133. New Carbonyl Compounds in the High-Boiling Fraction of Lavender Oil

3rd Communication[1])

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Summary

The occurrence of a series of new constituents which can be considered as *Diels-Alder* adducts of methyl vinyl ketone and ocimene (→**1–4**), myrcene (→**9,10**) or β-farnesene (→**11,12**), respectively, was reported. Furthermore, the structures of four isomeric cyclohexene derivatives could be established as adducts **21–24** of (*E,Z*)- and (*E,E*)-1,3,5-undecatriene and methyl vinyl ketone. Another series of constituents having the norbornane skeleton represents adducts **25–32** and **33–40** of methyl cyclopentadiene and 1-octen-3-one or methyl vinyl ketone, respectively. In accordance with *Alder*'s *endo*-rule the *endo*-isomers are preponderant in the natural as well as in the synthetic mixtures. Most of these constituents could also be identified in a lavender absolute as well as in a freshly prepared hexane extract of lavender flowers (*Lavandula officinalis* CHAIX).

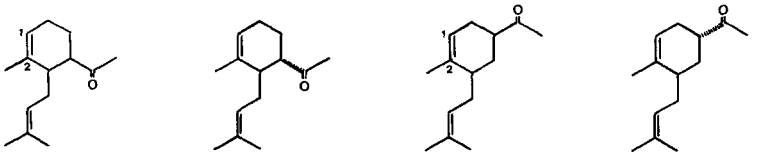
Introduction. – In addition to the new lavender constituents with santalane, cadinane, caryophyllane, cedrane and other skeletons described in [1] and [2] we now discuss a further series of carbonyl compounds **1–4** and **9–40** identified in the same natural product. As will be shown, these new natural products can be considered as *Diels-Alder* adducts of dienes and dienophiles most of them also identified as main or minor constituents in lavender oil. The isolation of the corresponding high-boiling carbonyl fraction is described in [1].

A. Ocimene as Diene. – The separation of the high-boiling carbonyl fraction by column chromatography (hexane/Et_2O 40:1) led to the elution of fractions containing an unsaturated methyl ketone of mol. wt. 206. The spectral data of the purified product were identical with those of the cyclohexene derivative **1**, which was recently discussed by *Giraudi et al.* [3] as a so-called nor-sesquiterpene ketone of lavender oil. Already in 1973, *Mookherjee & Trenkle* [4] isolated this interesting compound in connection with the investigation of lavandin oil as so-called peak 21-A in small amount and published the corresponding IR and mass spectra. Due to the lack of material,

[1]) Partially presented at the IXth International Congress of Essential Oils, Singapore, March 13–17, 1983.

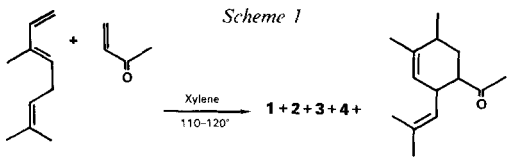
NMR analysis of this peak could not be performed, and therefore, a structural assignment was not possible at that time.

From the fractions containing **1**, a related compound of the same mol. wt. and similar spectral data could be isolated which proved to be the isomeric 2,3,5-substituted cyclohexene derivative **3** with *cis*-orientation of the acyl and alkenyl substituents. Furthermore, the investigation of the same fractions with the aid of GLC/MS measurements also allowed the identification of the corresponding *trans*-isomers **2** and **4** as trace constituents[2][3]).



1 (0.7%) **2** (trace) **3** (0.3%) **4** (trace)

Scheme 1



trans-Ocimene **5–8**

The structures of **1–4** were established by spectral comparison with synthetic specimens obtained by *Diels-Alder* reaction of ocimene and methyl vinyl ketone *(Scheme 1)*. For this reason, ocimene 80 (contains 75–80% *trans*-ocimene) was treated with an excess of methyl vinyl ketone in xylene at 110–120 °C for 72 hours to give in 50% yield a mixture **1–8** exhibiting a green herbaceous odor with woody aspects. All isomers were isolated in purities > 90% by column chromatography and subsequent preparative GLC. Their structures were elucidated by careful analysis of the corresponding 400-MHz-^{1}H-NMR spectra, including corresponding decoupling experiments.

Equilibration of pure **1** with KOMe in MeOH led to a mixture of **1** and **2** in the ratio of 1:4. The analogous experiment with pure **3** yielded a mixture of **3** and **4** in the ratio of 2:3.

The high amount of the tetrasubstituted cyclohexene derivatives **5–8** shows that the *Diels-Alder* reaction with methyl vinyl ketone was preceded to over 80% by isomerization of ocimene to allo-ocimene even under the relatively mild reaction conditions used. To suppress this side reaction as far as possible, the same experiment was repeated at 70 °C. After 200 hours, a conversion of 10% was detectable, the mixture

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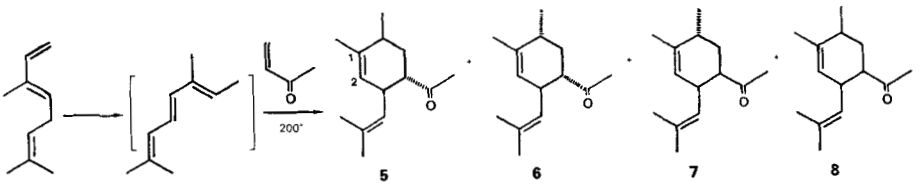
[2]) The percentages in parentheses given beneath the corresponding formula are approximate values based on the total carbonyl fraction of lavender oil.

[3]) To facilitate a direct comparison of the spectral data, the same arbitrary numbering was used for **1–4**, for **5–8** *(Scheme 2)*, for **21–24** *(Scheme 6)*, and for **25–40** (*Scheme 7* and *8*).

Scheme 2

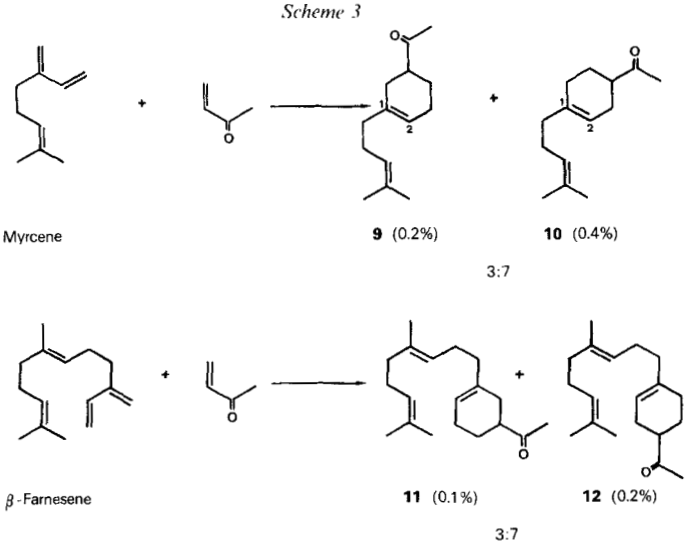


showing now a threefold increase of **1** and **3**. If the reaction was performed in an autoclave, however, ocimene completely isomerized to allo-ocimene, and only the four tetrasubstituted isomers **5–8** were formed in good yield (80%) in a ratio of 1:3:10:3 *(Scheme 2)*. The direct reaction of allo-ocimene and methyl vinyl ketone under the same conditions gave a mixture of **5–8** in nearly the same ratio.

The occurrence of the discussed 2,3,4- as well as the 2,3,5-substituted cyclohexene derivatives gives a good hint that **1–4** can really be considered as *Diels-Alder* adducts of *trans*-ocimene present to 3.1% in lavender oil and methyl vinyl ketone. The following series of related constituents will support this hypothesis.

B. Myrcene and β-Farnesene as Dienes. – GLC/MS measurements of fractions containing the discussed ocimene adducts **1–4** allowed to localize two further cyclic methyl ketones of the same mol. wt. and similar fragmentation pattern. The spectra interpretation of the isolated products allowed to presume the presence of the myrcene/methyl vinyl ketone adducts **9** and **10**[4]) *(Scheme 3)*. These structures were confirmed by corresponding *Diels-Alder* synthesis (autoclave, 200°C, without catalyst) which gave **9** and **10** in a similar ratio as found in lavender oil. The synthetic mixture of **9** and **10**, which

Scheme 3

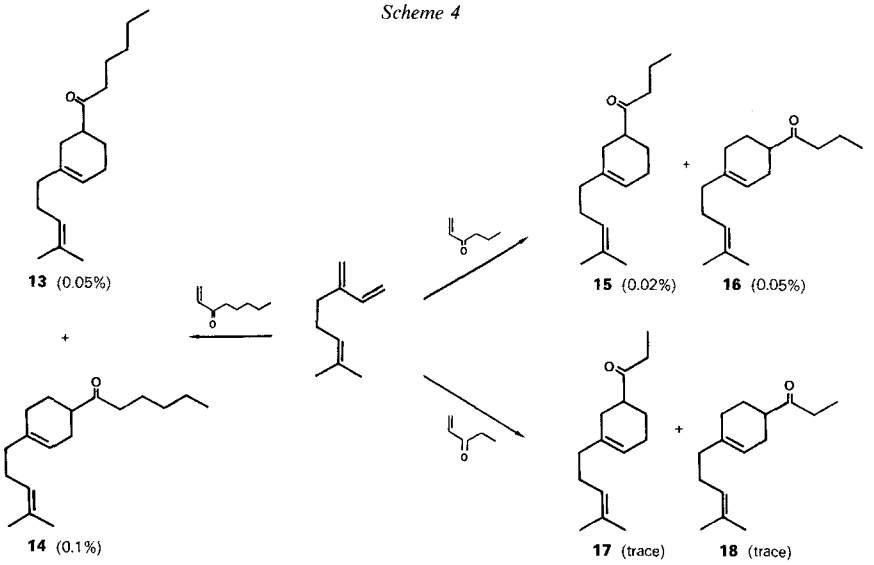


[4]) To facilitate a direct comparison of the spectral data, the same arbitrary numbering was used for all myrcene and β-farnesene adducts **9–20**.

is known from literature [5], exhibits a green herbaceous odor with woody aspects. The natural specimens of **9** and **10** as well as the already discussed ocimene adducts **1** and **3** have very low optical rotation values which may be due to impurities.

From fractions of the same polarity range (also hexane/Et_2O 40:1), two other new isomeric constituents showing much longer retention times and mol. wt. of 274 could be isolated. Apart from different integration values for the typical NMR signals and the different mol. wt., the spectral features were reminiscent of those of **9** and **10**, and therefore, the *Diels-Alder* adducts **11** and **12** of β-farnesene and methyl vinyl ketone could be presumed. The structural proof for these two positional isomers representing 0.1 and 0.2% of the total carbonyl fraction, respectively, was given again by synthesis as shown in *Scheme 3*. Myrcene and β-farnesene have already been known for a long time as constituents of lavender oil (0.5 and 1.2%, respectively).

