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Synthesis of Some Conjugated Caradienes from 3-Carene by the Wittig Reaction and Their Reactivity in the Diels-Alder Reaction

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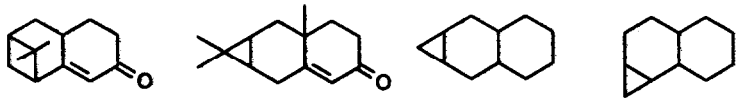
The applicability of the Wittig reaction for the preparation of conjugated *cis*-caradienes was studied by the preparation of 4-methyl-3(10)-carene (**27**). The method was applied for the study of the synthesis of 3-vinyl-3-apocarene (**6**), 4-methylene-3(10)-carene (**7**), 4-methyl-2-methylene-3(10)-carene (**8**), 4-isopropenyl-3-carene (**9**) and 4-isopropenyl-3-caren-2a-ol (**11**) starting from 3-carene (**20**). The reactivity of conjugated *cis*-caradienes **6**, **7** and **9** in the Diels-Alder reaction has also been studied.

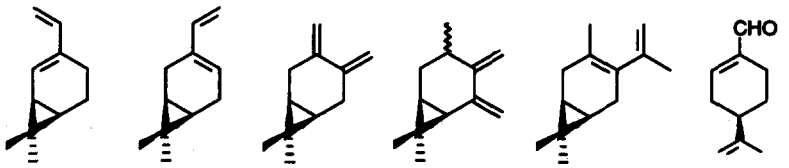
Various patents describe the synthesis of fragrance substances with a bridged or fused decalin skeleton. Very often these compounds have functional groups such as carbonyl, hydroxy and epoxy groups and C=C bonds.[1] Some typical structures are given below. The ketone **2** is a derivative of the parent hydrocarbon **3** tricyclo[5.4.0.0^{3,5}]undecane. Two medicines popular in the Far East, Chinese Spikenard oil[2] (*Nardostachys jatamansi*) and the root of *Aristolochia debilis* [3] contain sesquiterpenoids, which are derivatives of tricyclo[5.4.0.0^{2,4}]undecane (**4**).



1[1a] **2**[1b] **3** **4**

The tricyclo[5.4.0.0^{3,5}]undecane **3** and the tricyclo[5.4.0.0^{2,4}]undecane **4** ring systems can be synthesized by two main routes: the Robinson annulation of suitable caranones and the Diels-Alder reaction. The Robinson annulation reaction is the most commonly used method to synthesize compounds with decalin structure, and therefore derivatives of **3** and **4** have mainly been prepared by this route.[4]

Studies dealing with the Diels-Alder reaction of caradienes or carenones are sparse.[5] However, interesting derivatives of tricyclo[7.1.1.0^{2,7}]undecane **1** have been prepared from dienes with pinane skeleton using different dienophiles. The synthesis of conjugated caradienes **5** - **9** suitable for the Diels-Alder reaction was taken as the subject of this study. Earlier attempts to prepare these dienes through aminomethylation of 3-carene and *cis*-4-caranone proved unsuccessful because of complicated product mixtures.[6] In the present work the Wittig reaction of α,β-unsaturated carbonyl compounds obtained from 3-carene was chosen as the method to prepare conjugated *cis*-caradienes.

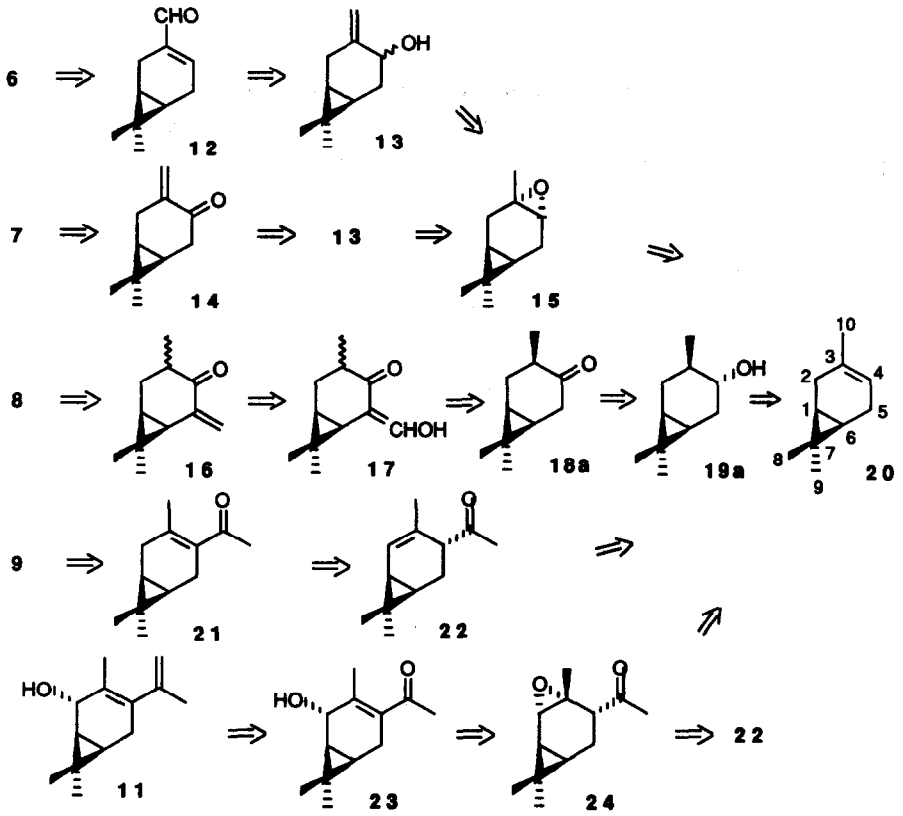


RESULTS AND DISCUSSION

The two conjugated caradienes **5** and **6** are known. **5** was synthesized from (-)-perillaldehyde (**10**).[5a,b] Rienäcker *et al.*[5c] have reported the reaction of **6** with 4-methyl-1,2,4-triazoline-3,5-dione, but they did not give any details about the preparation or spectral data of **6**. The conjugated dienes **7**, **8** and **9** were still unknown. Retrosynthetic analysis of **6**, **7**, **8** and **9** reveals possible synthetic pathways starting from 3-carene (**20**) (Scheme 1).

