40. Investigation of the Cyclopentenone Formation *via* the α-Alkynone Cyclisation: Synthesis of the Acorone Intermediate 8-Methylspiro[4.5]deca-3,7-dien-2-one

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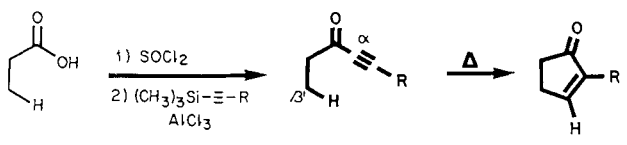
As a further application of the cyclopentenone formation **A**→**C** *via* the thermal α-alkynone cyclisation **B**→**C** and in order to test the fate of an isolated C,C-double bond within a molecule under these conditions, we investigated the synthesis of the acorone intermediate **3** starting from the known carboxylic acid **1**. The α-alkynone **2** was obtained from **1** *via* the acyl chloride **6** and a Pd(II)-catalysed route (22%). The thermolysis of **2** at 550° provided the target molecule **3** (48%) together with the product **9** (20%) of a competing intramolecular ene reaction and its dimer **10** (4%). At a higher thermolysis temperature (650°), the spiro ketone **3** was found to be unstable, affording the *retro-Diels-Alder* fragments 4-methylidene-2-cyclopentenone (**12**) (33%) and isoprene (32%). A further example of the influence of an isolated double bond on the yield of the cyclopentenone-formation sequence **A**→**C** was provided by the comparison of the annelation **14**→**20** (5% overall with Pd(II)-catalysed acylation) with that of its non-olefinic analogue **17**→**21** (53% overall with *Friedel-Crafts* acylation).

1. Introduction. – The cyclopentenone-formation sequence **A**→**C** *(Scheme 1)*, which was made possible by the discovery [1] of the thermal α-alkynone cyclisation step **B**→**C**, has been applied to the synthesis of various cyclopentanoid systems [1] [2] including natural products [3] [4]. So far the acids **A** and the α-alkynones **B** used in this sequence contained no other functional groups. In order to establish the synthetic scope of this annelation, the compatibility with the reaction conditions of functional groups and other structural elements aside from the reacting substructures must be examined. We first chose to investigate the influence of an isolated C,C-double bond located several bonds away from the reactive moiety (COOH or COC≡C) on the annelation sequence **A**→**C**. To that purpose we considered the synthesis of 8-methylspiro[4.5]deca-3,7-dien-2-one (**3**),

Scheme 1



A **B** **C**

R = H, D, CH_3, $Si(CH_3)_3$

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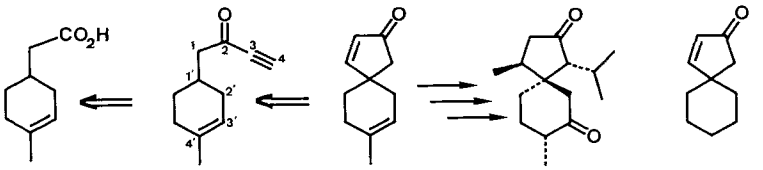
Scheme 2

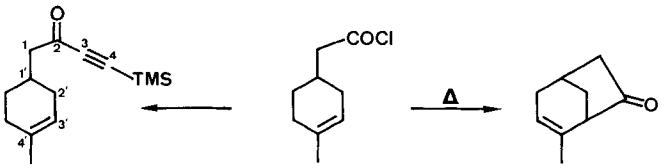


1 **2** **3** **4** **5**

a known intermediate for the synthesis of the spiro sesquiterpene acorone (**4**) [5–7]. Our approach, shown in *Scheme 2*, envisaged the thermolysis of the α-alkynone **2**, the latter being obtained by acylation from the carboxylic acid **1**. Since **1** is easily available by a *Diels-Alder*-addition route [8], this plan carried the potential of an expedient method for the synthesis of **3**.

As far as the α-alkynone cyclisation **2**→**3** is concerned, a positive precedent was available in the high-yield preparation of the spiro system **5** by this method [1]. On the other hand, a negative effect had to be considered due to the presence of two multiple bonds in **2** (competing intramolecular ene reaction (*cf.* [9])) and of the cyclohexene moiety in **2** or in **3** (competing or subsequent *retro-Diels-Alder* reaction (*cf.* [10])). Moreover, even the acylation **1**→**2** by the *Birkofer* method [11] might not be unproblematic, since *Friedel-Crafts* conditions were known to convert the acyl chloride **6** (see below) into **8** [8] [12]. In the present work we apply an alternative synthesis of α-alkynones and investigate the thermal behaviour of two α-alkynones (including **2**), both containing an isolated double bond.

