10° under Ar. After 1 h at −10° → 0° the reaction mixture was poured into cold water. Extraction with ether, work-up and chromatography (CH_2Cl_2) gave the bicyclic ketone **8** (oil, mixture of stereoisomers, 292 mg, 63%), Rf (CH_2Cl_2) 0.23, GC. (180°): 10.19. - IR.: 2934, 1710, 1264, 1235, 944. - ^{1}H-NMR.: 1.4–3.0 (14 H); 5.72 (*m*, 2 H). - MS.: (M^+ not observed), 119 (90), 117 (93), 103 (100), 86 (57), 84 (100), 75 (97).

cis-*Bicyclo[4.4.0]-3,7-decadien-2-one* (**9**). A solution of $NaIO_4$ (214 mg, 1 mmol) in water (1 ml) was added slowly to a stirred solution of **8** (178 mg, 0.91 mmol) in methanol (10 ml) at −25° under Ar. After 3 h at −25° the reaction mixture was poured into cold water. Extraction with CH_2Cl_2 and work-up gave a crude sulfoxide which was heated in CCl_4 under reflux for 2.5 h. Evaporation of the solution and chromatography (CH_2Cl_2) gave the dienone **9** (oil, 82 mg, 62%), Rf (CH_2Cl_2), 0.26 GC. (180°): 9.9. - IR.: 3020, 2920, 1676, 1390, 1257, 1130. - ^{1}H-NMR.: 1.5–3.0 (8 H); 5.64 (*d*×*m*, *J* = 10, 1 H); 5.68 (*d*×*m*, *J* = 10, 1 H); 6.05 (*d*×*t*, *J* = 10 and 2 H); 6.91 (*d*×*t*, *J* = 10 and 4, 1 H). Addition of varying amounts of $Eu(FOD)_3$, combined with decoupling experiments, indicates a vicinal coupling of the angular protons $J \simeq 9$ Hz in agreement with the assigned *cis*-fusion. - MS.: 148 (80, $C_{10}H_{12}O^+$), 133 (38), 107 (28), 94 (35), 80 (100), 79 (65).

All-cis-*bicyclo[4.4.0]dec-7-en-2-ol* (**10**). $NaBH_4$ (10.3 mg, 0.27 mmol) was added portionwise to a stirred solution of the bicyclic dienone **9** (20 mg, 0.135 mmol) in ethanol (4 ml) at 25°. After 20 min at 25° the mixture was heated under reflux for 15 min and then was poured into cold water. Extraction with CH_2Cl_2 gave the all-*cis*-alcohol **10** identical (TLC., GC., ^{1}H-NMR., IR.) to a sample, previously prepared [2].

cis-*Bicyclo[4.4.0]dec-7-en-2-one* (**11**). A solution of **10** (30 mg, 0.197 mmol) in CH_2Cl_2 (4 ml) was added in one portion to a rapidly stirred slurry of pyridinium chlorochromate (63 mg, 0.31 mmol) in dry CH_2Cl_2 (10 ml) containing dry NaOAc (41 mg, 0.5 mmol) at 25° under Ar. After 1 h at 25° the reaction mixture was poured into ether. Filtration through *Celite*, evaporation and chromatography gave the bicyclic enone **11** (oil, 27 mg, 92%) identical to a sample, prepared previously [2].

5-(Methylthio)-1,9-decadien-3-one (**7b**). A solution of **6d** (1.39 g, 4.46 mmol) in methanol (10 ml) was added slowly to a stirred solution of KF (290 mg, 5 mmol) in methanol (15 ml) at − 10° under Ar. The reaction mixture was allowed to attain − 5° during 30 min. Evaporation and chromatography (toluene/EtOAc 19:1) furnished **7b** (oil, 630 mg, 71%), Rf (toluene/EtOAc 19:1) 0.43. - IR.: 2930, 1683, 1405, 960, 920. - ^{1}H-NMR.: 1.58 (*m*, 4 H); 2.08 (*s*, 3 H); 2.12 (*m*, 2 H); 2.5–3.3 (3 H); 4.9–5.2 (2 H); 5.6–6.5 (4 H). - MS.: 198 (19, $C_{11}H_{18}OS^+$), 183 (61), 151 (66), 150 (68), 107 (51), 95 (100).

(4E)-1,4,9-Decatrien-3-one (**12**). A solution of *m*-chloroperbenzoic acid (80%, 258 mg, 1.2 mmol) in CH_2Cl_2 (9 ml) was added dropwise to a stirred solution of **7b**, (198 mg, 1 mmol) in CH_2Cl_2 (15 ml) at −78° under N_2. After 1 h at −78° the reaction mixture was poured into 10% aq. Na_2SO_3-solution. Extraction with ether, work-up and distillation at 120° (bath)/11 Torr afforded the dienone **12** (pale yellow oil, 96 mg, 66%), Rf (toluene/EtOAc 19:1) 0.40. - GC. (150°): 8.17. - IR.: 1670, 1635, 1617, 1409, 988. - ^{1}H-NMR.: 1.64 (*qa*, *J* = 7, 2 H); 2.21 (*m*, 4 H); 4.9–5.2 (2 H); 5.6–6.1 (2 H); 6.1–7.2 (4 H). - MS.: (M^+ not observed), 136 (9), 122 (20), 108 (59), 96 (50), 82 (41), 55 (100).