The preparation of starting materials. The carbonyl compounds **12**, **14**, **16**, **21**, and **23** used in the Wittig reaction were synthesized from 3-carene (**20**) as presented in Scheme 1.

Scheme 1

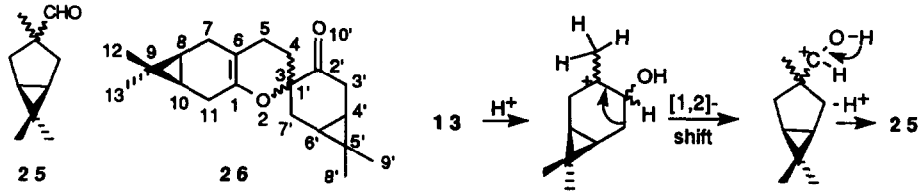


3-caren-10-al (12). Gollnick and Schade[7] and Kropp[8] have reported that the oxidation of *trans*-3(10)-caren-4-ol (**13a**) according to Brown and Garg[9] yielded 3-caren-10-al (**12**) instead of the corresponding ketone **14**. Isaeva and Andreeva,[10] however, had stated earlier that the chromic acid oxidation of **13a** yielded the corresponding ketone **14**.

The chromium (VI) oxidation of α,β-unsaturated alcohols may lead to several products.[11] The corresponding α,β-unsaturated ketone in the case of 3(10)-caren-4-ols, is 3(10)-caren-4-one (**14**). Cr(VI) reagents have been observed to add oxygen at the C=C bond leading to an epoxide which subsequently rearranges to a carbonyl compound.[11] This mechanism could explain the formation of 3-caren-10-al (**12**).

The chromic acid oxidation[7] of a mixture of 3(10)-caren-4-ols prepared by the isomerization of 3α,4α-epoxycarane (**15**) with aluminium isopropoxide[12] yielded the product mixture containing 8 % of 3,6,6-trimethylbicyclo[3.1.0]hexane-3-carboxaldehyde (**25**), 39 % of 3(10)-caren-4-one (**14**), 50 % of 3-caren-10-al (**12**) and 3 % of an unknown product. Separation of the components by steam distillation or distillation under reduced pressure caused the dimerization of the ketone **14** to **26**.

Scheme 2



The aldehyde **25** is known as a rearrangement product of 3α,4α-epoxycarane (**15**) effected by Lewis acids.[13] In this oxidation the acidic reaction conditions could lead to the formation of a carbocation intermediate followed by the [1,2]-shift of the 4,5-bond resulting in ring contraction (Scheme 2).

As a consequence of the dimerization of **14**, 3-caren-10-al (**12**) was isolated by steam distillation as a pure compound and used for the Wittig reaction.

3(10)-caren-4-one (14). Because the ketones **12** and **14** could not be separated on a larger scale, the oxidation of 3(10)-caren-4-ols was carried out by CrO_3/3,5-dimethylpyrazole.[14] The mixture oxidized in 1.5 h with 80 % yield to 3(10)-caren-4-one (**14**) (89 %), 3(10)-caren-10-al (**12**) (7 %), and unidentified products (4 %). The ketone **14** and the aldehyde **12** were identified by comparison of GC retention times and mass spectra to those of the authentic samples.

3(10)-caren-4-one (**14**) was used in the Wittig reaction immediately after its preparation because of its great tendency to dimerize.

The carbonyl compounds **16**,[15] **21**,[16] and **23**[16] were prepared according to the literature methods.

The Wittig reaction. The Wittig reaction is a widely used method in the preparation of alkenes, dienes, and polyenes.[17] With aldehydes and ketones the simplest ylide, methylenetriphenylphosphorane, yields corresponding alkenes with a terminal C=C bond.

The Wittig reaction proceeds more rapidly in DMSO than in other solvents, and the yield of alkene is frequently superior. Benzene, however, is an undesirable side product.[18]

Some ketones with at least one α-position fully substituted by bulky alkyl groups have been reported to be inert to methylenetriphenylphosphorane or react only slightly.[19] Low yields have been encountered with easily enolizable ketones.[18b,19f,g,20] According to Adlercreutz and Magnusson[21] the yield was reduced by the competitive enolate formation. In the presence of α-protons the preferred enolization over the Wittig reaction is the consequence of the steric hindrance in the reaction between the ylide and the carbonyl compound.[20a]

Fitjer and Quabeck[22] have performed the Wittig reaction for a series of sterically hindered ketones using potassium *tert*-butoxide as a base. Excellent yields of isolated products (90 - 96 %) were reported for the ketones that had not reacted under other reaction conditions or had given low yields. No formation of benzene was detected.

Despite its utility in the preparation of natural products the Wittig reaction has hitherto been little used in carane chemistry.[23] In this aspect the procedures of Greenwald *et al.*[18a] [**method A** (methylsulfinyl carbanion in DMSO)] and Fitjer and Quabeck[22] [**method B** (potassium *tert*-butoxide in diethyl ether)] were applied to several suitable carane compounds.

4-Methyl-3(10)-carene (**27**) is known to form upon the pyrolysis of 4-acetoxymethylcarane (**28**),[24] but its preparation by Wittig reaction has not been reported. *cis*-4-Caranone (**18a**) was chosen as a model compound to compare the methods A[18a] and B.[22] Both methods produced a mixture of two isomeric 4-methyl-3(10)-carenes (**27**) and contained some *cis*-4-caranone which had partly isomerized to the *trans*-4-caranone. The ratio of the two isomers of **27** resulting from these two methods was clearly different.

Method A yielded *cis:trans* 28:72 and method B 76:24, respectively. In the method A the isomerization of the starting material **18a** was more pronounced (*cis:trans* 88:12) than in the method B (*cis:trans* 94:6). A typical Wittig reaction of **18a** by the methods A and B is presented in Table 1.