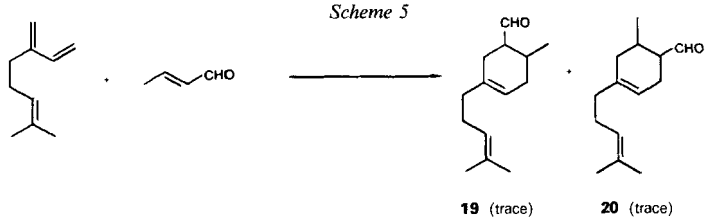
Scheme 4



The hypothesis in mind that dienes and dienophiles occurring in lavender oil might be accompanied by corresponding *Diels-Alder* adducts facilitated the elucidation of further constituents summarized in *Scheme 4*. Two isomers showing key fragments at *m/z* 99 were eluted as front fractions with hexane/Et_2O 40:1 and could be isolated in small amounts. They proved to be the *Diels-Alder* adducts **13** (0.05%) and **14** (0.1%) of myrcene and 1-octen-3-one. Furthermore, GLC/MS measurements of the same fractions followed by coinjections with synthetic specimens also allowed the identification of the corresponding adducts with 1-hexen-3-one, **15** (0.022%) and **16** (0.05%), and with 1-penten-3-one, **17** (trace) and **18** (trace), respectively. The free dienophiles 1-octen-3-one, 1-hexen-3-one and 1-penten-3-one could also be identified as minor constituents in the more volatile part of the carbonyl fraction.

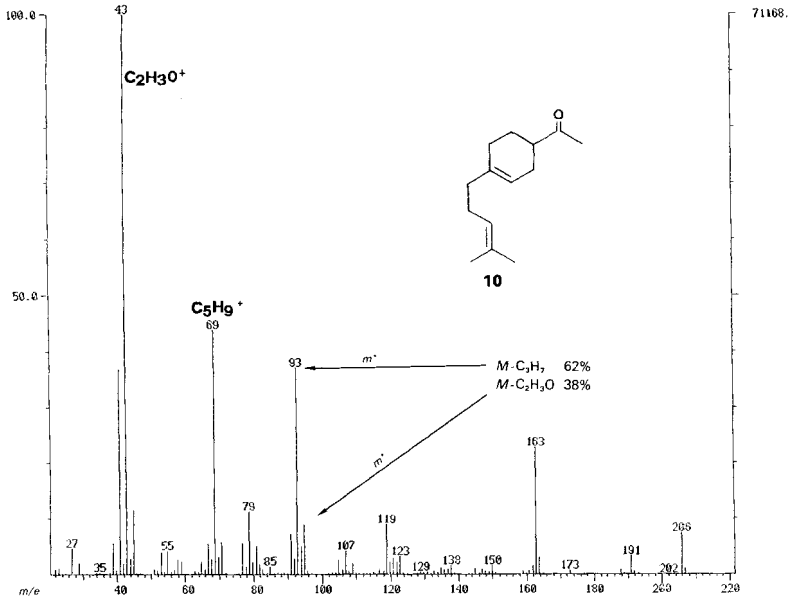
Finally, the same GLC/MS measurements allowed to localize two isomeric compounds with mol. wt. of 206 and key fragments at *m/z* 69 *(Scheme 5)*. Apart from the absence of a typical acylium ion, the general fragmentation pattern was similar to those

Scheme 5



19 (trace) **20** (trace)

2:3



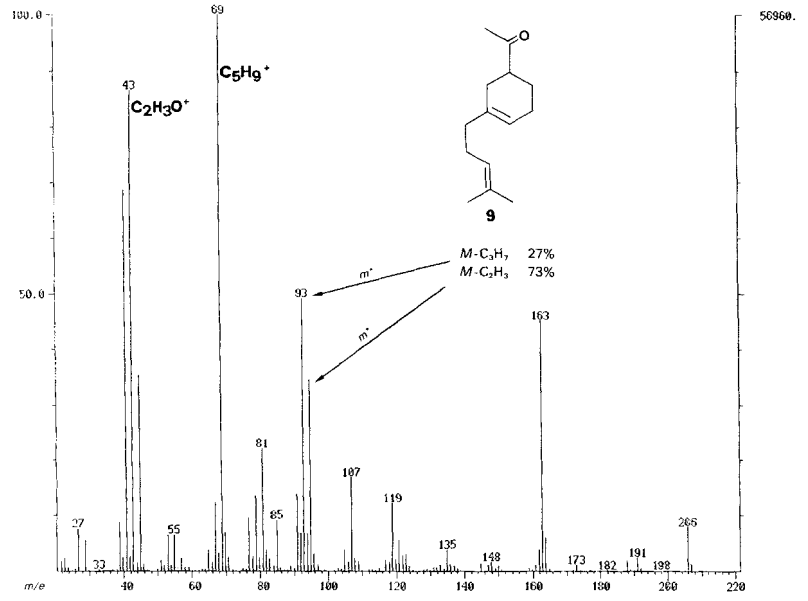


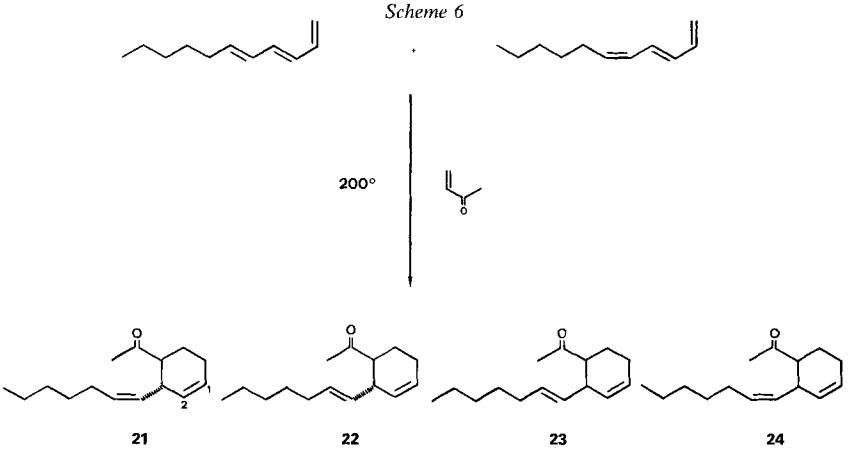
Figure. *Mass spectra (70 eV) of* **9** *and* **10**

of the *Diels-Alder* adducts discussed above. Therefore, the structure of a cyclic aldehyde derived from myrcene or ocimene was very likely. Corresponding synthetic work allowed to establish the structures **19** and **20** for these trace constituents in question. The mixture **19/20** exhibits a similar odor as the commercially available *Diels-Alder* adducts of myrcene and acrolein or methacrolein, respectively.

Vicarious for the general mass fragmentation of the adducts derived from myrcene and ocimene, those of **9** and **10** will now be discussed in more detail *(Figure)*. Not knowing the structures for these components, the general fragmentation pattern would rather suggest structures of nor-sesquiterpene derivatives than of *Diels-Alder* products. In fact, for components of this latter type, a primary *retro-Diels-Alder* reaction in the mass spectrometer would be expected leading to fragment ions *m/z* 136 and 70. However, in the spectra of **9** and **10**, these ions are only of very low intensity, and therefore, the fragmentation behavior was investigated in more detail. The peak *m/z* 163 is composed of two fragments which was demonstrated by high resolution mass analysis. Interestingly enough, the $M^+ - C_2H_3O$ fragment plays a major role in the spectrum of the 1,5-substituted isomer **9**, whereas the $M^+ - C_3H_7$ fragment is clearly dominant in the 1,4-substituted isomer **10**. The further fragmentation of *m/z* 163 was studied by linked-scan measurements demonstrating metastable transitions from *m/z* 163 to 93 and 95 among others. The loss of a neutral particle with the mass 70 could indicate a *retro-Diels-Alder* reaction involving the elimination of methyl vinyl ketone from the O-containing species *m/z* 163. Correspondingly, the ion *m/z* 95 could be the product of isoprene elimination from the O-free species *m/z* 163.

C. (*E,Z*)- and (*E,E*)-1,3,5-Undecatriene as Dienes. – In a fraction containing the discussed 2,3,4-substituted *Diels-Alder* adduct **1** of *trans*-ocimene and methyl vinyl ketone as major constituent, four isomeric trace constituents of mol. wt. 220 showing key fragments at *m/z* 43 and 57, respectively, were enriched to 15%. They are present together to about 0.07% in the total carbonyl fraction in a ratio of 1:1:3:10. The dominating isomer showing the longest retention time could be isolated in a small quantity (2 mg), and the spectral data were compatible with the structure of the cyclohexene derivative **24** *(Scheme 6)*. This structure appeared reasonable since we also

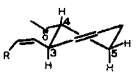
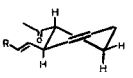
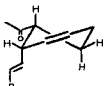
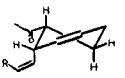
Scheme 6



21 **22** **23** **24**

(2:2:3:8)

Table 1. *Some ^{1}H-NMR Characteristics of* **21–24**[3])

	 **21**	 **22**	 **23**	 **24**
δ of H_{ax}–C(4) [ppm]	2.44	2.47	2.67	2.71
$J_{4ax,5ax}$ [Hz]	12	12	12	12
$J_{4ax,5eq}$ [Hz]	4	4	4	4
$J_{4ax,3quasi\text{-}ax}$ [Hz]	10	10	–	–
$J_{4ax,3quasi\text{-}ax}$ [Hz]	–	–	6	6
IR absorption at 970 cm^{-1}	no	yes	yes	no

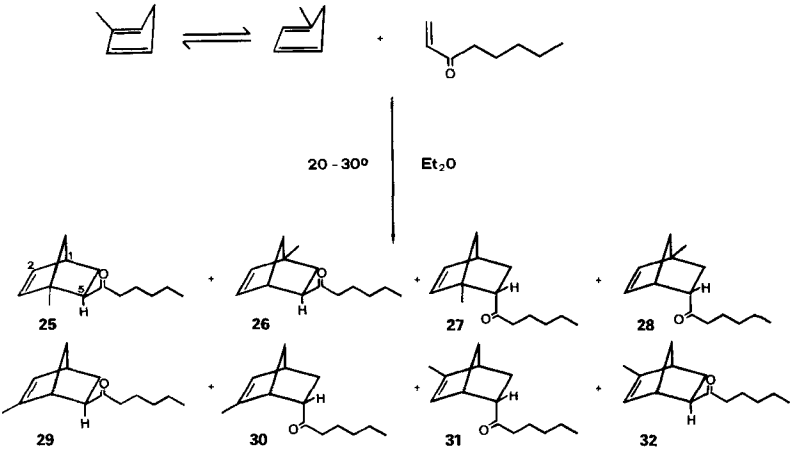
could identify the (*E,Z*)- and (*E,E*)-1,3,5-undecatriene as new lavender constituents of about 0.003%.