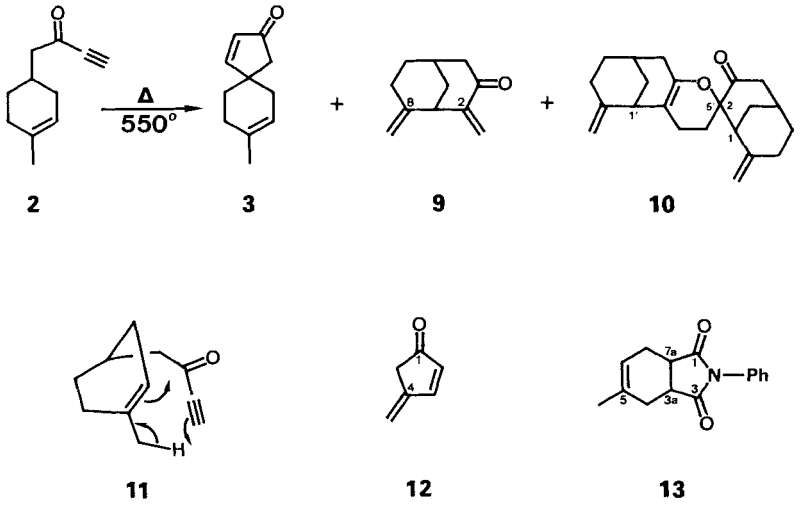
Scheme 3



7 TMS = $Si(CH_3)_3$ **6** **8**

2. Synthesis and Thermolysis of 2. – The acyl chloride **6** was obtained (*ca.* 82%) by treatment of the sodium salt of the carboxylic acid **1** [8] with oxalyl chloride [13]. The crude product was only 82% pure; according to GC and GC/MS it contained about 7% of **8** and 11% of 3 other unidentified components. Crude **6** could not be distilled without partial conversion to **8**; in fact, we found that prolonged heating of **6** in benzene, even without any *Lewis* acid, converted it completely into **8** (*cf.* [8]). Attempts to acylate bis(trimethylsilyl)acetylene with crude **6** according to the general *Friedel-Crafts* procedure [1] afforded, at best, 4% (from **1**) of the silyl-α-alkynone **7**. The crude product consisted of a *ca.* 1:4 mixture **7**/**8**, from which **7** could only be separated by chromatography. In order to suppress the intramolecular acylation **6**→**8**, the recently described procedure of *Logue* and *Teng* [14] was attempted: Acylation of tributyl[(trimethylsilyl)ethynyl]stannane with **6** under bis(triphenylphosphine)palladium(II) dichloride catalysis, but with shorter heating than in [14], did indeed afford more of **7**, but still in only

Scheme 4

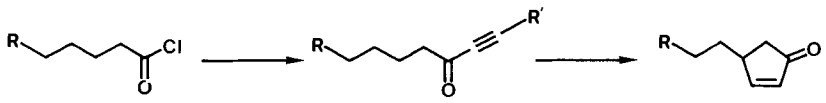


31% yield from **1**. The low yield of this acylation is still unexplained, but it is not due to a competing intramolecular acylation of **6** since **8** was not found among the products. Hydro-desilylation [3] of **7** afforded the free α-alkynone **2** (72%).

The α-alkynone **2** was subjected to thermolysis in a flow system as described in [15]. The optimum temperature for obtaining a maximum yield (34%) of spiro ketone **3** was found to be 550°. This temperature led to a separable mixture of 4 components *(Scheme 4)*: recovered **2** (29%), the known [5–7] spiro ketone **3** (34%), the bicyclic ketone **9** (15%), and a dimer **10** of the latter (3%); the yields of **3**, **9**, and **10** based on non-recovered **2** were 48, 20, and 4%, respectively. The bicyclic ketone **9** appears to be the product of an intramolecular ene reaction, within **2**, of the acceptor-activated (*cf.* [9]) acetylenic moiety (conjugated carbonyl group) and the methyl-substituted olefinic moiety (see **11**, *Scheme 4*). Of the 6 site- and regioselective modes of this intramolecular ene reaction, only the one shown in **11** leads to a product with two exocyclic methylidene groups. The presence of these groups in **9** is evident from the olefinic region in the ^{1}H-NMR spectrum; this and the IR band at 1695 cm^{-1} show that one of these double bonds belongs to an α,β-unsaturated ketone substructure. The ease of dimerisation of **9** to **10** confirms this substructure since α-methylidene ketones are known to undergo *Diels-Alder* dimerisations [16].