In the case of method A a sample from the reaction mixture contained some benzene. *cis*-4-Caranone reached the end of the reaction in three hours neither heating (75 °C) nor extension of the reaction time (40 h) increased the yield of **27**. The unequal ratio of *cis* and *trans* isomers of **27** may be derived from the different pK_a's of methylsulfinyl carbanion and potassium *tert*-butoxide. In method B the carbonyl addition may occur faster than the enolization by potassium *tert*-butoxide and *cis*-4-caranone mainly methylenated to*cis*-4-methyl-3(10)-carene. **18a** enolizes easily with methylsulfinyl carbanion and the epimerized *trans*-4-caranone seems to react faster than *cis*-4-caranone.

The greater reactivity of *trans*-4-caranone in the Wittig reaction can be explained by examining the Newman projection of *trans*-4-caranone (**18b**) along the C-3,C-4-bond.

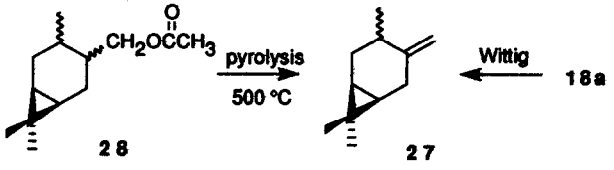
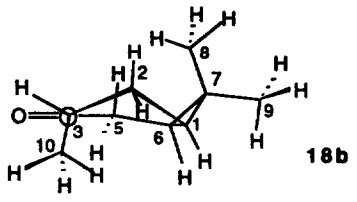


Table 1. The Wittig Reaction of cis-4-Caranone (18a) According to Methods A[18a] and B.[22]

Method	Temp.	Time/h	Composition of the product mixture/%		Yield of 27/%	
			27 (*cis:trans*)	Unreacted 18 (*cis:trans*)	Unknown	
A	rt	18	88 (28:72)	9 (88:12)	3	68
B	rt	18	83 (76:24)	17 (94:6)		77



18b

In the *cis* isomer the carbonyl and methyl group are spatially rather close to each other and therefore, the approach of methylenetriphenylphosphorane is hindered. In the case of the *trans* isomer the ylide has more space to approach and to form *trans*-4-methyl-3(10)-carene (**27**) through a "4-centered mechanism".[25]

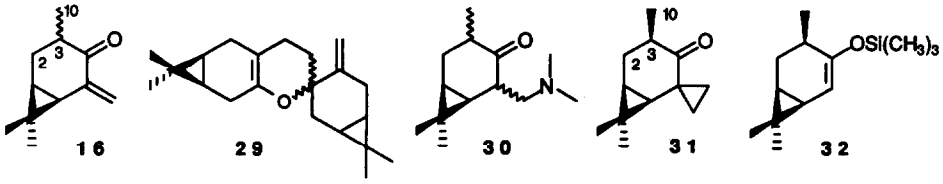
Cis- and *trans*-4-methyl-3(10)-carene (**27**) were identified by their 1D and 2D ^{1}H and ^{13}C NMR spectra.

The yields in both methods were lower than expected. This is probably due to the observed enolization, and in method A due to the decomposition of the ylide. It can be concluded that both methods can be equally well applied in the Wittig reaction of caranals and caranones.

3-Vinyl-3-apocarene (**6**). Conjugated caradiene **6** was prepared from 3-caren-10-al (**12**) according to the method A. The Wittig reaction proceeded smoothly. After stirring for 16 h at room temperature the starting compound had reacted completely and only one product, 3-vinyl-3-apocarene (**6**) was produced. In this case methylenetriphenylphosphorane could freely approach the carbonyl group in **12**, and as a result the yield (84 %) was better than in the Wittig reaction of **18a**.

4-Methylene-3(10)-carene (**7**).The Wittig reaction of 3(10)-caren-4-one (**14**) proved to be problematic. The Wittig reaction was performed by both methods A and B. GC-MS analysis showed that by both methods the reaction conditions caused dimerization of the starting compound **14** and led to cycloaddition of the desired product 4-methylene-3(10)-carene (**7**) with **14**. The π-electrons of the methylene group at the α-position influence the approach of the Wittig reagent because the conjugation to the carbonyl group leads to competitive reactions such as [4+2] cycloadditions (products **26** and **29**). The separation of the very reactive conjugated diene **7** did not succeed without its subsequent dimerization. The formation of 4-methylene-3(10)-carene (**7**) was confirmed by the diene synthesis with maleic anhydride. The adduct **29** was separated and identified from the 1D and 2D ^{1}H and ^{13}C NMR spectra. Upon gentle heating (36 °C method B) **14** partly dimerized to **26**.

4-Methyl-2-methylene-3(10)-carene (8). Attempts to prepare 4-methyl-2-methylene-3(10)-carene (8) through the Wittig reaction of the aminoketone **30** according to the method of Greenwald *et al.*[18a] resulted in deamination and the formation of the spiro compound **31**.[6,26]



Some sterically hindered α,β-unsaturated ketones have been reported to react with the conjugate addition to the C=C bond.[27] 94 % of the aminoketone **30** prepared through the silylenolether **32** had the *cis* form with respect to the methyl group at C-3. As in the case of 4-caranone (**18**) the *cis* methyl isomer of **30** is more hindered than the *trans* isomer and the bulky aminomethyl group on the side of the carbonyl group further increased the steric hindrance around the carbonyl group. This steric crowding retarded the Wittig reaction and the basic reaction conditions deaminated the starting compound **30** partly to **16**. The α,β-unsaturated ketone **16** favoured conjugate addition with methylenetriphenylphosphorane and yielded spiro[caran-5,1'-cyclopropan]-4-one (**31**). Comparison of some ^{1}H NMR chemical shifts and the coupling constants of **31** with the corresponding values of the *cis* and *trans* isomers of **16**[15] established that the spiro ketone **31** had the methyl group at C-3 in the *cis* position (Table 2).

Because the diene **8** was not obtained from the aminoketone **30**, and the methylene ketone **16** only partly reacted to **31**, it is likely that **16** is less reactive than **30** in the Wittig reaction.

Both methods A and B were utilized in the reaction of 5-methylene-4-caranone (**16**). An overnight reaction (18 h) of **16** with methylenetriphenylphosphorane in DMSO at room temperature using methylsulfinyl carbanion as a base resulted in a product mixture which according to GC-MS analysis contained 66 % of 4-methyl-3(10)-carene (**27**), 26 % of **16**, 4 % of the spiro compound **31** and 3 % of triphenylphosphine, but no diene **8**.