In fact, the *Diels-Alder* reaction of a 3:2 mixture of (*E,Z*)- and (*E,E*)-1,3,5-undecatriene with methyl vinyl ketone yielded a mixture of 4 isomers in a ratio of 2:2:3:8 which, after isolation and spectral interpretation, proved to be the cyclohexene derivatives **21–24** found in lavender oil. The product mixture of **21–24** is characterized by a green, fatty odor.

The *trans*- and *cis*-substitution at C(3),C(4)[3]), respectively, the position and geometry of the double bond in the side chain, and the position of the ring double bond in **21–24** can clearly be established by interpretation of their 400-MHz-^{1}H-NMR spectra (*Table 1*). Furthermore, the IR spectra independently confirm the geometry of the double bond in the side chain. As demonstrated in *Table 1*, the analysis of the coupling pattern of H_{ax}–C(4) with its neighboring protons was of central importance for the structural elucidation of **21–24**.

D. Methylcyclopentadiene as Diene. – Besides the discussed *Diels-Alder* adducts of myrcene and ocimene (**13–18**) and different new sesquiterpene derivatives (see [1] [2]), the investigation of the front fractions eluted with hexane/Et_2O 40:1 also revealed the

Scheme 7



25/26/27/28/29/30/31/32 ≈ 1:0.4:6:1:1:12:4:2

presence of six isomeric components with mol. wt. 206 in a ratio of 1:6:1:12:4:2 representing together 0.1% of the total carbonyl fraction. The dominating isomer could be isolated (2 mg) in a purity of *ca.* 80% accompanied by three of its isomers. Their nearly identical MS are characterized by a typical base fragment at *m/z* 80 indicating a *retro-Diels-Alder* reaction and key fragments at *m/z* 99 (hexanoylium ion), 107 ($M^+ - 99$), and 127 ($M^+ - 79$) which let us presume isomeric norbornene derivatives as shown in *Scheme 7*.

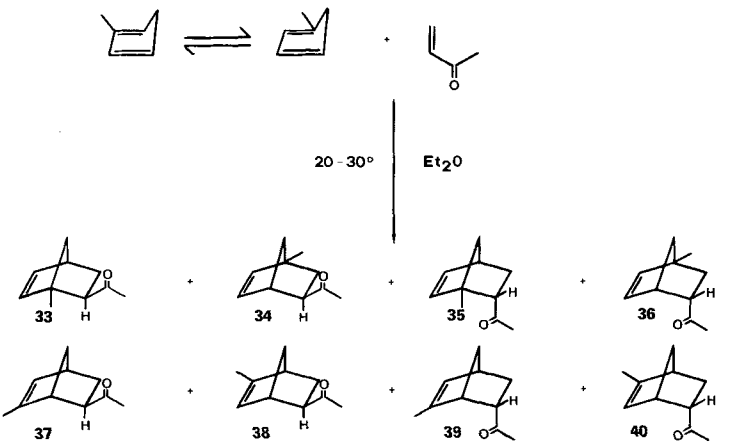
This assumption was verified by *Diels-Alder* reaction of methylcyclopentadiene (freshly prepared by distillation of the dimer) and 1-octen-3-one in Et_2O which spontaneously took place at normal pressure and room temperature. The reaction mixture consisting of 8 isomers in a ratio of 1:0.4:6:1:1:12:4:2 was carefully separated by column chromatography and subsequent preparative GLC, and the structures of the individual isomers **25–32** were established by spectroscopic means. The isomers **25**, **27**, and **29–32** proved to be identical with the constituents localized in lavender oil. Interestingly enough, they occur in the same ratio as found in the synthetic mixture.

The *endo*- and *exo*-configuration of the hexanoyl substituent, respectively, and the position of the CH_3-group in **25–32** can clearly be established by interpretation of their 400-MHz-^{1}H-NMR spectra. As illustrated by *Table 2*, the analysis of the coupling pattern of H–C(5) to its neighbouring protons was of central importance for the structural elucidation.

Table 2. *Some ^{1}H-NMR Characteristics of* **25–32**[3])

	25	**26**	**27**	**28**	**29**	**30**	**31**	**32**
δ of H–C(5) [ppm]	2.41	2.48	2.79	3.12	2.34	3.01	3.07	2.41
$J_{5endo,4}$ ($\sim 90°$)	–	0	–	–	0	–	–	0
$J_{5exo,4}$	–	–	–	4.2	–	4.4	4.8	–
$J_{5endo,6exo}$ ($\sim 120°$)	4.2	4.8	–	–	4.5	–	–	4.0
$J_{5endo,6endo}$ ($\sim 10°$)	8.8	8.8	–	–	9.0	–	–	8.8
$J_{5exo,6exo}$ ($\sim 10°$)	–	–	9.5	8.4	–	8.8	8.8	–
$J_{5exo,6endo}$ ($\sim 120°$)	–	–	5.1	4.2	–	4.4	4.8	–

Scheme 8



33/34/35/36/37/38/39/40 ≈ 1:0.3:7:1:1:2:13:5

Furthermore, GLC/MS measurements of the more volatile part of the carbonyl fraction followed by coinjections with synthetic specimens also allowed the identification of the corresponding acetyl isomers **35**, **39**, and **40** as trace constituent *(Scheme 8)*. In accordance with *Alder*'s *endo*-rule the *endo*-isomers are again preponderant in the natural as well as in the synthetic mixtures. The complete mixture of the synthetically prepared isomers **33–40** is characterized by a powerful herbaceous, camphoraceous odor.

Final Remarks. – Finally, the question has to be considered whether all these *Diels-Alder* adducts found in lavender oil are directly formed in the plant cell or afterwards during oil production. Cross-comparison with production lots of earlier years (1973 and 1977) have shown that these constituents are regularly present in lavender oil in which they certainly contribute olfactory facets to the total odor impression.

Furthermore, most of these constituents could also be identified in a commercially available lavender absolute (**1–4**, **9–12**, **24**, **27**, and **30–31**) as well as in a freshly prepared hexane extract of lavender flowers (**1–4**, **9–12**). Therefore, it can be assumed that these *Diels-Alder* adducts represent genuine constituents of *Lavandula officinalis* CHAIX rather than artefacts formed during the preparation of the oil or extract samples, respectively.

We wish to express our gratitude to Dr. *E. Billeter* and Mrs. *G. Scribano* for many in-depth NMR studies and valuable discussions and Dr. *J. Schmid* for his efforts in interpreting corresponding mass spectra.

Experimental Part

(with the valuable collaboration of Mr. *E. Stocker* and Mr. *R. Thoma*)

General. ^{1}H-NMR: *Bruker WH-400.* Measurements were run in $CDCl_3$ with TMS (0 ppm) as internal standard. Abbreviations: *s* = singlet; *d* = doublet; *t* = triplet; *q* = quadruplet; *quint.* = quintuplet; *m* = multiplet; f.s. = fine structure; br. = broad; ax = axial; eq = equatorial; *J* = apparent coupling constant in Hz; allylic protons in cyclohexenes should be considered as quasi-ax and quasi-eq although only described as ax and eq, respectively. For further general information see [1].

A. Ocimene as Diene. – *Methyl Methyl-(methylbutenyl)cyclohexenyl Ketones* **1–4** *and Dimethyl-(methylpropenyl)cyclohexenyl Methyl Ketones* **5–8**. A solution of 54.0 g (0.40 mol) of ocimene 80 (containing 75–80% trans ocimene) and 64.0 g (0.91 mol) of methyl vinyl ketone in 200 ml of xylene was stirred for 72 h at 110–120°. The methyl vinyl ketone distilled off during the reaction period was periodically readded to the mixture. Usual workup and subsequent distillation gave 40.7 g (49.4%) of a mixture containing **1**, **2**, **3**, **4**, and **5–8** in a ratio of 3:2:3:4:56, b.p. 72–78°/0.05 Torr. Chromatography of this mixture on silica gel (1000 g) with hexane/Et_2O 40:1→30:1 and subsequent prep. GLC allowed to isolate all isomers in purities > 90%.

Methyl cis-*3-Methyl-2-(3'-methyl-2'-butenyl)-3-cyclohexenyl Ketone* (**1**): IR ($CHCl_3$): 1705, 1165, 1150, 850. ^{1}H-NMR: see [3]. MS: 206 (2, M^+), 163 (18), 135 (5), 112 (3), 107 (5), 95 (28), 93 (43), 91 (6), 79 (8), 77 (7), 69 (34), 53 (5), 45 (13), 43 (100), 41 (35).

Methyl trans-*3-Methyl-2-(3'-methyl-2'-butenyl)-3-cyclohexenyl Ketone* (**2**): IR ($CHCl_3$): 1705, 1160, 1100. ^{1}H-NMR: see [3]. MS: 206 (1, M^+), 163 (18), 107 (2), 95 (11), 93 (37), 91 (5), 79 (6), 77 (5), 69 (21), 53 (2), 45 (10), 43 (100), 41 (21).

Methyl cis-*4-Methyl-5-(3'-methyl-2'-butenyl)-3-cyclohexenyl Ketone* (**3**): IR ($CHCl_3$): 1705, 1165. ^{1}H-NMR (400 MHz)[3]: 1.25 (*td*, $J_{4ax,5ax} \approx J_{4ax,4eq} = 13$, $J_{4ax,2ax} = 12$, H_{ax}–C(4)); 1.60 (*s*, CH_3–C(2)); 1.67, 1.70 (2 br. *s*, 2 CH_3–C(3')); 1.97 (*m*, 1H–C(1')); 2.00 (*m*, H_{eq}–C(4)); 2.10 (*m*, 2H–C(6)); 2.16 (*s*, CH_3CO–C(5)); 2.20 (*m*, H_{eq}–C(3)); 2.30 (*m*, 1H–C(1')); 2.55 (*m*, H_{ax}–C(5)); 5.04 (*tm*, H–C(2')); 5.46 (br. *s*, H–C(1)). MS: 206 (12, M^+), 163 (4), 138 (4), 137 (5), 123 (3), 121 (3), 119 (4), 107 (4), 95 (9), 93 (59), 91 (9), 79 (6), 77 (9), 69 (27), 53 (4), 45 (22), 43 (100), 41 (28).