In order to investigate the effect of the temperature on the α-alkynone cyclisation of **2**, thermolyses were carried out on a small scale ($\leqslant$ 4 mg) at a lower and a higher temperature: At 450°, **2** remained largely unchanged; at 650°, all of **2** had reacted, but the spiroketone **3** was not detected, which left the possibility that **3** was, in fact, formed but was not stable at higher temperatures. To confirm this and to find the cause of this instability, **3** was thermolysed at 650°. As one of the products of this reaction we isolated 4-methylidene-2-cyclopentenone (**12**, 33%); it was purified for spectral analysis but, due to its volatility, could not be separated from the solvent. The ketone **12** represents the dienophile fragment of the *retro-Diels-Alder* cleavage of the cyclohexene moiety of **3**; the

Scheme 5



14 R = CH_2=CH $Si(CH_3)_3$ **15** R = CH_2=CH, R' = $Si(CH_3)_3$ **20** R = CH_2=CH
16 R = CH_2=CH, R' = H

17 R = Et $Si(CH_3)_3$ **18** R = Et, R' = $Si(CH_3)_3$ **21** R = Et
19 R = Et, R' = H

corresponding diene fragment isoprene was isolated as the known [17] *Diels-Alder* adduct **13** (32%) by capturing it in the crude thermolysate of **3** with *N*-phenylmaleimide.

3. Synthesis and Thermolysis of 16 and 19. – As a further test of the influence of an isolated double bond on the cyclopentenone formation, the synthesis and thermolysis of the straight-chain olefinic alkynone **16** were compared to those of its non-olefinic analogue **19**. No attempt was made to apply the *Birkofer* method (*cf.* [11]) to the preparation of the olefinic silylalkynone **15** from the unsaturated acyl chloride **14**, since *Lewis*-acid catalysis had been shown [18] to cyclise **14** to β-chlorocycloheptanone. The Pd(II)-catalysed acylation of tributyl[(trimethylsilyl)ethynyl]stannane [14] proved to be applicable to both **14** and **17** affording the silylalkynones **15** (44%) and **18** (58%), respectively. While this method was inferior to the *Birkofer* method for the preparation of the non-olefinic silylalkynone **18** (98%), it was nevertheless capable of making available the olefinic silylalkynone **15**. Hydro-desilylation of **15** and **18** afforded the alkynones **16** (62%) and **19** (75%), respectively.

The thermolysis of the olefinic alkynone **16** at 620°/14 Torr afforded 18% of the alkenylcyclopentenone **20**. No by-products attributable to an intramolecular ene process or another side reaction were discovered. Under the same conditions, the non-olefinic alkynone **19** produced 56% of the alkylcyclopentenone **21** (72% based on non-recovered **19**).

The present work shows that the cyclopentenone-formation sequence with a modified acylation step **A**→**B** and the usual thermal cyclisation step **B**→**C** can make available alkenylcyclopentenones, but it also suggests that the presence of the extra C,C-double bond in the product depresses the yield.

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Experimental Part

1. *General.* See [2].

2. *4-Methyl-3-cyclohexene-1-acetyl Chloride* (**6**). To a stirred suspension of *ca.* 9.6 mmol of NaH (obtained by washing 0.42 g of a *ca.* 55% oil dispersion 3 times with dry benzene) in 30 ml of dry benzene was added, dropwise at 0°, a soln. of 1.01 g (6.5 mmol) of 4-methyl-3-cyclohexene-1-acetic acid (**1**) [8] in 20 ml of benzene. The mixture was stirred for 1 h at r.t., cooled to 0°, and treated dropwise with a soln. of 1.64 g (12.9 mmol) of oxalyl chloride [13] in 20 ml of benzene. The mixture was allowed to warm to r.t. within 0.5 h, filtered, and concentrated to leave 1.12 g (*ca.* 6.5 mmol) of crude **6** (*cf.* [8]) as an orange oil. GC (*SE-52*, 100°) of crude **6** showed 5 peaks in the integration ratio of 7:5:82:3:3 (order of elution), 2 of which were identified by GC/MS (*SE-54*, 100°, 70 eV) as **8** (1st peak) (see *Exper. 4*) and **6** (3rd peak). IR (film): 3010*w*, 2960*m*, 2920*s*, 2860*m*, 2840*m*, 2830*m*, 1800*s* (C=O), 1440*m*, 970*m*,

720*s*. Exhaustive bulb-to-bulb distillation of 98 mg of crude **6** at 175–185°/14 Torr gave 76 mg of a clear, colourless oil containing **8** and **6** in a ratio of 18:69 (GC (*SE-52*, 130°)). Due to this instability, crude **6** was used immediately in the preparation of **7**.