The reaction of **16** with the ylide by method B did not yield the diene **8**. When the methylene ketone **16** was

Table 2. Some ^{1}H Chemical Shifts and Coupling Constants of Spiro[caran-5,1'-cyclopropan]-4-one (31) and 5-Methylene-cis- and trans-4-caranone (16). Target Nuclei in Parenthesis.[a]

Compound	Proton/δ_H								Ref.
	10	3				2a		2e	
		J_{HH}/Hz				J_{HH}/Hz			
31	0.90	2.46	6.6 (10),	13.4 (2a),	6.0 (2e)	1.31	14.6 (2e)	2.22	27
cis-**16**	1.00	2.31	6.5 (10),	13.2 (2a),	6.5 (2e)	1.32	14.4 (2e)	2.31	15
trans-**16**	1.21	2.35	7.2 (10),	5.0 (2a),	2.5 (2e)	1.39	15.0 (2e)	2.03	15

[a] See **31** for the numbering of the nuclei, a = axial, e = equatorial.

added to the reaction mixture the yellow colour of the ylide solution disappeared and a white precipitate was obtained. In addition to the starting compound 5-methylene-4-caranone (**16**) the reaction product contained some triphenylphosphine. In the beginning the isomer ratio of **16** was cis:trans 32:68 and at the end of the reaction 67:34, respectively. The change in the isomer ratio was obviously caused by the basic reaction conditions. The white precipitate could mainly be a methyltriphenylphosphonium salt formed from methylenetriphenylphosphorane due to proton transfer through enolization. The protonated methylenetriphenylphosphorane thermally decomposes[28] in GC and appears as a triphenylphosphine peak in mass spectrum. In the case of methylenetriphenylphosphorane the hydrolytic cleavage at the end of the Wittig reaction should yield methyldiphenylphosphonium oxide.[29] GC-MS analysis, however, did not indicate the presence of this phosphonium oxide with *m/z* 216.

Because neither of the methods A and B promoted the Wittig reaction of **16** in the desired direction, *n*-butyllithium was used as a base. The reaction was performed in anhydrous diethyl ether at room temperature.[30] According to GC-MS analysis the product mixture contained 28 % of a compound with *m/z* 162, 7 % of **27**, 44 % of the starting compound **16**, 6 % of **31**, 2 % of triphenylphosphine, 8 % of *n*-butyldiphenylphosphine oxide and 5 % of a compound with *m/z* 326. The structure of the compound with *m/z* 162 was not determined. It could be either the diene **8** or 5-vinyl-4-carene. The latter would be the result of the rare 1,4-addition of the Wittig reagent as described in the review of Maerker.[20a] The compound with *m/z* 326 could be **33** the adduct of **16** and **8**, or the adduct of **16** and 5-vinyl-4-carene. *n*-Butyldiphenylphosphine oxide was formed from the reaction product of methylenetriphenylphosphorane and *n*-butyllithium.

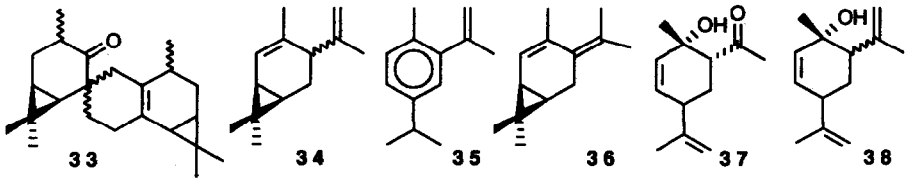
The Wittig reaction of hindered ketones has been promoted thermally.[22] In the case of the aminoketone **30** and 5-methylene-4-caranone (**16**), heating is excluded because it would increasingly lead to [4+2] cycloaddition as mentioned above for **14**. As a consequence the Wittig reaction does not apply to the preparation of the conjugated diene **8**.

4-Isopropenyl-3-carene (**9**). Two approaches were used to prepare 4-isopropenyl-3-carene (**9**):

1) from 4-acetyl-3-carene (**21**)
2) from Wittig reaction of 4α-acetyl-2-carene (**22**) with subsequent isomerization of 4-isopropenyl-2-carene (**34**) to 4-isopropenyl-3-carene (**9**)

Friedel-Crafts acylation of 3-carene easily produces 4α-acetyl-2-carene (**22**).[16] The ketone **22** partly isomerizes under basic conditions (CH_3ONa/CH_3OH or NaH/C_6H_6) to the *cis*-epimer of **22** and 4-acetyl-3-carene (**21**). In the presence of NaH ca. 10 % of an aromatic ketone with *p*- or *m*-cymene structure was found in the mixture.[31]

The Wittig reaction of 4-acetyl-3-carene (**21**) was carried out on a mixture of **21**, and **22** (75:25, respectively) using the method A. The product mixture contained 51 % of **34**, 44 % of **9**, and 5 % of an unknown compound with *m/z* 176. Some isomerization must have occurred during the reaction because the ratio of the starting compounds and that of the corresponding alkenes was different. The Wittig reaction of the pure 4α-acetyl-2-carene (**22**) yielded (method A) in one hour a product mixture which contained 54 % of **34**, 20 % **9**, 9 % of **35**, 8 % of **21**, 5 % of **22**, and 4 % of an unknown compound and same compounds were also found by method B.



33 34 35 36 37 38

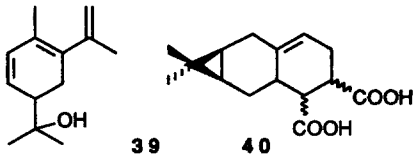
The presence of **9** and **21** in the product mixture confirmed that the basic reaction conditions caused the partial isomerization of the starting compound **22** to **21**. The larger part of **34** than **9** in the reaction product indicates the relative rate of reaction for 4α-acetyl-2-carene (**22**) is greater than that for **21** and that the Wittig reaction of these compounds is slower than equilibration. The lower reactivity of 4-acetyl-3-carene (**21**) presumably depends on the conjugation of the carbonyl group and the C=C bond.