Methyl trans-*4-Methyl-5-(3'-methyl-2'-butenyl)-3-cyclohexenyl Ketone* (**4**): IR: 1610, 1185, 1168, 1150, 1108, 800. ^{1}H-NMR (400 MHz)[3]: 1.51 (*td*, $J_{4ax,5ax} \approx J_{4ax,4eq} = 13$, $J_{4ax,3eq} = 5$, H_{ax}–C(4)); 1.64 (*s*, CH_3–C(2)); 1.70, 1.72 (2 br. *s*, 2 CH_3–C(3')); 1.88 (*dt*, $J_{4eq,4ax} = 13$, $J_{4eq,5ax} \approx J_{4eq,3eq} = 2$, H_{eq}–C(4)); 1.95 (*m*, 1H–C(1')); 2.01 (*m*, H_{eq}–C(3)); 2.12 (*m*, 2H–C(6)); 2.15 (*s*, CH_3CO–C(5)); 2.26 (*m*, 1H–C(1')); 2.61 (*m*, H_{ax}–C(5)); 5.12 (*tm*, H–C(2')); 5.40 (br. *s*, H–C(1)). MS: 206 (4, M^+), 163 (6), 150 (3), 137 (4), 135 (3), 107 (6), 106 (5), 95 (7), 93 (50), 91 (8), 79 (5), 77 (7), 69 (21), 53 (3), 45 (21), 43 (100), 41 (23).

*4,*t-*5-Dimethyl-*t-*2-(2'-methyl-1'-propenyl)-3-cyclohexen-*r-*1-yl Methyl Ketone* (**5**): IR: 1715, 1180, 1166, 1158, 1122, 1085, 1040, 1012, 857, 832. ^{1}H-NMR (400 MHz)[3]: 1.08 (*d*, $J = 7$, CH_3–C(6)); 1.60 (*dt*, $J_{5eq,5ax} = 13$, $J_{5eq,4ax} = J_{5eq,6eq} = 2$, H_{eq}–C(5)); 1.63, 2 × 1.67 (each *s* with f.s., CH_3–C(1), 2 CH_3–C(2')); 1.81 (*td*, $J_{5ax,5eq} = J_{5ax,4ax} = 13$, $J_{5ax,6eq} = 5$, H_{ax}–C(5)); 2.11 (*m*, H–C(6)); 2.12 (*s*, CH_3CO–C(4)); 2.47 (*ddd*, $J_{4ax,5ax} = 13$, $J_{4ax,3ax} = 9.5$, $J_{4ax,5eq} = 2.5$, H_{ax}–C(4)); 3.20 (*m*, H_{ax}–C(3)); 4.83 (*dm*, $J_{1',3ax} = 9$, H–C(1')); 5.06 (br. *s*, H–C(2)). MS: 206 (4, M^+), 191 (6), 173 (5), 163 (79), 149 (9), 137 (12), 121 (41), 119 (25), 109 (22), 107 (100), 105 (24), 95 (13), 93 (19), 91 (25), 79 (13), 77 (13), 69 (20), 57 (74), 43 (59), 41 (24).

*4,*c-*5-Dimethyl-*t-*2-(2'-methyl-1'-propenyl)-3-cyclohexen-*r-*1-yl Methyl Ketone* (**6**): IR: 1715, 1190, 1160, 1130, 1112, 1044, 993, 840, 822, 808. ^{1}H-NMR (400 MHz)[3]: 1.02 (*d*, $J = 7$, CH_3–C(6)); 1.35 (*td*, $J_{5ax,4ax} = J_{5ax,5eq} = 13$, $J_{5ax,6ax} = 11$, H_{ax}–C(5)); 1.61, 1.65, 1.67 (each *s* with f.s., CH_3–C(1), 2 CH_3–C(2')); 1.87 (*ddd*, $J_{5eq,5ax} = 13$, $J_{5eq,6ax} = 5$, $J_{5eq,4ax} = 2.5$, H_{eq}–C(5)); 2.10 (*s*, CH_3CO–C(4)); 2.17 (*m*, H_{ax}–C(6)); 2.42 (*ddd*, $J_{4ax,5ax} = 13$, $J_{4ax,3ax} = 9.5$, $J_{4ax,5eq} = 2.5$, H_{ax}–C(4)); 3.19 (*tm*, $J_{3ax,4ax} = 9.5$, H_{ax}–C(3)); 4.84 (*dm*, $J_{1',3ax} \approx 9$, H–C(1')); 5.07 (br. *s*, H–C(2)). MS: 206 (70, M^+), 191 (36), 188 (7), 173 (7), 163 (98), 149 (14), 135 (20), 121 (88), 119 (23), 107 (100), 105 (29), 91 (30), 79 (17), 77 (16), 69 (26), 57 (21), 43 (73), 41 (27).

*4,*t-*5-Dimethyl-*c-*2-(2'-methyl-1'-propenyl)-3-cyclohexen-*r-*1-yl Methyl Ketone* (**7**): IR ($CHCl_3$): 1708, 1180, 1168, 1155, 1110, 1078, 1008, 975, 865, 835. ^{1}H-NMR (400 MHz)[3]: 1.03 (*d*, $J = 7$, CH_3–C(6)); 1.60 (*dm*, $J_{5eq,5ax} = 13$, H_{eq}–C(5)); 1.65, 1.68, 1.69 (each *s* with f.s., CH_3–C(1), 2 CH_3–C(2')); 1.89 (*td*, $J_{5ax,5eq} = J_{5ax,4ax} = 13$, $J_{5ax,6eq} = 6$, H_{ax}–C(5)); 2.06 (*s*, CH_3CO–C(4)); 2.15 (*quint.*, $J \approx 6.5$, H_{eq}–C(6)); 2.74 (*ddd*, $J_{4ax,5ax} = 13$, $J_{4ax,3eq} = 5$, $J_{4ax,5eq} = 2$, H_{ax}–C(4)); 3.40 (*m*, H_{eq}–C(3)); 4.88 (*dm*, $J_{1',3eq} \approx 9$, H–C(1')); 5.19 (*dm* $J_{2,3eq} = 5$, H–C(2)). MS: 206 (8, M^+), 191 (4), 163 (19), 150 (38), 137 (100), 121 (77), 119 (18), 107 (92), 105 (26), 95 (26), 93 (21), 91 (26), 79 (16), 77 (15), 69 (21), 57 (38), 43 (95), 41 (35).

*4,*c-*5-Dimethyl-*c-*2-(2'-methyl-1'-propenyl)-3-cyclohexen-*r-*1-yl Methyl Ketone* (**8**): IR: 1712, 1165, 1152, 1075, 1065, 1000, 860, 834. ^{1}H-NMR (400 MHz)[3]: 1.05 (*d*, $J = 7$, CH_3–C(6)); 1.44 (*td*, $J_{5ax,4ax} = J_{5ax,5eq} = 13$, $J_{5ax,6ax} = 11$, H_{ax}–C(5)); 1.66, 1.69 (each *s* with f.s., 2 CH_3–C(2')); 1.67 (*s* with f.s., CH_3–C(1)); 1.88 (*ddd*, $J_{5eq,5ax} = 13$, $J_{5eq,6ax} = 5$, $J_{5eq,4ax} = 2.5$, H_{eq}–C(5)); 2.04 (*s*, CH_3CO–C(4)); 2.10 (*m*, H_{ax}–C(6)); 2.70 (*ddd*, $J_{4ax,5ax} = 13$, $J_{4ax,3eq} = 5$, $J_{4ax,5eq} = 2.5$, H_{ax}–C(4)); 3.43 (*m*, H_{eq}–C(3)); 4.89 (*dm*, $J_{1',3eq} \approx 9$, H–C(1')); 5.26 (*dm*, $J = 4$, H–C(2)). MS: 206 (27, M^+), 191 (13), 173 (6), 163 (50), 149 (9), 136 (25), 121 (100), 107 (58), 105 (19), 93 (32), 91 (22), 79 (13), 77 (12), 69 (15), 57 (11), 55 (12), 43 (56), 41 (22).

Equilibration of **1**. A solution of 20 mg of **1** in 2 ml of MeOH containing 5 mg of KOMe was heated under reflux for 3 h. Usual workup led to 15 mg of a 1:4 mixture **1/2**.

Equilibration of **3**. The analogous experiment with 30 mg of pure **3** led to **3/4** (26 mg) in the ratio of 2:3.

Selective Synthesis of **5–8**. In a stainless steel autoclave, 50.0 g (0.37 mol) of ocimene 80, 77.2 g (1.10 mol) of methyl vinyl ketone, and 0.20 g of hydroquinone were mixed and the air in the vessel was displaced by N_2. The temp. was raised to 210–220° and maintained at this range for 6 h. The maximum pressure recorded was 9.8 atm. Distillation of the product gave 60.6 g (79.5%) of **5–8** in a ratio of 1:3:10:3, b.p. 72–74°/0.05 Torr. The individual isomers were isolated by CC on silica gel using hexane/Et_2O 40:1→30:1 and subsequent prep. GLC. Spectral data see above.

B. Myrcene and β-Farnesene as Dienes. – *Methyl Ketones* **9** *and* **10**. *Diels-Alder* reaction of 70.0 g (0.51 mol) of myrcene and 72.2 g (1.03 mol) of methyl vinyl ketone (autoclave, 200°, 4 h, p_{max} 6 atm) led to 77.0 g (72.6%) of a 3:7 mixture **9/10**, b.p. 92–93°/0.05 Torr. For analysis, **9** and **10** were separated by prep. GLC.

Methyl 3-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Ketone (**9**): IR: 1712, 1670, 1165, 1130, 1105, 1060, 830, 775. ^{1}H-NMR (400 MHz)[4]: 1.55 (*m*, H_{ax}–C(4)); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.90–2.16 (*m*, 9H); 2.17 (*s*, CH_3CO–C(5)); 2.57 (*m*, H–C(5)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 206 (8, M^+), 163 (46), 135 (4), 119 (13), 107 (17), 95 (35), 93 (50), 91 (14), 85 (9), 81 (22), 79 (14), 77 (10), 69 (100), 45 (35), 43 (87), 41 (70).

Methyl 4-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Ketone (**10**): IR: 1712, 1670, 1165, 1132, 1103, 1050, 820, 795. ^{1}H-NMR (400 MHz)[4]: 1.55 (*m*, H_{ax}–C(5)); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.92–2.19 (*m*, 9H); 2.18 (*s*, CH_3CO–C(4)); 2.52 (*m*, H–C(4)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 206 (7, M^+), 191 (3), 163 (23), 119 (9), 107 (4), 95 (9), 93 (37), 91 (7), 81 (5), 79 (11), 77 (6), 69 (44), 45 (12), 43 (100), 41 (37).