3. *4-Methylbicyclo[3.2.1]oct-3-en-6-one* (**8**). Reflux of 66 mg (0.38 mmol) of distilled **6** (containing **6**/**8** in a ratio of 69:18) in 4 ml of dry benzene for 16 h and evaporation left a pale brown oil which, after bulb-to-bulb distillation at 140°/14 Torr ([8]: b.p. 160°/19 Torr), yielded 48 mg (100%, pure by anal. GC (*SE-52*, 100°)) of **8** as a pale yellow oil. IR, ^{1}H-NMR: as reported in [8]. MS (70 eV): 136 (25, M^+), 107 (5), 92 (100), 79 (48), 68 (16), 51 (8), 39 (17).

4. *Attempted Preparation of* **7** *Using* Friedel-Crafts *Conditions*. Acylation analogous to [3] of 0.85 g (4.99 mmol) of bis(trimethylsilyl)acetylene with 0.86 g (4.99 mmol) of crude **6** gave *ca.* 0.8 g of a crude oil. IR: 2 bands at 1675 and 1745 in a ratio of *ca.* 1:4 indicating the presence of **7** and **8**, resp. After column chromatography (silica gel, hexane/AcOEt 9:1), 80 mg (4% from I) of **7** and 268 mg (24% from **1**) of **8** (identified by their spectral data, see *Exper. 5* and *3*) were isolated.

5. *1-(4-Methyl-3-cyclohexenyl)-4-(trimethylsilyl)-3-butyn-2-one* (**7**). Acylation analogous to [14] of 2.52 g (6.5 mmol) of tributyl[(trimethylsilyl)ethynyl]stannane (freshly prepared according to [14]) with crude **6** (*ca.* 5.3 mmol, obtained from 6.5 mmol of **1**) and 82 mg (0.12 mmol) of bis(triphenylphosphine)palladium(II) dichloride (*Fluka AG*) by refluxing in $ClCH_2CH_2Cl$ for 5 min and workup yielded a dark brown oil. (Heating for 2 h as described in [14] resulted in lower yields.) Column chromatography (silica gel, hexane/AcOEt 99:1) and bulb-to-bulb distillation at 120°/0.1 Torr afforded 476 mg (31% from **1**) of **7** as a clear, colourless oil (purity: 95% by anal. GC (*SE-52*, 130°)). UV (EtOH): 202 (4800), 216 (sh, 5900), 225 (7400), 231 (sh, 6600). IR (film): 3010*m*, 2960*s*, 2910*s*, 2850*m*, 2830*m*, 2150*m* (C≡C), 1680*s* (C=O), 1440*m*, 1400*m*, 1380*m*, 1255*s*, 1220*m*, 1125*m*, 1095*s*, 1060*m*, 870*s*, 850*s*, 760*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.38 (br. *s*, H–C(3′)); 2.51 (*d*, J = 6.9, $H_2C(1)$); 2.30–1.20 (*m*, 7H); 1.65 (*s*, CH_3–C(4′)); 0.24 (*s*, $(CH_3)_3Si$). MS (70 eV): 219 (2, $M^+ - 15$), 125 (4), 94 (100), 79 (50), 73 (11). Anal. calc. for $C_{14}H_{22}OSi$ (234.40): C 71.73, H 9.46; found: C 71.32, H 9.06.

6. *1-(4-Methyl-3-cyclohexenyl)-3-butyn-2-one* (**2**). Hydro-desilylation analogous to [3] of 300 mg (1.28 mmol) of **7** and bulb-to-bulb distillation at 110°/14 Torr gave 150 mg (72%) of **2** as a clear, colourless oil (pure by anal. GC (*SE-52*, 130°)). UV (EtOH): 204 (6000). IR (film): 3260*s* (H–C≡), 3010*m*, 2960*m*, 2920*s*, 2830*m*, 2095*s* (C≡C), 1680*s* (C=O), 1440*m*, 1400*m*, 1375*m*, 1215*m*, 1130*m*, 1090*m*, 1060*m*, 920*w*, 800*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.38 (br. *s*, H–C(3′)); 3.24 (*s*, H–C≡); 2.54 (*d*, J = 7, $H_2C(1)$); 2.40–1.60 (*m*, 7H); 1.64 (*s*, CH_3–C(4′)). MS (70 eV): 94 (100, $M^+ - 66$), 79 (84), 67 (16), 41 (14). Anal. calc. for $C_{11}H_{14}O$ (162.23): C 81.44, H 8.70; found: C 81.65, H 8.92.