The isomerization of 4-isopropenyl-2-carene (**34**) to 4-isopropenyl-3-carene (**9**) was attempted with K-*tert*-butoxide in DMSO at different temperatures. The reaction was carried out for a mixture of **34** and **9** (9:1, respectively). At ambient temperature (25 - 40 °C) **9** was initially observed to isomerize partly to **34** which slowly started to form a new compound. At 70 °C **34** isomerized in two hours to this same compound but **9** remained unreacted. The isomerized product was identified as 4-isopropylidene-2-carene (**36**).

The transoid diene **36** is not capable of [4+2] cycloaddition reaction. Therefore the preparation of 4-isopropenyl-3-carene (**9**) starting from 4α-acetyl-2-carene (**22**) through isomerization of 4-isopropenyl-2-carene (**34**) cannot be achieved this way. The Wittig reaction of 4-acetyl-3-carene (**21**) yielded the corresponding diene **9**, but the yield was low because of the competitive isomerization reaction of the starting compound under basic conditions.

4-Isopropenyl-3-caren-2α-ol (**11**). 4-Acetyl-3-caren-2α-ol (**23**) is produced by treating the easily available epoxide **24** with alkaline medium.[31,32] The Wittig reaction of **23** was performed using methods A and B. In addition to **23** the starting material contained 8 % of **37**. The reaction was slightly exothermic and led rapidly (method A two hours and B one hour) to a complicated product mixture. The crude product from the method A contained 51 % of the desired product, 4-isopropenyl-3-caren-2α-ol (**11**), 10 % of **38**, 7 % of **35**, 7 % of **9**, 5 % of **23**, 4 % of **34**, 2 % of **37**, and 14 % of unknown products. The product mixture from the method B contained 25 % of **11**, 22 % of **39**, 12 % of **38**, 13 % of **35**, 6 % of **9**, 4 % of **34**, 7 % of presumably a derivative of acetophenone with *m/z* 190 and 11 % of unknown products.

Attempts to separate the product **11** by distillation at reduced pressure, by flash chromatography, and by preparative thin layer chromatography (PTLC) failed and resulted in the isomerized product **39**. This was not unexpected because the starting compound **23** was also found to be sensitive to heat and acid and could not be purified by distillation.[32a] Purification of **11** was also attempted through a *p*-nitrobenzoate derivative, but it decomposed to **35** in GC, TLC and on standing. The presence of **11** in the crude product was verified with MS and with TLC. Upon spraying with ethanolic anisaldehyde-H_2SO_4 solution **11** appeared as a dark blue spot and **39** as a purple one. Compounds **11** and **39** had clearly different mass spectra. The base peak of **39** with *m/z* 59 corresponding to the $[(CH_3)_2C{=}OH]^+$ ion was deduced according to Stevenson's Rule from the loss of the largest radical attached to the α-carbon of an alcohol. The compound **39** had a very small molecular ion peak, $M^{+\cdot}$, typical for a tertiary alcohol. **11** also had a small molecular ion peak, but the loss of H_2O from



39 40

$M^{+\cdot}$ of **11** was prominent whereas $(M - 18)^+$ of **39** was hardly perceptible. $(M - 18)^+$ was followed by the loss of $CH_3\cdot$ in both molecules. Because of this loss the most intense fragment of **11** was *m/z* 159 while in the mass spectrum of **39** this fragment was negligible.The formation of **39** could be thought as a consequence of the homoallylic rearrangement of **11**.[33]

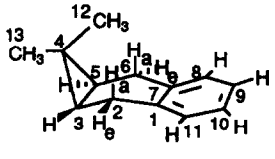
The Wittig reaction of 4-acetyl-3-caren-2α-ol (**23**) has no practical use because of many side products and the great tendency of **11** to rearrange to **39**.

The Diels-Alder reaction of conjugated dienes.

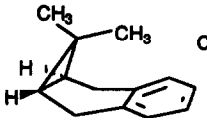
The suitability of the conjugated caradienes **6**, **7** and **9** for the preparation of tricyclo[5.4.0.$0^{3,5}$]undecane derivatives **3** was studied by the reaction with maleic anhydride or tetracyanoethylene.

The diene synthesis of 3-vinyl-3-apocarene (**6**) with maleic anhydride in dry benzene occurred under reflux in three hours. The direct hydrolysis of the resulting anhydride yielded the corresponding dicarboxylic acid **40**, m.p. 180 - 185 °C (decomp.).

The melting point of **40** depended on the solvent from which it was recrystallized. Upon crystallization from aqueous ethanol the dicarboxylic acid became a liquid at about 143 °C. When crystallized from absolute ethanol-petroleum ether mixture it decomposed at 180 - 185 °C. Thermogravimetric analysis (TG, DTG) (25 - 300 °C) of the two different samples of **40** showed that in aqueous conditions the acid binds two moles of water and in anhydrous conditions one mole of ethanol to itself. Decarboxylation[34] of the disodium salt of **40** by $K_3[Fe(CN)_6]$ in 5 % NaOH yielded benz-3-apocarene (**41**). The structure of the novel hydrocarbon **41** was verified with MS, 1D and 2D ^1H and ^{13}C NMR spectra. There are two possible conformations for **41** (a and b). The structure a is more probable than b, because the anisotropy of the aromatic ring has only a negligible effect on the geminal *syn* methyl group compared to the corresponding methyl group of 3-carene (0.81 ppm *syn*-CH_3 and 1.11 ppm *anti*-CH_3 for **41** and 0.76 ppm and 1.04 ppm, respectively for 3-carene[35]). In structure b the effect of the ring current would be notable. H,H-COSY spectrum showed that the protons H-2, H-3, and H-5 as well as H-3, H-5, and H-6 were respectively coupled. The splitting pattern of the proton quartet with four additional weak "inside lines" points out to a long-range coupled [AA'MM'XX'] system.[36] The coupling between H-2e and H-3, as well as H-6e and H-5 is 8 Hz, and the coupling between and H-2a and H-3, as well as H-6a and H-5 is 5 Hz. This indicates that the dihedral angles (H-2e)-(C-2)-(C-3)-(H-3) and (H-6e)-(C-6)-(C-5)-(H-5) are smaller than the dihedral angles (H-2a)-(C-2)-(C-3)-(H-3) and (H-6a)-(C-6)-(C-5)-(H-5). The ring structure was rather flat and very symmetric. The distance between axial H-2 and -6 and the geminal *syn*-methyl group in the structure a was increased because of the flatness of the saturated six-membered ring. **41** has a plane of symmetry in both conformations and shows only eight carbon signals in the ^{13}C spectrum. A similar flatness and symmetry were reported for the structure **41** where the geminal methyl groups were replaced by two bromine atoms.[37]

