Printed in Great Britain
Pergamon Press plc

CARBOCATIONIC CYCLISATIONS AND REARRANGEMENTS IN THE DAMASCONE SERIES

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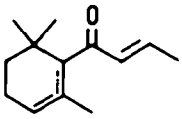
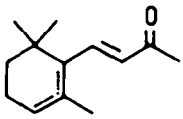
(*Received in Germany* 15 *July* 1988)

Abstract: A regio- and stereoselective synthesis of the tertiary chloride 7 is described, involving the Lewis acid catalysed addition of the allyl chloride 6 to isobutene as a key step. Acid catalysed cyclisation of 7 yields the damascenoid compounds 12-15.

As C_{13} compounds, the damascones 1, like the ionones 2 are not members of the terpene family. Their structural relationship to terpenes is obvious, however, and they have been suggested to be metabolites of carotenes.[1] Because of their occurence as natural fragrance and aroma constituents, they are of commercial interest, and several syntheses to damascones and damascenoid compounds have been developed, often based on intermediates of the technical vitamin A synthesis.[2-10]



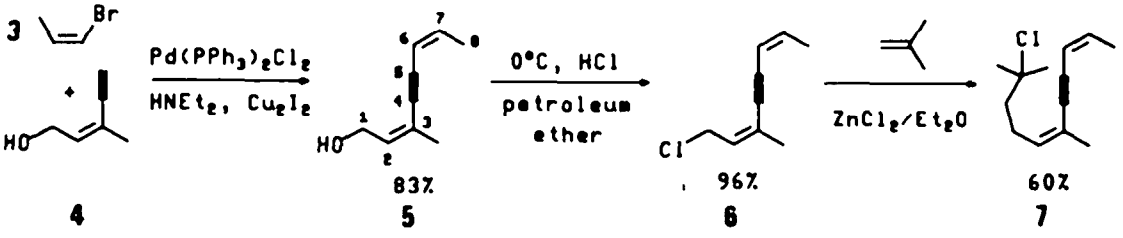
1



2

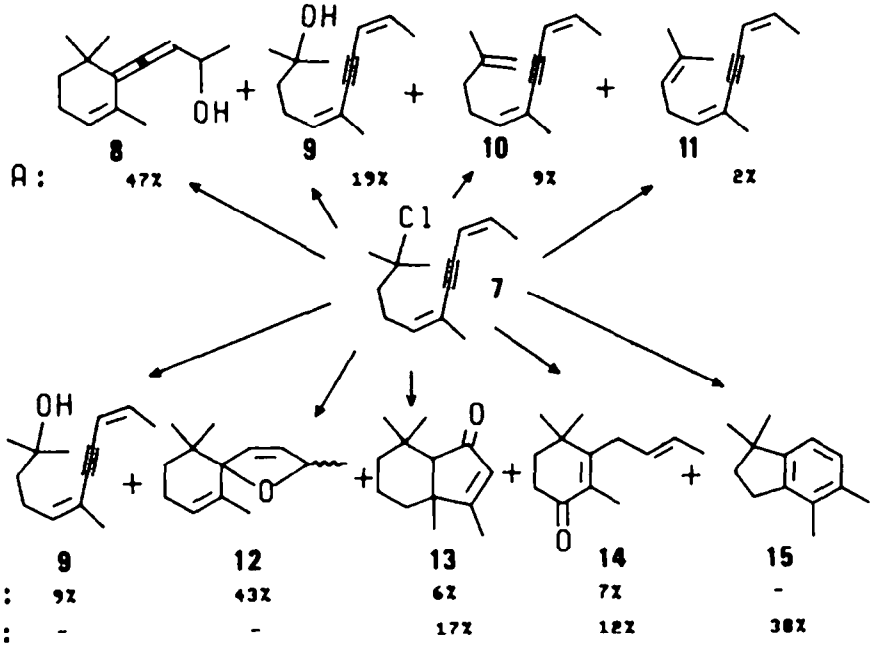
In this work, we report on the synthesis of the dienyne 7, a new precursor of damascenoid compounds. Its acid catalysed cyclisation is found to give mixtures of compounds, some of which are known as constituents of black tea aroma (13)[20], of Osmanthus absolute (14)[21], and of Virginia tabacco (14)[21] while others have been used as precursors for the synthesis of aroma compounds (8, 12).[18,19]