7. *Thermolysis of* **2**. Thermolysis of 589 mg (3.63 mmol) of **2** at 550°/14 Torr for 1.5 h was carried out in the apparatus described in [15]. Column chromatography (silica gel, hexane/AcOEt 95:5) of the thermolysate afforded 168 mg (29%) of recovered **2**, 202 mg (34%; 48% based on non-recovered **2**) of *8-methylspiro[4.5]deca-3,7-dien-2-one* (**3**) as a colourless oil after bulb-to-bulb distillation at 60°/0.1 Torr ([7]: b.p. 55–60°/0.1 Torr), 86 mg (15%; 20% based on non-recovered **2**) of *2,8-dimethylidenebicyclo[3.3.1]nonan-3-one* (**9**) as a colourless oil, and 35 mg (3%; 4% based on non-recovered **2**) of *8,12′-dimethylidenespiro[bicyclo[3.3.1]nonane-2,5′-(6′-oxatricyclo[7.3.1.0^{2,7}]tridec-2′(7′)-en)]-3-one* (**10**), after recrystallisation from hexane as white plates, m.p. 113.2–114.9°. Attempts to distil **9** resulted in partial dimerisation to **10** (^{1}H-NMR (60 MHz)). **3**: IR, ^{1}H-NMR, MS: identical to those reported [5–7]. UV (EtOH): 220 (5300). ^{13}C-NMR (20 MHz, $CDCl_3$): 209.1 (*s*, C=O) ([6]: 195.6), all other signals the same as in [6].

9: IR (film): 3070*w*, 2930*s*, 2860*m*, 1695*s* (C=O), 1645*m*, 1620*m*, 1450*m*, 1405*m*, 1290*m*, 1155*m*, 1130*m*, 1065*m*, 930*m*, 895*m*, 810*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.83 (*d*, J = 1.9, H–C=C(2)); 5.15 (*dd*, J = 1.8, 0.6, H–C=C(2)); 4.66 (*t*, J = 1.8, H–C=C(8)); 4.50 (*t*, J = 1.8, H–C=C(8)); 3.39 (br. *s*, H–C(1)); 3.00–1.50 (*m*, 9H). GC/MS (*SE-54*, 100°, 70 eV): 162 (66, M^+), 147 (17), 134 (16), 119 (40), 105 (49), 91 (100), 79 (73), 65 (26), 53 (34), 39 (58).

10: UV (EtOH): 202 (9500), 218 (sh, 4600), 270 (2900). IR ($CHCl_3$): 3060*m*, 2900*s*, 2850*s*, 1710*s* (C=O), 1643*m* (C=C), 1440*m*, 1150*s*, 1063*m*, 1005*m*, 895*s*, 650*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.71 (br. *s*, 2H); 4.59 (*m*, 2H); 3.02 (*dd*, J = 14, 6, 1H); 2.78–1.20 (*m*, 23H). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 209.9 (*s*, C=O); 150.7 (*s*); 146.7 (*s*); 144.7 (*s*); 111.3 (*t*); 108.1 (*s*); 106.0 (*t*); 78.8 (*s*); 50.2 (*d*); 44.8 (*t*); 43.9 (*d*); 34.8 (*t*); 33.7 (*t*); 33.5 (*t*); 32.7 (*t*); 31.6 (*d*); 30.6 (*t*); 28.4 (*t*); 28.1 (*t*); 27.6 (*d*); 24.8 (*t*); 20.8 (*t*). MS (70 eV): 324 (100, M^+), 296 (6), 267 (6), 239 (7), 231 (11), 213 (29), 187 (24), 175 (13), 162 (20), 145 (11), 131 (11), 119 (19), 105 (29), 91 (60), 79 (40), 67 (15), 53 (19), 41 (33). Anal. calc. for $C_{22}H_{28}O_2$ (324.25): C 81.49, H 8.64; found: C 81.48, H 8.77.

Thermolysis of 2 mg (0.012 mmol) of **2** as before, but at 450°/14 Torr, gave a thermolysate as a pale yellow oil which contained **2**, **9**, and **3** in a ratio of 55:25:9 (order of elution in anal. GC (*SE-52*, 100°)). Thermolysis of 4 mg

(0.026 mmol) at 650°, as above, gave a crude pale yellow oil which contained **9** and **12** in a ratio of 44:56, but no **2** or **3** (anal. GC (*SE-52*, 100°)).