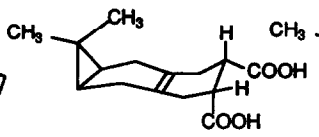


a

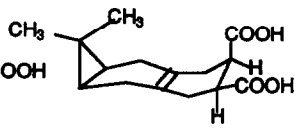


b

4 1



anti



syn

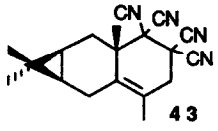
4 2

The formation of 4-methylene-3(10)-carene (**7**) in the Wittig reaction was confirmed by the reaction with maleic anhydride. The compound mixture containing 36 % of **7** reacted in dry benzene at room temperature in 18 h. Hydrolysis of the resulting anhydride and the acidification with HCl precipitated the dicarboxylic acid **42**, m.p. 186 - 188 °C. This dicarboxylic acid was a mixture of two isomers. Each carbon and geminal methyl proton signals had a small accompanying signal. The difference between the chemical shifts (^{1}H and ^{13}C) was largest between the geminal *syn*-methyl groups. The upfield shift of 0.05 ppm (^{1}H) might be a consequence from an additional anisotropic effect of a carbonyl group, when one of the two carboxyl groups is in the axial position and at *cis* side with respect to the cyclopropyl ring. The two isomers were the *anti* and *syn* conformations of the dicarboxylic acid **42**. The ratio of the *anti* and *syn* adducts, 3:1, respectively, was calculated from the peak intensities of the geminal methyl groups in ^{1}H NMR spectrum. The present ^{1}H and ^{13}C NMR chemical shifts were consistent with the values presented previously.[6,38]

Decarboxylation[34] of 4,4-dimethyltricyclo[5.4.0.0^{3,5}]undec-1(7)-en-9,10-dicarboxylic acid (**42**) yielded a hydrocarbon with identical spectral data (MS, ^{1}H and ^{13}C NMR) to those of benz-3-apocarene (**41**) and thus confirmed that **7** has a conjugated diene structure.

The diene synthesis of 4-isopropenyl-3-carene (**9**) was performed for a mixture of **9** (41 %) and **34**. The reaction with maleic anhydride neither without a solvent in a sealed tube at different temperatures (100 - 130 °C, 11 - 24 h), nor in dry benzene, or *m*-xylene yielded any adduct, or else gave a product mixture with only a very low yield.

Probably due to the steric hindrance of the methyl group at C-3 of the diene **9** maleic anhydride was not sufficiently reactive as a dienophile. Therefore, tetracyanoethylene was used in place of maleic anhydride. Diels-Alder reaction of 4-isopropenyl-3-carene (**9**) with tetracyanoethylene in dry benzene under reflux was completed in 30 min. The adduct **43**, purified by sublimation had melting point of 228 °C.



4 3

Conclusions

The synthesis of the *cis*-caradienes 3-vinyl-3-apocarene, 4-methylene-3(10)-carene, 4-methyl-2-methylene-3(10)-carene, 4-isopropenyl-3-carene, and 4-isopropenyl-3-caren-2α-ol by the Wittig reaction have been

studied. The Wittig reaction of *cis*-4-caranone was used to compare the two procedures; methylsulfinyl carbanion in DMSO (method A), and potassium-*tert*-butoxide in diethyl ether (method B). In both cases the strongly basic reaction conditions led to the isomerization of the starting compound and subsequently to the formation of *cis*- and *trans*-4-methyl-3(10)-carene. Both methods could be equally well applied in the Wittig reaction of the preceding carbonyl compounds with methylenetriphenylphosphorane.

The Wittig reaction of 3-caren-10-al proceeded smoothly and yielded only 3-vinyl-3-apocarene. The synthesis of the other mentioned *cis*-caradienes encountered difficulties such as enolization, dimerization and conjugate addition to the C=C bond, which led to complicated product mixtures or hindered the Wittig reaction.

3-Vinyl-3-apocarene, 4-methylene-3(10)-carene, and 4-isopropenyl-3-carene reacted in the Diels-Alder reaction with maleic anhydride or tetracyanoethylene in the expected way.

Experimental

General. 3-Carene used in this study was obtained from a distillation fraction of the sulfate turpentine of Veitsiluoto Oy, Finland (Oulu Oy). Gas chromatographic analyses were performed on a 25-m fused, methyl silicone, dimethylsilicone, or nitroterephthalate modified polyethylene glycol capillary column. Chromatographic separations were accomplished by standard flash chromatography[39] techniques (Merck silica gel 60, 230 - 400 mesh) or by pre-coated preparative layer chromatography plates of 2 mm thickness (Merck silica gel 60 F_{254}). The progress of the reactions was monitored by thin layer chromatography (TLC) (Merck pre-coated glass supported silica gel 60 F_{254} plates, 0.25 mm layer). Short wave length ultraviolet light and/or spraying with an ethanolic mixture of anisaldehyde (5 %) and conc. sulfuric acid (5 %), and keeping in oven (120 °C) 10 - 45 s were used to visualize the spots. NMR spectra were recorded on a Jeol GX-400, Bruker AM-200, or Jeol FX-100 MHz spectrometer. Chemical shifts are given in ppm relative to TMS and coupling constants in Hz. Unless otherwise noted, the solvent, $CDCl_3$ (δ = 7.26 ppm) was used as an internal standard. The signs of the coupling constants were not determined. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet), m_c (multiplet centred at) and br (broad). For protons a = axial, e = equatorial, *c* = *cis*, *t* = *trans*. Electron ionization (EI) and chemical ionization (CI) mass spectra were determined on a Kratos MS80RF Autoconsole at an ionization voltage of 70 eV and 150 eV, respectively. CI was performed with ammonia or isobutane as reagent gas. The temperature at the ionization chamber was 250 °C. The sample was injected through a gas chromatograph. Boiling points and melting points are uncorrected. Thermogravimetric runs (TG, DTG) were carried out on a thermobalance (Mettler TG 50) in a temperature range 25 - 300 °C. The sample quantity varied between 6.1 and 6.5 mg. The dynamic runs were made under N_2 with the flow rate 200 ml/min, and with the heating rate 2 °C/min.