Results. Pd(II) catalysed coupling[22,23] of 3-methyl-pent-2(Z)-en-4-yn-1-ol (4) (trade name: 1'-pentol) with 1(Z)-bromopropene (3) gave 83% of 5 in a stereoselective reaction. Since the configuration of the 6,7-double bond is lost in the cyclised products, the use of stereochemically pure 3 is not necessary, and it has been shown that the same cyclisation products are obtained, when a mixture of 1-bromopropenes is used instead of the pure (Z)-isomer. Treatment of 5 with concentrated hydrochloric acid in petroleum ether yielded 96% of 6, which shows a higher S_N1 reactivity than tertiary alkyl chlorides and, therefore, gives the 1:1 product 7 with isobutene[24-27] in presence of the weak Lewis acid $ZnCl_2 \cdot Et_2O$.[28]



Attemps to cyclise 7 with BCl_3 or $SnCl_4$ at -78°C or with $ZnCl_2$ at 0°C yielded complex mixtures of products which have not been identified. Treatment of 7 with silver trifluoroacetate in hexane and successive workup with ethanolic KOH afforded the cyclic allene alcohol 8 along with the acyclic compounds 9-11. The predominant formation of cyclised compounds was observed when the tertiary chloride 7 was heated in aqueous formic acid. While the tertiary alcohol 9 was isolated with the cyclised compounds 12-14 under relatively mild conditions ($HCO_2H:H_2O$:THF =2:1:2), only cyclic compounds were observed (13-15), when 7 was heated in 90% aqueous formic acid under reflux.

Scheme 1

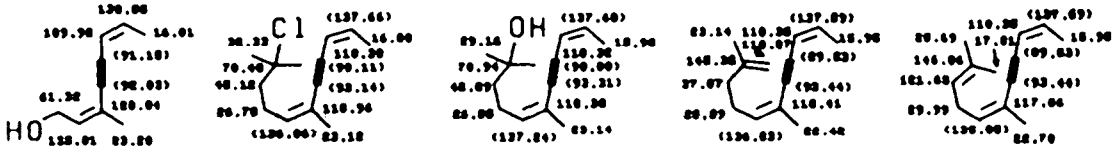


A: 1. $AgCF_3CO_2$/hexane, 2. EtO^-;

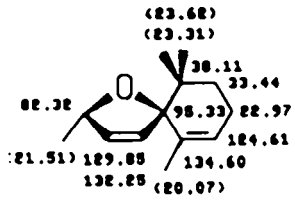
B: HCO_2H/H_2O/THF=2/1/2, 19h reflux;

C: HCO_2H/H_2O=9:1; 0.5h reflux;

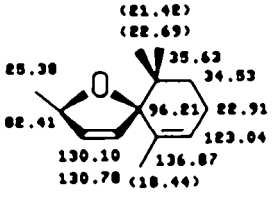
Structural Assignments. Compounds 7 and 9-11 show ^{13}C NMR spectra closely similar to that of their precursor 5, indicating that the configuration at the two double bonds had remained unchanged.



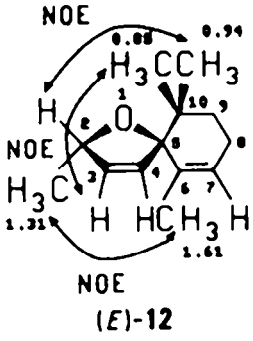
The ^{1}H NMR spectra of (Z,E)-12 are in accord with the spectrum reported for the mixture of the two diastereoisomers.[1] Though differences in the ^{13}C NMR spectra between the isomers can be found, the relative stereochemistry could not be assigned on this basis.



(E)-12



(Z)-12



(E)-12

Nuclear Overhauser effects between the allylic methyl protons (δ 1.61) and the methyl doublet at δ 1.31 as well as an NOE between 2-H and the methyl group at δ 0.94 suggested the stereochemical assignment of the (E)-isomer.

The cyclopentenone structure of 13 was derived from the strong infrared absorptions at 1689 and 1619 cm^{-1} and the UV absorption at λ_{max} = 223.0 (log ε = 4.03). Its ^{1}H NMR and mass spectroscopic data are in accord with literature reports.[8] The butenyl-cyclohexenone 14 has previously been detected as a constituent of Osmanthus absolute.[11] We have now corroborated the suggested structure by ^{1}H NMR spin decoupling experiments and a ^{13}C NMR spectrum. UV absorptions at 229, 267 and 276 nm and an AB system at δ 6.91 and 7.01 (J_{AB}=7.6 Hz, 2 H) in the ^{1}H NMR spectrum indicated 15 to be a compound with two adjacent aromatic protons. Since 15 as well as structural alternatives had been synthesised by cyclialkylation procedures,[12] an unequivocal assignment on the basis of ^{1}H NMR chemical shifts was possible.