8. *Thermolysis of* **3**. Thermolysis as in *Exper. 7* of 94 mg (0.58 mmol) of **3** at 650°/14 Torr provided a pale yellow oily thermolysate which contained no more **3** (anal. GC (*SE-52*, 100°)). This was treated with a soln. of 100 mg (0.58 mmol) of *N*-phenylmaleimide in 4 ml of dry benzene at r.t. for 65 h. Concentration and chromatography (silica gel, hexane/AcOEt 9:1) of the residue afforded 63 mg (63%) of recovered N-*phenylmaleimide*, 18 mg (33%) of *4-methylidenecyclo-2-pentenone* (**12**; pure by anal. GC (100°)) which was a clear, colourless oil still containing solvent after bulb-to-bulb distillation at 85°/80 Torr, and 44 mg (32%) of *3a,4,7,7a-tetrahydro-5-methyl-2-phenyl-1H-isoindole-1,3(2H)-dione* (**13**) as a pale yellow solid (pure by anal. GC (180°)) which gave small white needles on recrystallisation from Et_2O, m.p. 94.2–96.2° ([17]: m.p. 94°). **12**: IR (film): 2920*w*, 1710*s* (C=O), 1660*m*, 1640*m*, 1545*m* (C=C), 1395*m*, 1345*m*, 1280*m*, 1175*m*, 1150*m*, 1075*m*, 935*m*, 900*m*, 870*w*, 820*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.74 (*dd*, J = 5.4, H–C(3)); 6.32 (*dd*, J = 5.6, 1.0, H–C(2)); 5.41 (*s*, H–C=C(4)); 5.30 (*s*, H–C=C(4)); 2.98 (*s*, $H_2C(5)$). GC/MS (*SE-54*, 50°, 70 eV): 94 (75, M^+), 86 (2), 79 (2), 73 (2), 66 (75), 57 (20), 55 (21), 51 (17), 43 (100), 42 (27). **13**: UV (EtOH): 205 (11100), 216 (sh, 8800), 260 (1100). IR (paraffin oil): 3070*w*, 3030*w*, 2930*s*, 2850*s*, 1765*w* (C=O), 1705*s* (C=O), 1655*m* (C=C), 1595*m*, 1500*m*, 1455*m*, 1395*s*, 1320*m*, 1205*s*, 1155*m*, 960*m*, 900*m*, 805*m*, 765*m*, 700*s* (*cf.* [17]). ^{1}H-NMR (200 MHz, $CDCl_3$): 7.52–7.28 (*m*, 3H), 7.28–7.12 (*m*, 2H, 5 arom. H); 5.60 (br. *s*, H–C(5)); 3.30–3.10 (*m*, H–C(3a), H–C(7a)); 2.72–2.48 (*m*, 2H); 2.38–2.14 (*m*, 2H); 1.71 (*s*, CH_3–C(5)). ^{13}C-NMR (50.4 MHz, $CDCl_3$): 179.1 (*s*, C=O); 178.9 (*s*, C=O); 136.3 (*s*); 132.0 (*s*); 128.8 (*d*); 128.3 (*d*); 126.2 (*d*); 120.0 (*d*); 39.5 (*d*); 39.0 (*d*); 28.7 (*t*); 24.3 (*t*); 23.3 (*q*). MS (70 eV): 241 (75, M^+), 212 (7), 198 (8), 174 (7), 121 (26), 107 (6), 94 (100), 79 (62), 65 (14), 51 (15), 45 (15), 41 (16), 39 (23). Anal. calc. for $C_{15}H_{15}NO_2$ (241.28): C 74.67, H 6.27, N 5.81; found: C 74.40, H 6.53, N 5.70. The spectral data were identical to those of an authentic sample prepared by treating isoprene with *N*-phenylmaleimide as described above.

9. *1-(Trimethylsilyl)-8-nonen-1-yn-3-one* (**15**). Acylation of 5.25 g (13.55 mmol) of tributyl[(trimethylsilyl)ethynyl]stannane (freshly prepared according to [14]) with 1.99 g (13.55 mmol) of 6-heptenoyl chloride (**14**; pure by anal. GC (*SE-52*, 80°)) [19] and 171 mg (0.24 mmol) of bis(triphenylphosphine)palladium(II) dichloride (*Fluka AG*) according to [14], but after reflux in $ClCH_2CH_2Cl$ for only 0.5 h, gave a dark brown oil. Column chromatography (silica gel, hexane/AcOEt 99:1) and bulb-to-bulb distillation at 90°/0.06 Torr yielded 1.25 g (44%) of **15** as a clear, colourless oil (pure by anal. GC (*SE-52*, 100°)). UV (EtOH): 216 (sh, 5600), 224 (7400), 231 (sh, 6400). IR (film): 3080*m*, 2965*m*, 2940*m*, 2860*m*, 2150*m* (C≡C), 1680*s* (C=O), 1645*m* (C=C), 1410*m*, 1255*s*, 1215*m*, 1120*m*, 1095*m*, 995*m*, 910*m*, 850*s*, 765*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.80 (*ddt*, J = 16.9, 10.2, 6.6, H–C(8)); 5.10–4.90 (*m*, $H_2C(9)$); 2.57 (*t*, J = 7.1, $H_2C(4)$); 2.10 (*dt*, J = 6.9, 6.9, $H_2C(7)$); 1.70 (*tt*, J = 7, 7, $H_2C(5)$); 1.45 (*tt*, J = 7, 7, $H_2C(6)$); 0.25 (*s*, $(CH_3)_3Si$). MS (70 eV): 193 (10, $M^+ - 15$), 177 (6), 164 (7), 153 (9), 149 (8), 140 (30), 125 (100), 117 (19), 97 (49), 91 (14), 83 (18), 75 (71), 73 (58), 67 (11), 59 (16), 55 (12), 45 (11), 43 (18), 41 (19), 39 (14). Anal. calc. for $C_{12}H_{20}OSi$ (208.37): C 69.17, H 9.68; found: C 68.92, H 9.76.