General Procedures for the Wittig Reactions. Method A.[18a] 4-Methyl-3(10)-carene (3-methylene-4,7,7-trimethylbicyclo[4.1.0]heptane) (**27**). NaH (2.9 g, ca. 66 mmol, a 55 % mineral oil dispersion) was placed in a 500 ml round bottomed flask equipped with a thermometer, a rubber septum, reflux condenser fitted with a three way stopcock, and a magnetic stirrer. The system was flushed by evacuating and filling with pre-dried N_2. Anhydrous DMSO (25 ml) was added via syringe and the mixture was heated at 70 °C until the evolution of hydrogen ceased. The solution was cooled in an ice-water bath, and methyltriphenylphosphonium bromide (24.0 g, 67 mmol) in DMSO (50 ml) was added. The ylide was stirred at room temperature for 30 min. *Cis*-4-caranone (**18a**) (10.0 g, 66 mmol) in DMSO (10 ml) was added. The colour of the mixture changed from greenish to brown and the temperature rose to 30 °C. After stirring at room temperature for 4 h, the solution was poured into ice-water (600 ml). The aqueous phase was extracted with petroleum ether. The precipitated triphenylphosphine oxide (in organic phase) was filtered off. The combined organic extracts were washed with a 50 % saturated NaCl solution until the solution stayed neutral. After drying over $MgSO_4$ the petroleum ether was removed under reduced pressure. According to GC-MS analysis the residue (9.0 g) contained 88 % of two isomeric 4-methyl-3(10)-carenes (**27**), 9 % of *cis*- and *trans*-4-caranones (**18**), and 3 % of an unknown hydrocarbon with *m/z* 148. The mixture of *cis*- and *trans*-4-methyl-3(10)-carenes (28:72, respectively) distilled at 67 - 68 °C/12 Torr. Ref.[16] b.p. 70 °C/15 Torr. Yield 7.1 g (72 %). The identification based on the 1D and 2D ^1H and ^{13}C the NMR spectra was performed directly from the mixture. *Trans*-**27**: ^1H NMR (400 MHz): δ 4.58 (td, 1H, H-10A, $J_{10A,2a}$ = 2.4, $J_{10A,2e}$ = 0.5), 4.56 (td, 1H, H-10B, $J_{10B,2e}$ = 2.3, $J_{10B,2e}$ = 0.9), 2.56

(m_c, 1H, H-2a, J_{gem} = 16.2, $J_{2a,1}$ = 8.4, $J_{2a,10A}$ = 2.4), 2.20 (m_c, 1H, H-4), 2.15 (d, 1H, H-2e, J_{gem} = 16.1), 1.77 (ddd, 1H, H-5e, J_{gem} = 14.3, $J_{5e,6}$ = 9.3, $J_{5e,4}$ = 3.2), 1.52 (m_c, 1H, H-5a, J_{gem} = 14.3, $J_{5a,4}$ = 4.6), 1.07 (d, 3H, H-11, $J_{11,4}$ = 6.8), 0.97 (s, 3H, H-9), 0.89 (s, 3H, H-8), 0.71 (m_c, 1H, H-1, $J_{1,2a}$ = 8.6), 0.61 (m_c, 1H, H-6, $J_{6,1}$ = 9.2, $J_{6,5a}$ = 4.6). ^{13}C NMR (100 MHz): δ 153.3 (C-3), 105.8 (C-10), 35.7 (C-4), 28.9 (C-9), 28.2 (C-5), 25.9 (C-2), 21.1 (C-1), 19.4 (C-11), 17.9 (C-7), 16.8 (C-6), 14.5 (C-8). MS [*m/z*, (rel. intensity,%)]: $M^{+\cdot}$ 150 (28), 135 (30), 121 (10), 119 (3), 108 (18), 107 (100), 105 (12), 94 (32), 93 (77), 91 (41), 81 (16), 79 (77), 77 (22), 69 (34), 67 (34), 65 (11), 55 (22), 53 (25), 51 (9), 43 (22), 41 (43), 39 (36). *Cis*-**27**: ^{1}H NMR (400 MHz): δ 4.68 (m_c, 1H, H-10A), 4.52 (m_c, 1H, H-10B), 2.52 (m_c, 1H, H-2a, $J_{2a,1}$ = 7.6), 2.42 (d, 1H, H-2e, J_{gem} = 15.5), 2.05 (m_c, 1H, H-5a, $J_{5a,4}$ = 13.7, $J_{5a,6}$ = 9.6), 1.95 (m_c, 1H, H-4), 0.98 (d, 3H, H-11, $J_{11,4}$ = 6.5), 0.95 (s, 3H, H-9), 0.92-0.85 (m, 1H, H-5e), 0.87 (s, 3H, H-8), 0.78 (m_c, 1H, H-6, $J_{5e,6}$ = 4.4), 0.63 (m_c, 1H, H-1, $J_{1,6}$ = 8.6).^{13}C NMR (100 MHz): δ 153.6 (C-3), 104.7 (C-10), 34.5 (C-4), 31.2 (C-2), 30.7 (C-5), 28.8 (C-9), 21.3 (C-1), 20.7 (C-6), 18.7 (C-7), 17.9 (C-11), 14.7 (C-8). MS [*m/z*, (relative intensity,%)]: $M^{+\cdot}$ 150 (28), 135 (30), 121 (16), 119 (4), 108 (18), 107 (100), 105 (15), 94 (36), 93 (82), 91 (44), 81 (16), 79 (75), 77 (22), 69 (35), 67 (39), 65 (12), 55 (21), 53 (27), 51 (8), 43 (22), 41 (82), 39 (40).