Methyl Ketones **11** *and* **12**. *Diels-Alder* reaction of 9.18 g (0.048 mol) of β-farnesene (for synthesis see [6])

and 9.38 g (0.13 mol) of methyl vinyl ketone (autoclave, 200°, 4 h) yielded 8.2 g (65.5%) of a 3:7 mixture **11/12**, b.p. 127–130°/0.05 Torr. For analysis, **9** and **10** were separated by prep. GLC.

3-((E)-4',8'-Dimethyl-3',7'-nonadienyl)-3-cyclohexenyl Methyl Ketone (**11**): IR: 1715, 1670, 1162, 1118, 1108, 830. ^{1}H-NMR (400 MHz)[4]: 1.49 (*m*, H_{ax}–C(5)); 1.60 (*s*, CH_3–C(4')); 1.60, 1.68 (each *s*, 2 CH_3–C(8')); 1.90–2.16 (*m*, 13H); 2.18 (*s*, CH_3CO–C(5)); 2.58 (*m*, H–C(5)); 5.10 (*m*, H–C(3'), H–C(7')); 5.41 (br. *s*, H–C(2)). MS: 274 (3, M^+), 231 (7), 205 (2), 187 (2), 161 (3), 149 (6), 136 (20), 121 (10), 119 (10), 107 (13), 105 (11), 95 (24), 93 (31), 91 (16), 81 (41), 69 (100), 55 (10), 45 (22), 43 (76), 41 (55).

4-((E)-4',8'-Dimethyl-3',7'-nonadienyl)-3-cyclohexenyl Methyl Ketone (**12**): IR: 1713, 1670, 1164, 1132, 1108, 835, 815. ^{1}H-NMR (400 MHz)[4]: 1.56 (*m*, H_{ax}–C(5)); 1.59, 1.60, 1.68 (each *s*, CH_3–C(4'), 2 CH_3–C(8')); 1.92–2.19 (*m*, 13H); 2.18 (*s*, CH_3CO–C(4)); 2.53 (*m*, H–C(4)); 5.10 (*m*, H–C(3'), H–C(7')); 5.41 (br. *s*, H–C(2)). MS: 274 (2, M^+), 231 (5), 192 (3), 161 (3), 150 (7), 123 (7), 121 (6), 119 (8), 107 (5), 105 (8), 95 (12), 93 (31), 91 (13), 81 (29), 69 (82), 43 (100), 41 (44).

Diels-Alder *Adducts* **13** *and* **14** *of Myrcene and 1-Octen-3-one.* Reaction of 5.7 g (0.042 mol) of myrcene and 4.0 g (0.032 mol) of 1-octen-3-one (autoclave, 200°, 3 h) gave 5.0 g (60.2%) of a 3:7 mixture **13/14**, b.p. 127–130°/0.05 Torr. For analysis, **13** and **14** were separated by prep. GLC.

3-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Pentyl Ketone (**13**): IR ($CHCl_3$): 1705, 1670, 1128, 1078, 830. ^{1}H-NMR (400 MHz)[4]: 0.89 (*t*, J = 7, 3H); 1.21–1.38 (*m*, 4H); 1.48 (*m*, H_{ax}–C(4)); 1.58 (*m*, 2H); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.85–2.18 (*m*, 9H); 2.47 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.58 (*m*, H–C(5)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 262 (6, M^+), 219 (6), 191 (4), 163 (33), 147 (3), 135 (4), 119 (8), 107 (21), 105 (10), 99 (40), 95 (23), 93 (29), 83 (20), 81 (43), 79 (13), 71 (30), 69 (100), 55 (39), 43 (67), 41 (65).

4-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Pentyl Ketone (**14**): IR ($CHCl_3$): 1705, 1670, 1128, 1102, 1078, 830. ^{1}H-NMR (400 MHz)[4]: 0.89 (*t*, J = 7, 3H); 1.21-1.37 (*m*, 4H); 1.57 (*m*, 3H); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.90–2.18 (*m*, 9H); 2.46 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.52 (*m*, H–C(4)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 262 (5, M^+), 219 (7), 191 (5), 163 (11), 135 (2), 119 (7), 107 (3), 99 (100), 93 (7), 81 (9), 79 (7), 71 (54), 69 (34), 55 (11), 43 (59), 41 (39).

Diels-Alder *Adducts* **15** *and* **16** *of Myrcene and 1-Hexen-3-one.* Reaction of 14.8 g (0.11 mol) of myrcene and 7.4 g (0.076 mol) of 1-hexen-3-one (autoclave 200°, 3 h) led to 10.1 g (56.8%) of **15/16** (3:7), b.p. 110–112°/0.05 Torr. For analysis, **15** and **16** were separated by prep. GLC.

3-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Propyl Ketone (**15**): IR ($CHCl_3$): 1705, 1670, 1128, 1105, 1070. ^{1}H-NMR (400 MHz)[4]: 0.91 (*t*, J = 7, 3H); 1.48 (*m*, H_{ax}–C(4)); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.62 (*m*, 2H); 1.85–2.20 (*m*, 9H); 2.48 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.58 (*m*, H–C(5)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 234 (8, M^+), 216 (2), 191 (11), 163 (30), 147 (2), 135 (4), 121 (6), 119 (8), 107 (21), 105 (11), 95 (25), 93 (28), 85 (10), 81 (34), 79 (12), 71 (56), 69 (100), 55 (37), 43 (62), 41 (65).

4-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Propyl Ketone (**16**): IR ($CHCl_3$): 1705, 1670, 1128, 1102, 1080, 1020, 825. ^{1}H-NMR (400 MHz)[4]: 0.91 (*t*, J = 7, 3H); 1.55 (*m*, H_{ax}–C(5)); 1.59 (*m*, 2H); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.90–2.18 (*m*, 9H); 2.45 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.53 (*m*, H–C(4)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 234 (4, M^+), 191 (9), 163 (7), 135 (1), 123 (3), 119 (4), 107 (2), 93 (6), 81 (4), 79 (5), 71 (100), 69 (22), 55 (4), 43 (38), 41 (25).

Diels-Alder *Adducts* **17** *and* **18** *of Myrcene and 1-Penten-3-one.* Reaction of 27.2 g (0.20 mol) of myrcene and 25.2 g (0.30 mol) of 1-penten-3-one (autoclave, 200°, 3 h) led to 28.0 g (63.6%) of **17/18** (3:7), b.p. 94–96°/0.04 Torr. For analysis, **17** and **18** were separated by prep. GLC.

Ethyl 3-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Ketone (**17**): IR ($CHCl_3$): 1605, 1670, 1122, 1108, 1068, 1018, 982, 832. ^{1}H-NMR (400 MHz)[4]: 1.06 (*t*, J = 7, 3H); 1.50 (*m*, H_{ax}–C(4)); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.89 (*m*, H_{eq}–C(4)); 1.93–2.20 (*m*, 8H); 2.51 (*AB* of *ABX*$_3$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.59 (*m*, H–C(5)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 220 (10, M^+), 191 (3), 177 (9), 163 (30), 135 (4), 121 (5), 119 (6), 107 (20), 95 (29), 93 (36), 85 (11), 81 (27), 69 (100), 59 (34), 57 (72), 41 (59).

Ethyl 4-(4'-Methyl-3'-pentenyl)-3-cyclohexenyl Ketone (**18**): IR ($CHCl_3$): 1705, 1670, 1122, 1108, 1018, 982, 830. ^{1}H-NMR (400 MHz)[4]: 1.06 (*t*, J = 7, 3H); 1.55 (*m*, H_{ax}–C(5)); 1.60, 1.68 (each *s*, 2 CH_3–C(4')); 1.90–2.18 (*m*, 9H); 2.50 (*AB* of *ABX*$_3$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.53 (*m*, H–C(5)); 5.09 (*tm*, H–C(3')); 5.41 (br. *s*, H–C(2)). MS: 220 (6, M^+), 191 (3), 177 (6), 163 (7), 135 (2), 123 (3), 119 (4), 107 (3), 93 (11), 85 (3), 79 (6), 69 (25), 57 (100), 41 (23).

Diels-Alder *Adducts* **19** *and* **20** *of Myrcene and Crotonaldehyde.* Reaction of 81.4 g (0.60 mol) of myrcene and 84.0 (1.20 mol) of crotonaldehyde (autoclave, 200°, p_{max} 4 atm) led to a isomeric mixture **19/20**, b.p. 95–97/0.05 Torr (peak 1/peak 2 ratio *ca.* 2:3 on a *Pluronic* glass capillary column, assignment tentative according to NMR data of the mixture and GLC/MS analysis).

6-Methyl-3-(4'-methyl-3'-pentenyl)-3-cyclohexenecarbaldehyde (**19**; Peak 1): MS: 206 (4, M^+), 177 (12), 163 (5), 145 (2), 135 (3), 121 (5), 119 (6), 109 (7), 107 (20), 95 (6), 93 (7), 91 (9), 81 (6), 79 (8), 69 (100), 55 (7), 41 (58).

6-Methyl-4-(4'-methyl-3'-pentenyl)-3-cyclohexenecarbaldehyde (**20**; Peak 2): MS: 206 (8, M^+), 188 (3), 177 (3), 163 (7), 145 (2), 135 (3), 121 (7), 119 (14), 109 (9), 107 (21), 95 (4), 93 (9), 91 (11), 79 (9), 77 (5), 69 (100), 55 (8), 41 (67).