Reaction Mechanism. The formation of compounds 9-15 is rationalised by Scheme 2. Ionisation of 7 yields the tertiary carbenium ion 16 from which compounds 9-11 are derived. Cyclisation of 16 affords the ambident methyleneallyl ⟷ allenylcarbinyl cation 17 which may be attacked by nucleophiles at two different positions.

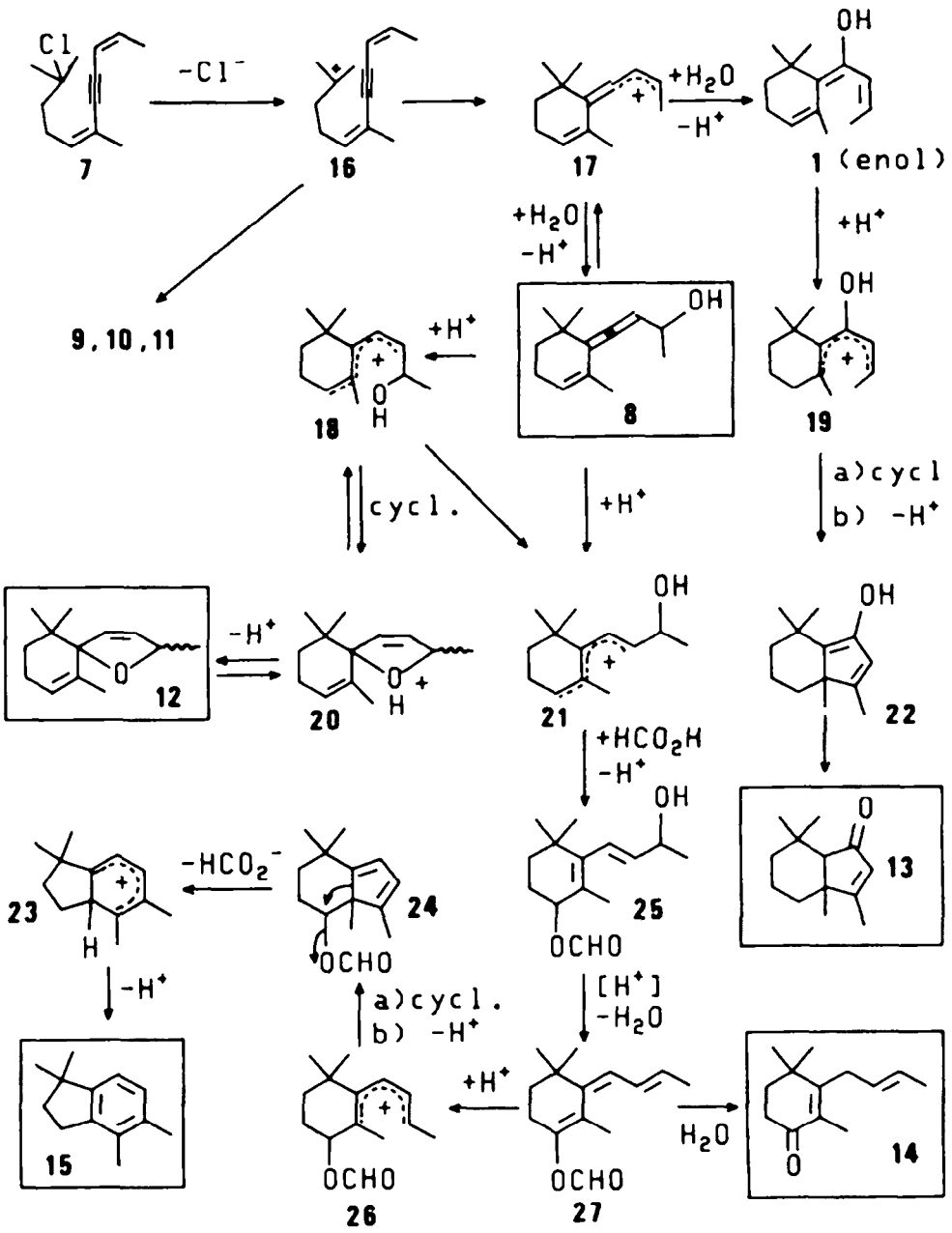
Compound 8, the only cyclic product formed in the silver trifluoroacetate initiated reaction, arises from attack of $CF_3CO_2^-$ at 17 and hydrolysis of the resulting ester. When the reaction is carried out in formic acid, 8 is not isolated; under these conditions, the central allenic position of 8 is protonated to yield the stereoisomeric pentadienyl cations 18 and 21, the former of which may cyclise with formation of the theaspirenes 12. In accord with this mechanism acid treatment of 8 has been reported to yield the theaspirenes 12.[13]

Compounds 12 are not observed when the cyclisation of 7 is carried out in 90% formic acid. It can be assumed, therefore, that under more acidic conditions the dihydrofuran ring of 12 is cleaved again, and the regenerated cation 18 undergoes stereomutation with formation of 21, which can also be formed from 8 directly. Cation 21 then combines with a nucleophile to give the allylic formate 25 (or the corresponding alcohol), which is converted into 27 by acid catalysed dehydration. The trienyl formate 27 may either be hydrolysed to give 14 or protonated to afford the pentadienyl cation 26 which undergoes electrocyclic ring closure and deprotonation.