10. *8-Nonen-1-yn-3-one* (**16**). Hydro-desilylation of 621 mg (2.98 mmol) of **15**, according to [3] gave, after bulb-to-bulb distillation at 100°/14 Torr, 251 mg (62%) of **16** as a clear, colourless oil (pure by anal. GC (*SE-52*, 100°)). UV (EtOH): 210 (4500), 272 (800). IR (film): 3265*s* (H–C≡), 3080*m*, 2980*m*, 2935*s*, 2860*m*, 2100*s* (C≡C), 1685*s* (C=O), 1645*m* (C=C), 1460*m*, 1410*m*, 1365*m*, 1210*m*, 1090*m*, 995*m*, 915*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.80 (*ddt*, J = 17, 10, 7, H–C(8)); 5.10–4.92 (*m*, $H_2C(9)$); 3.21 (*s*, H–C(1)); 2.61 (*t*, J = 7.5, $H_2C(4)$); 2.09 (*dt*, J = 7.1, 7.1, $H_2C(7)$); 1.71 (*tt*, J = 7.8, 7.8, $H_2C(5)$); 1.45 (*tt*, J = 7.4, 7.4, $H_2C(6)$). MS (70 eV): 135 (6, $M^+ - 1$), 121 (5), 107 (14), 93 (10), 81 (27), 68 (76), 53 (100), 41 (58). Anal. calc. for $C_9H_{12}O$ (136.19): C 79.37, H 8.89; found: C 79.09, H 9.17.

11. *Thermolysis of* **16**. Thermolysis as in *Exper. 7* of 251 mg (1.84 mmol) of **16** at 620°/14 Torr for 0.5 h, chromatography (silica gel, hexane/AcOEt 95:5) of the thermolysate, and bulb-to-bulb distillation of the single product fraction at 75°/14 Torr yielded 46 mg (18%) of *4-(3-butenyl)-2-cyclopentenone* **20** as a clear, colourless oil (purity: 96% by anal. GC (*Pluronic 64*, 80°)). UV (EtOH): 220 (12400). IR (film): 3080*m*, 2980*m*, 2925*s*, 2860*m*, 1715*s* (C=O), 1665*m*, 1645*m* (C=C), 1590*m* (C=C), 1455*m*, 1440*m*, 1410*m*, 1350*m*, 1185*s*, 1000*m*, 915*m*, 785*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.64 (*dd*, J = 5.7, 2.5, H–C(3)); 6.16 (*dd*, J = 5.7, 2.0, H–C(2)); 5.82 (*ddt*, J = 17, 10, 6.5, H–C(3')); 5.14–4.96 (*m*, $H_2C(4')$); 3.06–2.90 (*m*, H–C(4)); 2.55 (*dd*, J = 18.8, 6.3, H–C(5)); 2.30–2.10 (*m*, $H_2C(2')$); 2.02 (*dd*, J = 18.9, 2.2, H–C(5)); 1.82–1.40 (*m*, $H_2C(1')$). ^{13}C-NMR (25.2 MHz, $CDCl_3$): 209.5 (*s*, C=O); 168.0 (*d*); 137.5 (*d*); 133.7 (*d*); 115.4 (*t*); 40.9 (*d*); 40.9 (*t*); 33.9 (*t*); 31.8 (*t*). MS (70 eV): 136 (6, M^+), 121 (5), 108 (18), 94 (50), 82 (100), 67 (39), 53 (46), 41 (41). Anal. calc. for $C_9H_{12}O$ (136.19): C 79.37, H 8.88; found: C 79.09, H 8.86.

12. *1-(Trimethylsilyl-1-nonyn-3-one* (**18**). Acylation analogous to [14] of 3.83 g (9.89 mmol) of tributyl-[(trimethylsilyl)ethynyl]stannane (freshly prepared according to [14]) with 1.47 g (9.89 mmol) of heptanoyl chloride (**17**) and 125 mg (0.18 mmol) of bis(triphenylphosphine)palladium(II) dichloride (both from *Fluka AG*) gave, after