C. (*E,Z*)- and (*E,E*)-1,3,5-Undecatriene as Diene. – *Methyl Ketones* **21–24**. Reaction of 6.0 g (0.040 mol) of 1,3,5-undecatriene ((*E,Z*)/(*E,E*) ≈ 3:2) and 7.0 g (0.10 mol) of methyl vinyl ketone (autoclave, 200°, 4 h, p_{max} 5 atm) gave 6.25 g (70.5%) of **21–24** (2:2:3:8), b.p. 140–150°/12 Torr (bulb-to-bulb distillation). For analysis, the individual isomers were separated by prep. GLC.

trans-*2-((Z)-1'-Heptenyl)-3-cyclohexenyl Methyl Ketone* (**21**): IR ($CHCl_3$): 1710, 1210, 1165, 1035, 950, 700. ^{1}H-NMR (400 MHz)[3]: 0.88 (*t*, *J* = 7, 3H); 1.33–1.38 (*m*, 6H); 1.65 (*m*, H_{ax}–C(5)); 1.87 (*m*, H_{eq}–C(5)); 2.03 (*m*, 2H–C(3')); 2.08 (*m*, 2H–C(6)); 2.14 (*s*, CH_3CO–C(4)); 2.44 (*ddd*, $J_{4ax,5ax}$ = 12, $J_{4ax,3ax}$ = 10, $J_{4ax,5eq}$ = 4, H_{ax}–C(4)); 3.37 (*tm*, $J_{3ax,4ax} \approx J_{3ax,1'}$ = 10, $J_{3ax,2}$ = 4, H_{ax}–C(3)); 5.09 (*tt*, $J_{1',2'} \approx J_{1',3ax}$ = 10, $J_{1',3'} \approx$ 1.5, H–C(1')); 5.39 (*dq*, $J_{1,2}$ = 10, $J_{1,6} \approx J_{1,3ax} \approx$ 2.5, H–C(1)); 5.41 (*dt*, $J_{2',1'}$ = 10, $J_{2',3'}$ = 7, $J_{2',3} \approx$ 2.5, H–C(2')); 5.70 (*dm*, $J_{2,1}$ = 10, $J_{2,3ax}$ = 4, H–C(2)). MS: 220 (1, M^+), 205 (5), 177 (17), 149 (4), 135 (5), 121 (15), 107 (16), 99 (3), 93 (23), 91 (15), 79 (24), 71 (7), 67 (14), 57 (100), 43 (79).

trans-*2-((E)-1'-Heptenyl)-3-cyclohexenyl Methyl Ketone* (**22**): IR ($CHCl_3$): 1710, 1160, 970. ^{1}H-NMR (400 MHz)[3]: 0.87 (*t*, *J* = 7, 3H); 1.18–1.38 (*m*, 6H); 1.63 (*m*, H_{ax}–C(5)); 1.85 (*m*, H_{eq}–C(5)); 1.96 (*q*, $J_{3',2'}$ = 7, 2H–C(3')); 2.07 (*m*, 2H–C(6)); 2.14 (CH_3CO–C(4)); 2.45 (*ddd*, $J_{4ax,5ax}$ = 12, $J_{4ax,3ax}$ = 10, $J_{4ax,5eq}$ = 4, H_{ax}–C(4)); 3.04 (*m*, H_{ax}–C(3)); 5.24 (*ddt*, $J_{1',2'}$ = 16, $J_{1',3ax}$ = 9, $J_{1',3'} \approx$ 1.5, H–C(1')); 5.45 (*dt*, $J_{2',1'}$ = 16, $J_{2',3'}$ = 7, H–C(2')); 5.51 (*dq*, $J_{1,2}$ = 10, $J_{1,6} \approx J_{1,3ax} \approx$ 2, H–C(1)); 5.69 (*dm*, $J_{2,1}$ = 10, $J_{2,3ax}$ = 4, H–C(2)). MS: 220 (1, M^+), 205 (5), 177 (17), 149 (3), 135 (5), 121 (15), 107 (18), 99 (3), 93 (22), 91 (7), 79 (23), 71 (4), 67 (13), 57 (100), 43 (77).

cis-*2-((E)-1'-Heptenyl)-3-cyclohexenyl Methyl Ketone* (**23**): IR: 1710, 1167, 1155, 970. ^{1}H-NMR (400 MHz)[3]: 0.87 (*t*, *J* = 7, 3H); 1.18–1.38 (6H); 1.64 (*qd*, $J_{5ax,4ax} \approx J_{5ax,5eq}$ = 12, $J_{5ax,6}$ = 6, H_{ax}–C(5)); 1.79 (*m*, H_{eq}–C(5)); 1.94 (*q*, $J_{3',2'}$ = 7, 2H–C(3')); 2.02 (*m*, H–C(6)); 2.12 (*s*, CH_3CO–C(4)); 2.67 (*dq*, $J_{4ax,5ax}$ = 12, $J_{4ax,3eq}$ = 6, $J_{4ax,5eq}$ = 3, H_{ax}–C(4)); 3.17 (*m*, H_{eq}–C(3)); 5.18 (*ddt*, $J_{1',2'}$ = 15.5, $J_{1',3eq}$ = 9, $J_{1',3'} \approx$ 1.5, H–C(1')); 5.46 (*dt*, $J_{2',1'}$ = 15, $J_{2',3'}$ = 7, H–C(2')); 5.57 (*dm*, $J_{2,3eq}$ = 6, H–C(2)); 5.74 (*dm*, H–C(1)). MS: 220 (9, M^+), 205 (4), 177 (18), 149 (4), 135 (5), 121 (13), 107 (18), 99 (2), 93 (33), 91 (19), 79 (36), 71 (7), 67 (18), 57 (92), 43 (100).

cis-*2-((Z)-1'-Heptenyl)-3-cyclohexenyl Methyl Ketone* (**24**): IR: 1710, 1225, 1210, 1167, 1150, 1100, 1050, 860, 740, 715. ^{1}H-NMR (400 MHz)[3]: 0.88 (*t*, *J* = 7, 3H); 1.25–1.42 (*m*, 6H); 1.71 (*qd*, $J_{5ax,4ax} \approx J_{5ax,5eq}$ = 12, $J_{5ax,6}$ = 6, H_{ax}–C(5)); 1.84 (*m*, H_{eq}–C(5)); 2.01 (*m*, 2H–C(6)); 2.08–218 (*m*, 2H–C(3')); 2.08 (*s*, CH_3CO–C(4)); 2.71 (*dq*, $J_{4ax,5ax}$ = 12, $J_{4ax,3eq}$ = 6, $J_{4ax,5eq}$ = 4, H_{ax}–C(4)); 3.56 (*m*, H_{eq}–C(3)); 5.16 (*tt*, $J_{1',2'}$ = 11, $J_{1',3eq}$ = 10, H–C(1')); 5.39 (*dt*, $J_{2',1'}$ = 11, $J_{2',3'}$ = 7, H–C(2')); 5.53 (*dm*, $J_{2,3eq}$ = 3.5, H–C(2)); 5.72 (*m*, H–C(1)). MS: 220 (9, M^+), 205 (4), 177 (18), 149 (6), 135 (5), 121 (12), 107 (16), 99 (3), 93 (29), 91 (17), 79 (36), 71 (8), 67 (16), 57 (94), 43 (100).

D. Methylcyclopentadiene as Diene. – *Di- and Trinorbornenyl Pentyl Ketones* **25–32**. Methylcyclopentadiene (80.0 g, 1.0 mol; freshly prepared by distillation of the dimer) was added at 25–30° (weak external cooling) during 3 h to a solution of 63.0 g (0.50 mol) of 1-octen-3-one in 150 ml of Et_2O. Stirring was continued at r.t. for 2 h. Evaporation of the solvent and distillation gave 66.0 g (64%) of a mixture containing **25–32** in a ratio of 1:0.4:6:1:1:12:4:2, b.p. 84–86°/0.05 Torr. Chromatography of this mixture on silica gel with hexane/Et_2O 40:1→30:1 and subsequent prep. GLC allowed to isolate all isomers in purities > 90%.

*8,9-Dinorborn-5-en-2-*exo*-yl Pentyl Ketone* (**25**): IR: 1710, 1125, 1088, 1064, 1014, 997, 950, 710. ^{1}H-NMR (400 MHz)[3]: 0.89 (*t*, *J* = 7, 3H); 1.12 (*dm*, $J_{7s,7a}$ = 8.5, $J_{7s,6endo}$ = 3, $J_{7s,5endo}$ = 1.5, H_s–C(7)); 1.26 (*s*, CH_3–C(4)); 1.24–1.32 (*m*, 4H); 1.32 (*ddd*, $J_{6endo,6exo}$ = 12, $J_{6endo,5endo}$ = 8.5, $J_{6endo,7s}$ = 3, H_{endo}–C(6)); 1.56 (*m*, 2H); 1.82 (*d*, $J_{7a,7s}$ = 8.5, H_a–C(7)); 1.90 (*dt*, $J_{6exo,6endo}$ = 12, $J_{6exo,1} \approx J_{6exo,5endo}$ = 4, H_{exo}–C(6)); 2.42 (*dd*, $J_{5endo,6endo}$ = 8.5, $J_{5endo,6exo}$ = 4, $J_{5endo,7s}$ = 1.5, H_{endo}–C(5)); 2.47 (*AB* of *ABX*$_2$, $J_{AB} \approx$ 15, $J_{AX} \approx J_{BX} \approx$ 7, CO–CH_2); 2.82 (br. *s*, H–C(1)); 5.84 (*d*, $J_{3,2}$ = 5.5, H–C(3)); 6.13 (*dd*, $J_{2,3}$ = 5.5, $J_{2,1}$ = 3, H–C(2)); compare with ^{1}H-NMR of **35**. MS: 206 (6, M^+), 127 (17), 107 (9), 99 (2), 93 (3), 91 (3), 80 (100), 79 (18), 71 (4), 55 (15), 43 (10).

*8,9-Dinorborn-5-en-3-*exo*-yl Pentyl Ketone* (**26**): IR ($CHCl_3$): 1705, 1135, 1065, 700. ^{1}H-NMR (400 MHz)[3]: 0.90 (*t*, *J* = 7, 3H); 1.20 (*dm*, H_s–C(7)); 1.28 (*ddd*, $J_{6endo,6exo}$ = 11.5, $J_{6endo,5endo}$ = 8.8, $J_{6endo,7s}$ = 2.5, measured after addition of Eu(fod)$_3$, H_{endo}–C(6)); 1.30 (*d*, $J_{7a,7s}$ = 8, measured after addition of Eu(fod)$_3$, H_a–C(7)); 1.34

(*s*, CH_3–C(1)); 1.25–1.34 (*m*, 4H); 1.58 (*m*, 2H); 1.69 (*dd*, $J_{6exo,6endo}$ = 11.5, $J_{6exo,5endo}$ = 4.8, H_{exo}–C(6)); 2.47 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} = 7$, CO–$CH_2$); 2.50 (*ddd*, $J_{5endo,6endo}$ = 8.8, $J_{5endo,6exo}$ = 4.8, $J_{5endo,7s}$ = 1.5, measured after addition of Eu(fod)$_3$, H_{endo}–C(5)); 2.88 (br. *s*, $J_{4,3}$ = 3.8, $J_{4,5endo}$ = 0 (90°), H–C(4)); 5.93 (*d*, $J_{2,3}$ = 6, H–C(2)); 6.12 (*dd*, $J_{3,2}$ = 6, $J_{3,4}$ = 3.8, H–C(3)); compare with ^{1}H-NMR of **34**. MS: 206 (3, M^+), 127 (9), 107 (15), 99 (3), 92 (3), 91 (3), 80 (100), 79 (18), 71 (4), 55 (15), 43 (9).