The secondary formate 24, thus formed, is suggested to solvolyse with simultaneous 1,2-vinyl shift to give the benzenium ion 23, the precursor of 15.

Compound 8 as well as the products 12, 14, and 15 are thus explained via attack of a nucleophile at the sp^2 terminus of the allylic cation 17. The alternative nucleophilic attack at the sp carbon of 17 yields an enol of the damascone 1, which affords 13 in a Nazarov type cyclisation, as described previously.[1]

Scheme 2



Conclusion. The readily available chlorodienyne 7 represents a new precursor to damasconoid compounds, but conditions for the selective cyclisation have not yet been found. Since in presence of Brønsted acids, protonation of 8 to give 18 or 21 appears to be faster than the reionisation 8 → 17, the selective formation of 1 probably requires solvents of low acidity and high ionising power.

EXPERIMENTAL

General. IR: Shimadzu IR-435. - NMR: Varian XL 200; chemical shifts (δ) refer to internal TMS. - Mass Spectra: VG 70-250. - UV: Kontron Uvikon 860. - The preparative MPLC separations were carried out on 30 x 2.5 cm glass columns filled with Lichroprep Si 60, 15-25 μ (SiO_2 or RP 18) particles using a Gilson Model 302 pump, a Rheodyne 7125 injection valve, and a Latek RI 201 differential refractometer.

3-Methyl-2(Z),6(Z)-octadien-4-yn-1-ol (5). 3-Methyl-2(Z)-penten-4-yn-1-ol (4) (19.3 g, 200 mmol, FLUKA) and 1(Z)-bromopropene (22.5 g, 186 mmol, Janssen-Chemie) were dissolved in 300 mL of diethylamine (nitrogen atmosphere). A mixture of Cu_2I_2 (0.33 g, 0.87 mmol) and $Pd(PPh_3)_2Cl_2$ (0.59 g, 0.84 mmol) was added slowly with stirring (exothermic reaction!). A clear solution is formed from which a colourless salt precipitates after several minutes. After 2 h at ambient temperature, the mixture was poured onto 500 mL of ice/water. The layers were separated, and the aqueous layer was extracted with two 100 mL portions of ether. The combined organic layers were washed several times with 50 mL portions of 3% aqueous HCl until the aqueous layer had a pH < 7. After drying over Na_2SO_4 and evaporation of the solvent, distillation gave 5 (20.9 g, 83%), a colourless oil with bp. 48-49°C/0.1 mbar.
^{1}H NMR ($CDCl_3$): δ 1.89 (dd, J = 6.8 Hz, 1.7 Hz, 3 H, 8-H), 1.92 (dt, J = 1.5 Hz, 1.1 Hz, 3 H, 3-CH_3), 4.34 (dq, J = 6.8 Hz, 1.1 Hz, 2 H, 1-H), 5.62 (dq, J = 10.8 Hz, 1.7 Hz, 1 H, 6-H), 5.86 (tq, J = 6.8 Hz, 1.5 Hz, 1 H, 2-H), 6.01 (dq, J = 10.8 Hz, 6.8 Hz, 1 H, 7-H). - ^{13}C NMR: see "Structural Assignments". - IR neat: 3301, 3020, 2912, 2850, 2180, 1630, 1433, 1400, 1374, 1360, 1323, 1085, 1036, 997, 787, 762, 719 cm^{-1}.