reflux in $ClCH_2CH_2Cl$ for 15 min and workup, a dark brown oil. Column chromatography (silica gel, hexane/AcOEt 99:1) and bulb-to-bulb distillation at 150°/14 Torr provided 1.20 g (58%) of **18** as a pale yellow oil (pure by anal. GC (*SE-52*, 120°)). UV (EtOH): 216 (sh, 4900), 224 (6100), 231 (sh, 5300). IR (film): 2960*s*, 2930*s*, 2860*m*, 2150*m* (C≡C), 1680*s* (C=O), 1460*m*, 1410*m*, 1250*s*, 1210*m*, 1135*m*, 1085*m*, 845*s*, 760*m*, 700*m*, 665*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.55 (*t*, *J* = 7.3, $H_2C(4)$); 1.74–1.54 (*m*, $H_2C(5)$); 1.36–1.20 (*m*, 6H); 0.89 (br. *t*, $H_3C(9)$); 0.25 (br. *s*, $(CH_3)_3Si$). MS (70 eV): 210 (1, M^+), 195 (5), 181 (6), 179 (6), 167 (7), 153 (8), 140 (49), 125 (100), 109 (5), 97 (28), 83 (25), 73 (28), 67 (8), 57 (10), 44 (28). Anal. calc. for $C_{12}H_{22}OSi$ (210.38): C 68.50, H 10.54; found: C 68.75, H 10.80.

Acylation of 1.44 g (8.45 mmol) of bis(trimethylsilyl)acetylene according to [3] with 1.00 g (6.73 mmol) of **17** gave, after bulb-to-bulb distillation at 150°/14 Torr, 1.38 g (98%) of **18** as a pale yellow oil (pure by anal. GC (*SE-52*, 100°)).

13. *1-Nonyn-3-one* (**19**). Hydro-desilylation of 101 mg (0.48 mmol) of **18** according to [1], but using THF as solvent[2]), for 6 h at r.t. and bulb-to-bulb distillation at 110°/14 Torr afforded 50 mg (75%) of **19** as a clear, colourless oil (pure by anal. GC (*SE-52*, 100°)). UV (EtOH): 210 (4800). IR (film): 3260*m* (H–C≡), 2960*s*, 2930*s*, 2860*s*, 2100*s* (C≡C), 1685*s* (C=O), 1470*m*, 1405*m*, 1380*w*, 1210*m*, 1135*m*, 1085*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.21 (*s*, H–C(1)); 2.59 (*t*, *J* = 7.3, $H_2C(4)$); 1.80–1.60 (*m*, $H_2C(5)$); 1.44–1.22 (*m*, 6H); 0.89 (*t*, *J* = 6.8, $H_3C(9)$). MS (70 eV): 137 (2, $M^+ - 1$), 123 (11), 109 (6), 95 (11), 81 (20), 68 (100), 53 (24), 43 (25). Anal. calc. for $C_9H_{14}O$ (138.20): C 78.21, H 10.21; found: C 77.93, H 10.47.

14. *Thermolysis of* **19**. Thermolysis as in *Exper. 7* of 1.08 g (7.82 mmol) of **19** at 620°/14 Torr for 1 h and chromatography (silica gel, hexane/AcOEt 95:5) of the thermolysate yielded 230 mg (21%) of recovered **19** and, after bulb-to-bulb distillation at 98°/14 Torr, 608 mg (56%; 72% based on non-recovered **19**) of *4-butyl-2-cyclopentenone* (**21**) as a clear, colourless oil (pure by anal. GC (*Pluronic 64*, 80°)). UV (EtOH): 220 (11 100). IR (film): 3080*w*, 3050*w*, 2960*s*, 2930*s*, 2860*s*, 1720*s* (C=O), 1665*m*, 1590*m* (C=C), 1470*m*, 1410*m*, 1350*m*, 1185*s*, 955*m*, 905*m*, 835*m*, 780*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.64 (*dd*, *J* = 5.5, 2.7, H–C(3)); 6.14 (*dd*, *J* = 5.5, 1.8, H–C(2)); 3.02–2.86 (*m*, H–C(4)); 2.53 (*dd*, *J* = 19, 6.3, H–C(5)); 2.00 (*dd*, *J* = 19, 2, H–C(5)); 1.7–1.2 (*m*, 6H); 0.91 (br. *t*, *J* = 6.5, $H_3C(4')$). ^{13}C-NMR (25.5 MHz, $CDCl_3$): 209.6 (*s*, C=O); 168.4 (*d*); 133.3 (*d*); 41.3 (*d*); 40.9 (*t*); 34.3 (*t*); 29.6 (*t*); 22.6 (*t*); 13.8 (*q*). MS (70 eV): 138 (14, M^+), 110 (7), 95 (21), 82 (100), 68 (15), 53 (28), 41 (22). Anal. calc. for $C_9H_{14}O$ (138.20): C 78.21, H 10.21; found: C 78.10, H 10.12.

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[2]) Use of MeOH as described in [1] gave rise to a side product in *ca.* 10% yield, which by ^{1}H-NMR was thought to result from acetal formation.