*8,9-Dinorborn-5-en-2-*endo-*yl Pentyl Ketone* (**27**): IR ($CHCl_3$): 1705, 1132, 1078, 1000. ^{1}H-NMR (400 MHz)[3]): 0.88 (*t*, *J* = 7, 3H); 1.20–1.32 (*m*, H_s–C(7), H_a–C(7), 2 CH_2); 1.37 (*ddd*, $J_{6endo,6exo}$ = 12, $J_{6endo,5exo}$ = 5, $J_{6endo,7s}$ = 3, H_{endo}–C(6)); 1.42 (*s*, CH_3–C(4)); 1.52 (*quint.*, *J* = 7, 2H); 2.09 (*ddd*, $J_{6exo,6endo}$ = 12, $J_{6exo,5exo}$ = 9.6, $J_{6exo,1}$ = 4, H_{exo}–C(6)); 2.33 (*AB* of *ABX*$_2$, J_{AB} = 15, $J_{AX} \approx J_{BX}$ = 7, CO–CH_2); 2.79 (*dd*, $J_{5exo,6exo}$ = 9.6, $J_{5exo,6endo}$ = 5.2, measured after addition of Eu(fod)$_3$, H_{exo}–C(5)); 2.80 (br. *s*, $J_{1,6exo}$ = 4, $J_{1,2}$ = 3, H–C(1)); 5.80 (*d*, $J_{3,2}$ = 6, H–C(3)); 6.11 (*dd*, $J_{2,3}$ = 6, $J_{2,1}$ = 3, H–C(2)); compare with ^{1}H-NMR of **35**. MS: 206 (8, M^+), 127 (18), 107 (10), 99 (3), 93 (5), 92 (4), 80 (100), 79 (19), 71 (5), 55 (19), 43 (11).

*8,9-Dinorborn-5-en-3-*endo-*yl Pentyl Ketone* (**28**): IR ($CHCl_3$): 1705, 1132, 1075. ^{1}H-NMR (400 MHz)[3]): 0.89 (*t*, *J* = 7, 3H); 1.20–1.35 (*m*, H_s–C(7), H_a–C(7), 2 CH_2); 1.33 (*s*, CH_3–C(1)); 1.48–1.61 (*m*, H_{endo}–C(6), H_{exo}–C(6), CH_2); 2.38 (*t*, *J* = 7, CO–CH_2); 3.13 (*quint.*, $J_{5exo,6exo}$ = 8.8, $J_{5exo,6endo} \approx J_{5exo,4}$ = 4, H_{exo}–C(5)); 3.17 (br. *s*, $J_{4,5exo}$ = 4, $J_{4,3}$ = 3, H–C(4)); 5.81 (*dd*, $J_{3,2}$ = 6, $J_{3,4}$ = 3, H–C(3)); 5.93 (*d*, $J_{2,3}$ = 6, H–C(2)); compare with ^{1}H-NMR of **36**. MS: 206 (4, M^+), 135 (2), 127 (2), 114 (2), 107 (20), 99 (7), 92 (5), 80 (100), 79 (18), 71 (7), 55 (17), 43 (12).

*6-Methyl-8,9,10-trinorborn-5-en-2-*exo-*yl Pentyl Ketone* (**29**): IR ($CHCl_3$): 1705, 1130, 1070, 985. ^{1}H-NMR (400 MHz)[3]): 0.90 (*t*, *J* = 7, 3H); 1.28 (*m*, 4H); 1.32 (*m*, H_{endo}–C(6)); 1.36 (br. *s*, H_s–C(7), H_a–C(7)); 1.59 (*quint.*, *J* = 7, 2H); 1.77 (*s*, with f.s., CH_3–C(3)); 1.88 (*dt*, $J_{6exo,6endo}$ = 12, $J_{6exo,5endo} \approx J_{6exo,1}$ = 4.5, H_{exo}–C(6)); 2.34 (*dd*, $J_{5endo,6endo}$ = 8.5, $J_{5endo,6exo}$ = 4.5, H_{endo}–C(5)); 2.49 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX}$ = 7, CO–CH_2); 2.69 (br. *s*, H–C(4)); 2.89 (br. *s*, H–C(1)); 5.65 (br. *s*, H–C(2)). MS: 206 (8, M^+), 135 (2), 127 (12), 107 (12), 99 (4), 92 (6), 91 (5), 80 (100), 79 (20), 71 (5), 55 (18), 43 (13).

*6-Methyl-8,9,10-trinorborn-5-en-2-*endo-*yl Pentyl Ketone* (**30**): IR: 1710, 1130, 1090, 1030, 992, 920, 814, 780, 716. ^{1}H-NMR (400 MHz)[3]): 0.88 (*t*, *J* = 7, 3H); 1.20–1.35 (*m*, H_a–C(7), 2 CH_2); 1.48 (*dm*, $J_{7s,7a}$ = 8.2, $J_{7s,6endo} \approx 2$, H_s–C(7)); 1.50–1.62 (*m*, H_{endo}–C(6), CH_2); 1.68 (*ddd*, $J_{6exo,6endo}$ = 12, $J_{6exo,5exo}$ = 8.5, $J_{6exo,1}$ = 4, H_{exo}–C(6)); 1.73 (*s*, with f.s., CH_3–C(3)); 2.40 (*t*, *J* = 7, CO–CH_2); 2.63 (br. *s*, H–C(1)); 3.01 (*quint*, $J_{5exo,6exo}$ = 8.5, $J_{5exo,6endo} \approx J_{5exo,4}$ = 4.5, H_{exo}–C(5)); 3.13 (br. *s*, H–C(4)); 5.33 (br. *s*, H–C(2)); compare with ^{1}H-NMR of **39**. MS: 206 (7, M^+), 135 (1), 127 (13), 107 (6), 99 (3), 92 (6), 80 (100), 79 (17), 67 (3), 55 (6), 43 (9).

*5-Methyl-8,9,10-trinorborn-5-en-2-*endo-*yl Pentyl Ketone* (**31**): IR: 1710, 1130, 1095, 1080, 942, 827, 798, 785, 718. ^{1}H-NMR (400 MHz)[3]): 0.89 (*t*, *J* = 7, 3H); 1.22–1.38 (*m*, H_a–C(7), 2 CH_2); 1.48 (*dm*, $J_{7s,7a}$ = 8, H_s–C(7)); 1.52–1.62 (*m*, H_{endo}–C(6), CH_2); 1.60 (*s* with f.s., CH_3–C(2)); 1.68 (*ddd*, $J_{6exo,6endo}$ = 12, $J_{6exo,5exo}$ = 8.5, $J_{6exo,1}$ = 4, H_{exo}–C(6)); 2.46 (*AB* of *ABX*$_2$, J_{AB} = 15, $J_{AX} \approx J_{BX}$ = 7, CO–CH_2); 2.79 (br. *s*, H–C(1)); 3.00 (br. *s*, H–C(4)); 3.07 (*quint.*, $J_{5exo,6exo}$ = 8.5, $J_{5exo,6endo} \approx J_{5exo,4}$ = 4.5, H_{exo}–C(5)); 5.72 (br. *s*, H–C(3)); compare with ^{1}H-NMR of **40**. MS: 206 (9, M^+), 135 (2), 127 (10), 107 (15), 99 (5), 92 (7), 80 (100), 79 (19), 71 (5), 67 (2), 55 (18), 43 (12).

*5-Methyl-8,9,10-trinorborn-5-en-2-*exo-*yl Pentyl Ketone* (**32**): IR ($CHCl_3$): 1705, 1132, 1070, 1020, 994, 818. ^{1}H-NMR (400 MHz)[3]): 0.89 (*t*, *J* = 7, 3H); 1.18–1.33 (*m*, H_{endo}–C(6), 2 CH_2); 1.34 (*m*, H_s–C(7), H_a–C(7)); 1.58 (*quint.*, *J* = 7, 2H); 1.74 (*s* with f.s., CH_3–C(2)); 1.89 (*dt*, $J_{6exo,6endo}$ = 12, $J_{6exo,5endo}$ = 4.1, $J_{6exo,1} \approx 4.5$, H_{exo}–C(6)); 2.42 (*dd*, $J_{5endo,6endo}$ = 8.5, $J_{5endo,6exo}$ = 4, $J_{5endo,7s}$ = 2, H_{endo}–C(5)); 2.49 (*AB* of *ABX*$_2$, $J_{AB} \approx 15$, $J_{AX} \approx J_{BX} \approx 7$, CO–$CH_2$); 2.62 (br. *s*, H–C(1)); 2.86 (br. *s*, H–C(4)); 5.62 (br. *s*, H–C(3)). MS: 206 (10, M^+), 135 (2), 127 (23), 107 (12), 99 (4), 92 (10), 80 (100), 79 (28), 71 (5), 67 (3), 55 (24), 43 (15).

Di- and Trinorbornenyl Methyl Ketones **33–40**. Methylcyclopentadiene (96.0 g; 1.2 mol) was added at 25–30° (weak external cooling) during 3 h to a solution of 70.0 g (1.0 mol) of methyl vinyl ketone in 250 ml of Et_2O. Stirring was continued at r.t. for 2 h. Evaporation of the solvent and distillation furnished 97.8 g (65.2%) of a mixture containing **33–40** in a ratio of 1:0.3:7:1:1:2:13:5, b.p. 76–81°/12 Torr. Chromatography of this mixture on silica gel with hexane/Et_2O 40:1→30:1 and subsequent prep. GLC allowed to isolate all isomers in purities > 90%. *8,9-Dinorborn-5-en-2-*exo-*yl Methyl Ketone* (**33**): IR: 1708, 1185, 1162, 1085, 955, 822, 778, 716. ^{1}H-NMR (400 MHz)[3]): 1.13 (*dm*, $J_{7s,7a}$ = 8.5, $J_{7s,5endo} \approx 1.5$, $J_{7s,6endo}$ = 3, H_s–C(7)); 1.30 (*s*, CH_3–C(4)); 1.33 (*ddd*, $J_{6endo,6exo}$ = 11.5, $J_{6endo,5endo}$ = 8.5, $J_{6endo,7s}$ = 3, H_{endo}–C(6)); 1.75 (*d*, $J_{7a,7s}$ = 8.5, H_a–C(7)); 1.94 (*dt*, $J_{6exo,6endo}$ = 11.5, $J_{6exo,1}$ = 4.5, $J_{6exo,5endo}$ = 4.5, H_{exo}–C(6)); 2.21 (*s*, CH_3CO–C(5)); 2.45 (*dd*, $J_{5endo,6endo}$ = 8.5, $J_{5endo,6exo}$ = 4.5, $J_{5endo,7s}$ = 1.5, H_{endo}–C(5)); 2.82 (br. *s*, H–C(1)); 5–85 (*d*, $J_{3,2}$ = 5.5, H–C(3)); 6.14 (*dd*, $J_{2,3}$ = 5.5, $J_{2,1}$ = 3, H–C(2)). MS: 150 (9, M^+), 135 (1), 107 (8), 91 (7), 80 (100), 79 (32), 71 (14), 65 (3), 55 (5), 43 (15), 39 (6).