1-Chloro-3-methyl-2(Z),6(Z)-octadien-4-yne (6). Concentrated aqueous HCl (37%, 14.2 mL, 171 mmol) was added dropwise to a well stirred solution of 5 (10.5 g, 77.1 mmol) in 62 mL of petroleum ether (bp. 40-60°C) at 0°C. The mixture was stirred at 0°C for 17 h, and the organic layer was dried over Na_2SO_4. After evaporation of the solvent, the residue was distilled to give 6 (11.4 g, 96%), a colourless oil with bp. 30-31°C/4 mbar.
^{1}H NMR ($CDCl_3$): δ 1.92 (dd, J = 6.9 Hz, 1.7 Hz, 3 H, 8-H), 1.95 (dt, J = 1.5 Hz, 0.8 Hz, 3 H, 3-CH_3), 4.29 (dq, J = 7.8 Hz, 0.8 Hz, 2 H, 1-H), 5.66 (dq, J = 10.7 Hz, 1.7 Hz, 1 H, 6-H), 5.83 (tq, J = 7.8 Hz, 1.5 Hz, 1 H, 2-H), 6.05 (dq, J = 10.7 Hz, 6.9 Hz, 1 H, 7-H). - ^{13}C NMR ($CDCl_3$): δ 16.11 (q, C-8), 23.18 (q, 3-CH_3), 42.57 (t, C-1), 91.15, 92.64 (2 s, C-4,5), 109.83 (d, C-6), 123.88 (s, C-3), 130.77 (d, C-2), 139.26 (d, C-7). - IR (neat): 3023, 2940, 2913, 2950, 2180, 1666, 1626, 1435, 1400, 1375, 1365, 1346, 1257, 1235, 1217, 1155, 1032, 1000, 920, 832, 720 cm^{-1}.

10-Chloro-6,10-dimethyl-2(Z),6(Z)-undecadien-4-yne (7). Isobutene (17.8 g, 317 mmol) and a solution of $ZnCl_2$ (5.18 g) in ether (6.2 mL) were dissolved in CH_2Cl_2 (133 mL) which was precooled at -78°C.[**] A solution of 6 (7.73 g, 50.0 mmol) in CH_2Cl_2 (60mL) was added dropwise within 2 h. The mixture was kept at -78°C for 16 h and was then washed with 100 mL of 25% aqueous NH_4Cl solution. The organic layer was dried over $CaCl_2$ and the solvent was evaporated. Distillation of the residue yielded 7 (6.34 g, 60%), a slightly yellow oil with bp. 50-60°C (bath)/0.1 mbar.
^{1}H NMR ($CDCl_3$): δ 1.59 (s, 6 H, 11-H, 10-CH_3), 1.80 - 2.02 (m, 8 H, 1,9-H, 6-CH_3), 2.40 - 2.52 (m, 2 H, 8-H), 5.60 - 5.70 (m, 2 H, 3,7-H), 5.98 (dq, J = 10.7 Hz, 6.8 Hz, 1 H, 2-H). - ^{13}C NMR: see "Structural Assignments". - IR (neat): 3020, 2970, 2920, 2180, 1724, 1670, 1448, 1400, 1385, 1370, 1215, 1190, 1160, 1114, 1077, 1034, 820, 719 cm^{-1}.

Treatment of 7 with Silver Trifluoroacetate. A solution of 7 (2.11 g, 10.0 mmol) in 300 mL of dry hexane was cooled at -14°C and protected from light (aluminium foil). Approximately 20 portions of $AgCF_3CO_2$ (total: 2.21 g, 10.0 mmol) were added to the well stirred solution within 2 h. The cooling bath was removed, and stirring was continued for 17 h. The suspension was filtered, the AgCl was washed with 20 mL of hexane, and the solvent was evaporated to give 3.06 g of a yellow oil, which was added dropwise to a well-stirred solution of KOH (5.0 g, 89 mmol) in 70 mL of ethanol. After 1 h, 150 mL of water was added, and the products were extracted with two 75 mL portions of pentane. The organic layers were dried over Na_2SO_4, and the solvent was evaporated to afford 1.75 g of a yellow oil, which was separated by MPLC (RP 18, CH_3OH : H_2O = 10 : 1). We obtained 904 mg (47%) of 8, 365 mg (19%) of 9, and 194 mg (11%) of a 4:1 mixture of 10 and 11.

6,7-Dehydro-α-ionol [4-(2',6',6'-Trimethyl-2'-cyclohexen-1'-ylidene)-3-buten-2-ol] (8, 1:1 - mixture of diastereoisomers): Bp. 35-40°C (bath)/0.1 mbar (lit.[**] ca 44-46°C/0.01 Torr). -
^{1}H NMR ($CDCl_3$): δ 1.06, 1.07, 1.07 (3 s, 6 H, 6'-CH_3), 1.31 (d, J = 6.4 Hz, 3 H, 1-H), 1.49 (t,