5-(Methylthio)-1-penten-3-one (**7a**). KF (700 mg, 12 mmol) was added to a stirred solution of crude **4** (obtained from 1.6 g (8.1 mmol) of 3-triethylsilyloxy-1,4-pentadiene) in methanol (20 ml) at 0°. Subsequent stirring of the reaction mixture at 0° for 1 h, work-up and chromatography (CH_2Cl_2) gave the enone **7a**, (oil, 584 mg, 56% yield from 3-triethylsilyloxy-1,4-pentadiene), Rf (CH_2Cl_2) 0.39, GC. (SE-30, 140°): 3.17. - IR.: 2910, 1680, 1620, 1405, 1095, 985, 965, 915. - ^{1}H-NMR.: 2.12 (*s*, 3 H); 2.65–3.10 (4 H); 5.70–6.70 (3 H). - MS.: 130 (20, $C_6H_{10}OS^+$), 83 (46), 82 (57), 75 (33), 74 (10), 61 (30), 55 (100), 47 (21).

2-(5-Methylthio-3-oxopentyl)cyclohexanone (**15**). A mixture of the enone **7a** (584 mg, 4.5 mmol) and the enamine **14** [15] (820 mg, 5.4 mmol) in dry dioxane was stirred at 25° for 3 h. After addition of 2N aq. HCl (3 ml) the mixture was stirred for 15 h. Work-up and chromatography (toluene/EtOAc 9:1 → 3:1) gave **15** (oil, 544 mg, 53%), Rf (toluene/EtOAc 3:1) 0.42. - IR. (film): 2920, 2855, 1708, 1130. - ^{1}H-NMR.: 1.1–2.9 (17 H); 2.10 (*s*, 3 H). - MS.: 228 (8, $C_{12}H_{20}O_2S^+$), 178 (35), 86 (60), 85 (45), 84 (100), 83 (75), 55 (80), 47 (50).

2-(3-Oxo-4-pentenyl)cyclohexanone (**16**). A solution of *m*-chloroperbenzoic acid (90%, 440 mg, 2.4 mmol) in CH_2Cl_2 (5 ml) was added slowly over 15 min to a stirred solution of **15** (540 mg, 2.4 mmol) in CH_2Cl_2 (30 ml) at − 30°. Work-up (CH_2Cl_2) gave a crude sulfoxide (551 mg, 96% yield. - ^{1}H-NMR.: 1.2–2.9 (13 H); 2.60 (*s*, 3 H); 2.97 (*m*, 4 H)). A solution of this crude sulfoxide (80 mg, 0.33 mmol) in CCl_4 (6 ml) was heated under reflux for 4 h. Evaporation and chromatography (toluene/EtOAc 3:1) gave **16** (oil, 36 mg, 60%), Rf (toluene/EtOAc 3:1) 0.35. - IR. (film): 2930, 2857, 1705, 1684, 1620, 1452, 1407, 1132, 969. - ^{1}H-NMR.: 1.2–2.9 (13 H); 5.83 (*d* × *d*, *J* = 8.5 and 4, 1 H); 6.1–6.6 (2 H). - MS.: 180 (2, $C_{11}H_{16}O_2^+$), 151 (24), 111 (23), 84 (20), 83 (18), 70 (24), 55 (100), 41 (24).

2-Ethylbicyclo[4.4.0]dec-1-en-3-one (**17**). Methyllithium (1.9M in ether, 1.69 mmol) was added to a suspension of CuI (dried by heating at 140°/0.1 Torr for 1 h, 172 mg, 0.9 mmol) in dry ether (7 ml) at − 10° under Ar. To the clear solution, **16** (135 mg, 0.75 mmol) in dry ether (5 ml) was added dropwise with stirring at − 78°. Successive stirring of the mixture at − 60° for 90 min, at 0° for 1 h and work-up gave a crude product which was heated in THF (6 ml)/conc. aq. HCl (0.1 ml) for 2 h under reflux. Work-up and chromatography (pentane/ether 2:1) furnished the bicyclic enone **17** (oil, 117 mg, 88%), Rf (toluene/EtOAc 3:1) 0.48, GC. (SE-30, 180°): 6.8. - IR.: 2918, 2850, 1670, 1616, 1450, 1364, 1196. - ^{1}H-NMR.: 0.91 (*t*, *J* = 7, 3 H); 1.1–2.7 (14 H); 2.91 (*m*, 1 H). - MS.: (M^+ not observed), 178 (78), 150 (41), 149 (100), 121 (31), 107 (31), 93 (28), 91 (21), 79 (38).

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