*8,9-Dinorborn-5-en-3-*exo-*yl Methyl Ketone* (**34**): IR: 1705, 1172, 1138, 1082, 945. ^{1}H-NMR (400 MHz)[3]: 1.21 (*dm*, $J_{7s,7a}$ = 8.2, $J_{7s,5endo}$ = 1.5, $J_{7s,6endo}$ = 3, H_s–C(7)); 1.29 (*ddd*, $J_{6endo,6exo}$ = 11.5, $J_{6endo,5endo}$ = 8.8, $J_{6endo,7s}$ = 2.5, H_{endo}–C(6)); 1.29 (*d*, $J_{7a,7s}$ = 8.2, H_a–C(7)); 1.35 (*s*, CH_3–C(1)); 1.69 (*dd*, $J_{6exo,6endo}$ = 11.5, $J_{6exo,5endo}$ = 4.8, H_{exo}–C(6)); 2.20 (*s*, CH_3CO–C(5)); 2.50 (*ddd*, $J_{5endo,6endo}$ = 8.8, $J_{5endo,6exo}$ = 4.8, $J_{5endo,7s}$ = 1.5, H_{endo}–C(5)); 2.93 (br. *s*, $J_{4,3}$ = 3.5, $J_{4,5endo}$ = 0 (90°), H–C(4)); 5.93 (*d*, $J_{2,3}$ = 6, H–C(2)); 6.13 (*dd*, $J_{3,2}$ = 6, $J_{3,4}$ = 3.5, H–C(3)). MS: 150 (4, M^+), 107 (15), 92 (9), 91 (9), 80 (100), 79 (36), 71 (8), 58 (5), 55 (5), 43 (19), 39 (7).

*8,9-Dinorborn-5-en-2-*endo-*yl Methyl Ketone* (**35**): IR: 1710, 1170, 823, 720. ^{1}H-NMR (400 MHz)[3]: 1.27 (*d*, $J_{7a,7s}$ = 9, H_a–C(7)); 1.31 (*dt*, $J_{7s,7a} \approx 9$, $J_{7s,6endo}$ = 2.8, H_s–C(7)); 1.40 (*ddd*, $J_{6endo,6exo}$ = 11.8, $J_{6endo,5exo}$ = 4.5, $J_{6endo,7s}$ = 2.8, $J_{6endo,1} \approx 0$ (90°), H_{endo}–C(6)); 1.45 (*s*, CH_3–C(4)); 2.08 (*s*, CH_3CO–C(5)); 2.09 (*ddd*, $J_{6exo,6endo}$ = 11.8, $J_{6exo,5exo}$ = 9.8, $J_{6exo,1} \approx 4$, H_{exo}–C(6)); 2.80 (*dd*, $J_{5exo,6exo}$ = 9.8, $J_{5exo,6endo}$ = 4.5, H_{exo}–C(5)); 2.81 (br. *s*, $J_{1,6exo} \approx 4$, $J_{1,2}$ = 3.5, H–C(1)); 5.79 (*d*, $J_{3,2} \approx 6$, H–C(3)); 6.13 (*dd*, $J_{2,3} \approx 6$, $J_{2,1}$ = 3.5, H–C(2)). MS: 150 (9, M^+), 107 (7), 91 (6), 80 (100), 79 (32), 71 (12), 65 (3), 55 (3), 43 (14), 39 (6).

*8,9-Dinorborn-5-en-3-*endo-*yl Methyl Ketone* (**36**): IR: 1710, 1178, 1142, 1092, 735, 718. ^{1}H-NMR (400 MHz)[3]: 1.27 (*d*, $J_{7a,7s}$ = 8, H_a–C(7)); 1.33 (*s*, CH_3–C(1)); 1.36 (*dt*, $J_{7s,7a}$ = 8, $J_{7s,6endo} \approx 3$, $J_{7s,4} \approx 3$, H_s–C(7)); 1.52 (*dd*, $J_{6exo,6endo}$ = 11, $J_{6exo,5exo}$ = 8.8, H_{exo}–C(6)); 1.58 (*ddd*, $J_{6endo,6exo}$ = 11, $J_{6endo,5exo}$ = 4, $J_{6endo,7s}$ = 3, H_{endo}–C(6)); 2.12 (*s*, CH_3CO–C(5)); 3.13 (*quint.*, $J_{5exo,6exo}$ = 8.8, $J_{5exo,6endo} \approx J_{5exo,4}$ = 4, H_{exo}–C(5)); 3.18 (br. *s*, $J_{4,3} \approx J_{4,7s} \approx 3$, H–C(4)); 5.84 (*dd*, $J_{3,2}$ = 6, $J_{3,4}$ = 3, H–C(3)); 5.93 (*d*, $J_{2,3}$ = 6, H–C(2)). MS: 150 (3, M^+), 107 (24), 92 (14), 91 (11), 80 (100), 79 (36), 71 (3), 65 (3), 58 (7), 43 (17), 39 (7).

*Methyl 6-Methyl-8,9,10-trinorborn-5-en-2-*exo-*yl Ketone* (**37**): IR: 1710, 1172, 1020, 800. ^{1}H-NMR (400 MHz)[3]: 1.28–1.38 (*m*, H_s–C(7), H_a–C(7), H_{endo}–C(6)); 1.77 (*s* with f.s., CH_3–C(3)); 1.89 (*dt*, $J_{6exo,6endo} \approx 12$, $J_{6exo,5endo} \approx 4.5$, H_{exo}–C(6)); 2.23 (*s*, CH_3CO–C(5)); 2.35 (*dd*, $J_{5endo,6endo} \approx 9$, $J_{5endo,6exo} \approx 4.5$, H_{endo}–C(5)); 2.73 (br. *s*, H–C(4)); 2.80 (br. *s*, H–C(1)); 5.66 (br. *s*, H–C(2)). MS: 150 (2, M^+), 107 (20), 92 (14), 91 (12), 80 (100), 79 (43), 71 (7), 66 (16), 58 (9), 43 (37), 39 (12).

*Methyl 5-Methyl-8,9,10-trinorborn-5-en-2-*exo-*yl Ketone* (**38**): IR: 1710, 1172, 1020, 918, 870, 818, 778. ^{1}H-NMR (400 MHz)[3]: 1.24 (*ddd*, $J_{6endo,6exo}$ = 11.5, $J_{6endo,5endo}$ = 8.8, $J_{6endo,7s}$ = 2.5, H_{endo}–C(6)); 1.29 (*d*, $J_{7a,7s}$ = 8.5, H_a–C(7)); 1.36 (*dm*, $J_{7s,7a}$ = 8.5, $J_{7s,6endo} \approx 2.5$, $J_{7s,5endo}$ = 1.5, H_s–C(7)); 1.74 (*s* with f.s., CH_3–C(2)); 1.90 (*dt*, $J_{6exo,6endo}$ = 11.5, $J_{6exo,5endo}$ = 4.4, $J_{6exo,1}$ = 3.4, H_{exo}–C(6)); 2.21 (*s*, CH_3CO–C(5)); 2.44 (*dd*, $J_{5endo,6endo}$ = 8.8, $J_{5endo,6exo}$ = 4.5, $J_{5endo,7s}$ = 1.5, H_{endo}–C(5)); 2.62 (br. *s*, H–C(1)); 2.91 (br. *s*, H–C(4)); 5.62 (br. *s*, H–C(3)). MS: 150 (11, M^+), 107 (13), 91 (7), 80 (100), 79 (38), 71 (10), 65 (5), 55 (5), 51 (5), 43 (23), 39 (10).

*Methyl 6-Methyl-8,9,10-trinorborn-5-en-2-*endo-*yl Ketone* (**39**): IR: 1710, 1181, 1170, 1118, 992, 915, 812, 782, 730. ^{1}H-NMR (400 MHz)[3]: 1.30 (*d*, $J_{7a,7s}$ = 8, H_a–C(7)); 1.49 (*dm*, $J_{7s,7a}$ = 8, $J_{7s,6endo}$ = 2.5, H_s–C(7)); 1.52 (*ddd*, $J_{6endo,6exo}$ = 12, $J_{6endo,5exo}$ = 4.2, $J_{6endo,7s}$ = 2.4, H_{endo}–C(6)); 1.70 (*ddd*, $J_{6exo,6endo}$ = 12, $J_{6exo,5exo}$ = 8.5, $J_{6exo,1}$ = 3, H_{exo}–C(6)); 1.73 (*s* with f.s., CH_3–C(3)); 2.12 (*s*, CH_3CO–C(5)); 2.64 (br. *s*, $J_{1,6exo}$ = 3, H–C(1)); 3.01 (*quint.*, $J_{5exo,6exo}$ = 9, $J_{5exo,6endo}$ = 4.2, $J_{5exo,4}$ = 4, H_{exo}–C(5)); 3.14 (br. *s*, H–C(4)); 5.34 (br. *s*, H–C(2)). MS: 150 (9, M^+), 107 (5), 92 (6), 91 (8), 80 (100), 79 (41), 65 (4), 55 (5), 43 (19), 39 (11).

*Methyl 5-Methyl-8,9,10-trinorborn-5-en-2-*endo-*yl Ketone* (**40**): IR: 1710, 1182, 1170, 1138, 1118, 1108, 1035, 992, 800, 785. ^{1}H-NMR (400 MHz)[3]: 1.30 (*d*, $J_{7a,7s}$ = 8, H_a–C(7)); 1.50 (*dm*, $J_{7s,7a}$ = 8, $J_{7s,6endo}$ = 2.5, H_s–C(7)); 1.57 (*ddd*, $J_{6endo,6exo}$ = 11.5, $J_{6endo,5exo}$ = 4.4, $J_{6endo,7s}$ = 2.5, H_{endo}–C(6)); 1.63 (*s* with f.s., CH_3–C(2)); 1.68 (*ddd*, $J_{6exo,6endo}$ = 11.5, $J_{6exo,5exo}$ = 8.5, $J_{6exo,1}$ = 4, H_{exo}–C(6)); 2.18 (*s*, CH_3CO–C(5)); 2.80 (br. *s*, $J_{1,6exo}$ = 4, H–C(1)); 3.03 (br. *s*, H–C(4)); 3.08 (*quint.*, $J_{5exo,6exo}$ = 8.5, $J_{5exo,6endo}$ = 4.4, $J_{5exo,4}$ = 4.5, H_{exo}–C(5)); 5.72 (br. *s*, H–C(3)). MS: 150 (11, M^+), 107 (11), 92 (7), 91 (9), 80 (100), 79 (40), 71 (9), 65 (5), 55 (4), 43 (21), 39 (11).

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