J = 6.3 Hz, 2 H, 5'-H), 1.62 (br.s, 1 H, OH), 1.72 (mc, 3 H, 2'-CH_3), 2.08 - 2.19 (m, 2 H, 4'-H), 4.32 - 4.39 (m, 1 H, 2-H), 5.53 - 5.63 (m, 2 H, 3,3'-H). - ^{13}C NMR ($CDCl_3$): δ 21.23 (q, 2'-CH_3), 22.93 (t, C-4'), 23.47, 23.50 (2 q, C-1), 28.05, 28.56 (2q, 6'-CH_3), 32.48 (s, C-6'), 35.95 (t, C-5'), 66.40, 66.46 (2 d, C-2), 100.75, 100.78 (2 d, C-3), 116.89, 117.05 (2 s, C-1'), 124.75, 124.81 (2 d, C-3'), 127.86, 127.92 (2 s, C-2'), 199.20, 199.32 (2 s, C-4). IR (Film): 3325, 3014, 2962, 2917, 2869, 2845, 2720, 2655, 1940, 1470, 1450, 1434, 1379, 1361, 1334, 1313, 1285, 1221, 1201, 1171, 1123, 1111, 1075, 1056, 1037, 1019, 996, 978, 931, 857, 836, 820, 802, 787 cm^{-1}. - Mass spectrum (70 eV): m/z = 192 (35%, M^+), 148 (62), 133 (100), 119 (21), 105 (43), 92 (69), 91 (50), 77 (22), 65 (13), 45 (46). - Anal. Calcd for $C_{12}H_{20}O$(192.3): C, 81.20; H, 10.48. Found: C, 81.21; H, 10.47.

2,6-Dimethyl-5(Z),9(Z)-undecadien-7-yn-2-ol (9). - ^{1}H NMR ($CDCl_3$): δ 1.23 (s, 6 H, 1-H, 2-CH_3), 1.51 - 1.60 (m, 3 H, 3-H, OH), 1.85 - 1.92 (m, 6 H, 11-H, 6-CH_3), 2.27 - 2.43 (m, 2 H, 4-H), 5.65 (dq, J = 10.7 Hz, 1.6 Hz, 1 H, 9-H), 5.68 (tq, J = 7.5 Hz, 1.6 Hz, 1 H, 5-H), 5.97 (dq, J = 10.7 Hz, 6.8 Hz, 1 H, 10-H). - ^{13}C NMR: see "Structural Assignments". - IR (neat): 3346, 3018, 2961, 2913, 2849, 2179, 1661, 1654, 1635, 1627, 1611, 1466, 1460, 1448, 1433, 1400, 1371, 1364, 1342, 1292, 1266, 1196, 1149, 1133, 1077, 1032, 953, 902, 837, 767, 717 cm^{-1}.

Mixture (4:1) of 2,6-Dimethyl-1,5(Z),9(Z)-undecatrien-7-yne (10) and 2,6-Dimethyl-2,5(Z),9(Z)-undecatrien-7-yne (11). - ^{1}H NMR ($CDCl_3$): δ 1.66, 1.70 (2 mc, 1-H, 2-CH, of 11), 1.74 (mc, 2-CH_3 of 10), 1.86 - 1.94 (m, 6 H, 11-H, 6-CH_3), 2.10 (br.t, J = 7.7 Hz, 3-H of 10), 2.43 (br.q, J = 7.5 Hz, 4-H of 10), 2.97 (br.t, J = 7.7 Hz, 2 H, 4-H of 11), 4.71 (mc, 2 H, 1-H of 10), 5.09 - 5.21 (m, 1 H, 3-H of 11), 5.56 - 5.69 (m, 2 H, 5,9-H), 5.97 (dq, J = 10.8 Hz, 6.8 Hz, 1 H, 10-H).

Hydrolyses of 7 in Formic Acid/Water/THF. Compound 7 (2.32 g, 11 mmol) was added to a well-stirred homogeneous solution of 41.4 g of formic acid in 20 mL of water and 40 mL of tetrahydrofuran. The mixture was then heated under reflux for 19 h, cooled, and poured onto crushed ice. The cold mixture was washed with aqueous $NaHCO_3$ solution, extracted with CH_2Cl_2, dried (Na_2SO_4), concentrated and distilled (70-75°C (bath)/0.20 mbar) to give 1.85 g of a light yellow oil, which was further purified by MPLC (RP-18, methanol/water = 19/1) to afford 180 mg (9%) of 9, 150 mg (7%) of 14, 120 mg (6%) of 13, 410 mg (19%) of (Z)-12, and 500 mg (24%) of (E)-12.

(Z)-2,6,10,10-Tetramethyl-1-oxaspiro[4.5]deca-3,6-diene [(Z)-Theaspirane, (Z)-12]. - ^{1}H NMR ($CDCl_3$): δ 0.86, 0.95 (2 s, 6 H, 10-CH_3), 1.29 (d, J = 6.5 Hz, 3 H, 2-CH_3), 1.46 - 1.53 (m, 2 H, 9-H), 1.60 (br.s, 3 H, 6-CH_3), 2.01 (mc, 2 H, 8-H), 4.96 (br.q, J = 6.5 Hz, 1 H, 2-H), 5.40 (mc, 1 H, 7-H), 5.59 (dd, J = 6.1 Hz, 2.3 Hz, 1 H, 4-H), 5.77 (dd, J = 6.1 Hz, 1.3 Hz, 1 H, 3-H). - ^{13}C NMR: see "Structural Assignments". - IR (neat): 2963, 2917, 2839, 1453, 1089, 1077, 1054, 999 cm^{-1}. - Mass spectrum (70 eV): m/z = 192 (0.25%, M^+), 136 (100), 121 (47), 93 (24), 43 (13). - Anal. Calcd for $C_{12}H_{20}O$ (192.3): C, 81.20; H, 10.48. Found: C, 81.14; H, 10.45.

(E)-2,6,10,10-Tetramethyl-1-oxaspiro[4.5]deca-3,6-diene [(E)-Theaspirane, (E)-12]. - ^{1}H NMR ($CDCl_3$): δ 0.85, 0.94 (2 s, 6 H, 10-CH_3), 1.31 (d, J = 6.4 Hz, 3 H, 2-CH_3), 1.25 - 1.75 (m, 2 H, 9-H), 1.61 (br.s, 3 H, 6-CH_3), 2.03 (mc, 2 H, 8-H), 4.87 (br.q, J = 6.4 Hz, 1 H, 2-H), 5.54 (mc, 1 H, 7-H), 5.59 (dd, J = 6.2 Hz, 2.5 Hz, 1 H, 4-H), 5.84 (dd, J = 6.2 Hz, 1.3 Hz, 1 H, 3-H), - ^{13}C NMR : see "Structural Assignments". - IR (neat): 2963, 2919, 2841, 1453, 1349, 1088, 1077, 1055, 978 cm^{-1}. - Mass spectrum (70 eV): m/z = 192 (0.25%, M^+), 136 (100), 121 (50), 93 (23), 43 (14). - Anal. Calcd for $C_{12}H_{20}O$ (192.3): C, 81.20; H, 10.48. Found: C, 81.11; H, 10.53.

1,5,5,9-Tetramethyl-bicyclo[4.3.0]non-8-en-7-one (13)[9]. - ^{1}H NMR ($CDCl_3$): δ = 0.90 (br.s, 3 H, 5-CH_3), 1.18 (s, 3 H, 5-CH_3), 1.20 (q, J = 0.4 Hz, 3 H, 1-CH_3), 1.31 - 1.72 (m, 6 H, 2,3,4-H), 1.84 (mc, 1 H, 6-H), 2.00 (dq, J = 1.3 Hz, 0.4 Hz, 3 H, 9-CH_3), 5.78 (q, J = 1.3 Hz, 1 H, 8-H). - ^{13}C NMR ($CDCl_3$): δ = 14.32 (q, 9-CH_3), 17.36 (t, C-3), 24.59, 28.02 (2 q, 5-CH_3), 30.04 (t, C-4), 32.82 (q, 1-CH_3), 33.84 (s, C-5), 36.06 (t, C-2), 46.11 (s, C-1), 62.76 (d, C-6), 129.60 (d, C-8), 183.99 (s, C-9), 210.01 (s, C-7). - IR (neat): 3055, 2934, 2864, 1689, 1619, 1463, 1433, 1384, 1374, 1363, 1314, 1260, 1221, 1199, 1118, 1070, 1021, 1011, 971, 954, 927, 869, 837, 806 cm^{-1}. - UV (pentane): λ_{max} (log ε) = 223.0 (4.08). - Mass spectrum (70 eV): m/z = 192 (24%, M^+), 177 (41), 164 (4), 149 (5), 136 (5), 123 (52), 110 (100), 95 (9), 91 (10), 82 (13), 55 (15), 41 (27). - Anal. Calcd for $C_{12}H_{20}O$ (192.3): C, 81.20; H, 10.48. Found: C, 80.82; H, 10.53.

3-(2(E)-Buten-1-yl)-2,4,4-trimethyl-2-cyclohexen-1-one (14) (Megastigma-5,8(E)-dien-4-one)[11]. ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 6 H, 4-CH_3), 1.67 (br.d, J = 5.7 Hz, 3 H, 4'-H), 1.76 (br.s, 3 H, 2-CH_3), 1.82 (mc, 2 H, 5-H), 2.48 (mc, 2 H, 6-H), 2.92 - 2.99 (m, 2 H, 1'-H), 5.33, 5.48 (AB part of an ABX,Y_2-system with J_{ab} = 15.3 Hz, J_{ay} = 5.5 Hz, J_{ax} = 1.0 Hz, J_{bx} = 5.7 Hz, J_{by} = 0.9 Hz, 2 H, 2', 3'-H). - ^{13}C NMR ($CDCl_3$): δ = 11.43 (q, C-4'), 17.93 (q, 2-CH_3), 26.83 (q, 4-CH_3), 33.51 (t, C-5), 34.30 (t, C-1'), 36.37 (s, C-4), 37.36 (t, C-6), 126.66, 127.07 (2 d, C-2', 3'), 131.60 (s, C-2), 162.56 (s, C-3), 199.10 (s, C-1). - IR (neat): 3455, 3306, 3016, 2953, 2918, 2858, 1663, 1609, 1468, 1448, 1419, 1375, 1363, 1351, 1334, 1303, 1279, 1264, 1228, 1196, 1177, 1172, 1136, 1082, 1023, 1006, 964, 939, 878, 684 cm^{-1}. - UV (pentane): λ_{max} (log ε) = 239.5 (4.23). - Mass spectrum (70 eV): m/z = 192 (53%, M^+), 177 (19), 163 (12), 137 (100), 121 (32), 109 (41), 107 (22), 95 (20), 93 (20), 91 (18), 81 (17), 79 (20), 77 (20), 67 (18), 55

(37), 41 (43). - Anal. Calcd for $C_{13}H_{20}O$ (192.3): C, 81.20; H, 10.48. Found: C, 80.76; H, 10.44.

Solvolysis of 7 in 90% Formic Acid/Water. Compound 7 (1.05 g, 5.00 mmol) was added dropwise to a refluxing solution of 90% formic acid/water (50 mL) to give a dark red mixture. After 0.5 h, the heating was removed, and 100 mL of water was added. The products were extracted with three 20 mL portions of petroleum ether. The extracts were dried over Na_2SO_4, and the solvent was evaporated in vacuo to give 0.760 g of a yellow oil, which was passed over silica (petroleum ether : ether = 98 : 2) to give 330 mg (38%) of 15 with bp. 50-55°C (bath)/0.1 mbar. When the silica column was washed with ether, 420 mg of a mixture was obtained which was separated by MPLC (silica gel, hexane : ether = 80 : 20) to give 160 mg (17%) of 13 and 150 mg of slightly contaminated 14. MPLC of this fraction (RP 18, CH_3OH : H_2O = 85 : 15) gave 112 mg (12%) of pure 14.

1,1,4,5-Tetramethylindane (15)[22]. - ^1H NMR ($CDCl_3$): δ = 1.24 (s, 6 H, 1-CH_3), 1.91 (t, J = 7.2 Hz, 2 H, 2-H), 2.17 (d, J = 0.4 Hz, 3 H, aryl-CH_3), 2.25 (d, J = 0.3 Hz, 3 H, aryl-CH_3), 2.83 (t, J = 7.2 Hz, 2 H, 3-H), 6.91, 7.01 (AB-system, J = 7.6 Hz, 2 H, 6,7-H). All δ values in the previously described spectrum[22] (CCl_4, 60 MHz) were approximately 0.07 ppm smaller. - ^{13}C NMR ($CDCl_3$): δ = 15.78, 19.59 (2 q, 4,5-CH_3), 28.88 (q, 1-CH_3), 29.00 (t, C-3), 41.19 (t, C-2), 44.05 (s, C-1), 119.01 (d, C-7), 128.14 (d, C-6), 132.28 (s, C-5), 134.23 (s, C-4), 141.76 (s, C-9), 150.05 (s, C-8). - IR (neat): 3001, 2950, 2856, 1600, 1476, 1453, 1380, 1360, 1313, 1120, 1100, 998, 811, 785, 762 cm^{-1}. - UV (pentane): λ_{max} (log ε) = 229.0 (2.84), 267.0 (2.74). - Mass spectrum (70 eV): m/z = 174 (19%, M^+), 159 (100), 144 (7), 129 (7), 128 (8), 119 (4), 115 (5), 91 (4), 77 (3). - Anal. Calcd for $C_{13}H_{18}$ (174.3): C, 89.59; H, 10.41. Found: C, 89.33; H, 10.59.

Acknowledgement. We thank Roswitha Lammers for experimental assistance and Rainer Koschinsky for the NMR spectroscopic structural elucidations. A.-R. thanks the A.v. Humboldt Stiftung for a fellowship.

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