Method B.[22] Methyltriphenylphosphonium bromide (3.8 g, 11 mmol, dried at 120 °C) was added to a stirred suspension of potassium *tert*-butoxide (1.1 g, 10 mmol) in anhydrous ether (200 ml) under N_2. The yellow suspension was refluxed for 20 min. *Cis*-4-caranone (**18a**) (1.5 g, 10 mmol) in anhydrous diethyl ether (20 ml) was added at room temperature in small portions into the reaction mixture. Stirring was continued under reflux for 1 h and then at room temperature for 17 h. After 1 h GC showed that 50 % of *cis*-4-caranone was unreacted, and when the reaction was stopped after 18 h by adding water 17 % of 4-caranone remained. Precipitated triphenylphosphine oxide was filtered off and the filtrate washed with brine and dried over $MgSO_4$. After solvent evaporation the residue (1.4 g) contained (GC-MS) 83 % of 4-methyl-3(10)-carenes (**27**) and 17 % of 4-caranone (**18**). The ratio of *cis*- and *trans*-4-methyl-3(10)-carene was 76:24, respectively (GC).

3-Vinyl-3-apocarene (7,7-dimethyl-3-ethenylbicyclo[4.1.0]hept-3-ene) (**6**). The Wittig reaction of 3-caren-10-al (**12**) (6.6 g, 40 mmol) in DMSO (10 ml) was carried out with methylenetriphenylphosphorane (40 mmol), prepared from DMSO (70 ml), and NaH (1.75 g, ca. 40 mmol).[18a] During the reaction the temperature rose to 32 °C. The stirring of the reaction mixture was continued at room temperature for 16 h and then quenched by adding water. After the usual work-up the product (5.0 g, 84 %) was pure 3-vinyl-3-apocarene (**6**) (GC), b.p. 75 °C/8 Torr. Ref.[5c] ^{1}H NMR (200 MHz): δ 6.25 (dd, 1H, H-10, $J_{10,11t}$ = 17.3, $J_{10,11c}$ = 11.0), 5.52 (br s, 1H, H-4), 5.01 (d, 1H, H-11*c*, $J_{11c,10}$ = 11.5), 4.79 (d, 1H, H-11*t*, $J_{11t,10}$ = 17.3), 2.55-1.58 (m, 4H, H-2 and H-5), 0.98 (s, 3H, H-9), 0.80-0.58 (m, 2H, H-1 & H-6), 0.67 (s, 3H, H-8). ^{13}C NMR (50 MHz): δ 140.0 (C-10), 133.7 (C-3), 128.3 (C-4), 109.2 (C-11), 28.4 (C-9), 21.4 (C-2), 18.8 (C-5), 18.0 & 17.5 (C-1 & -6), 17.0 (C-7), 13.3 (C-8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 148 (9), 133 (14), 119 (5), 117 (5), 115 (5), 106 (13), 105 (100), 104 (30), 103 (10), 92 (22), 91 (42), 79 (43), 78 (12), 77 (27), 69 (7), 67 (9), 65 (12), 55 (9), 53 (13), 51 (12), 41 (39), 39 (32).

4-Methylene-3(10)-carene (7,7-dimethyl-3,4-dimethylenebicyclo[4.1.0]heptane) (**7**) Method A.[18a] Wittig reaction of 3(10)-caren-4-one (**14**) (8.0 g, 53 mmol) carried out as in the case of **18a** yielded 4.0 g of the crude product. According to GC-MS analysis it contained 36 % of the desired product, 4-methylene-3(10)-carene (**7**), 38 % of **29** (the adduct of **14** and **7**), 22 % of a hydrocarbon compound with *m/z* 150 (likely a base catalyzed isomerization product of **14**), and 4 % of unidentified minor products. The separation of **7** did not succeed without its subsequent dimerization. The adduct **29** was separated with flash chromatography (hexane) and identified from the mass spectrum, the 1D and 2D ^{1}H and ^{13}C NMR spectra. **29**: ^{1}H NMR (200 MHz): δ 4.8 (d, 2H, H-10´), 2.70 (ddt, 1H, H-3´A, *J*gem = 15.2, $J_{3'4'}$ = 7.8 $J_{3',10'}$ = 2.2), 2.40-1.47 (m, 10H, CH_2:s), 1.10-0.94 (m, 1H, CH_2), 1.10-0.52 (m, 4H, H-4´, -6´, -8 & -10), 1.05 (s, 3H, H-13), 0.97 (s, 3H, H-8´), 0.91 (s, 3H, H-9´), 0.83 (s, 3H, H-12). ^{13}C NMR (50 MHz): δ 151.3 (C-2´), 143.5 (C-1), 108.2 (C-10´), 101.7 (C-6), 74.4 (C-1´= C-3), 30.6, 29.8, 28.8, 25.2, 23.4, 22.9 (C-3´, -7´, -4, -5, -7, & -11), 28.8 & 28.3 (C-8´& 13), 22.3, 19.4, 18.0, 17.9 (C-4´, -6´, -8 & 10), 18.6 (C-5´), 16.4 (C-9), 14.2 (C-9´), 13.0 (C-12). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 298 (13), 217 (15), 216 (74), 201 (8), 173 (20), 160 (14), 149 (30), 148 (42), 147 (43), 145 (21), 133 (65), 131 (29), 121 (24), 119 (19), 117 (17), 107 (38), 105 (100), 93 (32), 91 (58), 81 (24), 79 (27), 77 (27), 67 (25), 55 (36), 53 (23), 43 (54), 41 (64). 4-Methylene-3(10)-carene (**7**): MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 148 (10), 133 (12), 119 (3), 117 (4), 115 (3), 106 (10), 105 (100), 104 (21), 92 (15), 91 (27), 79 (27), 77 (15), 69 (5), 67 (6), 65 (7), 55 (6), 53 (7), 51 (5), 41 (22), 39 (15).

Method B.[22] Upon reaction for 1 h the Wittig reaction of 3(10)-caren-4-one (**14**) (2.5 g, 17 mmol) yielded 2.0 g of the crude product. The GC-MS analysis of the product indicated 20 % of 4-methylene-3(10)-carene (**7**), 18 % **29**, 17 % of a compound with *m/z* 150, 40 % of **26** (the dimer of **14**), and 5 % of unidentified products. The dimer **26**: MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 300 (56), 257 (10), 203 (7), 190 (8), 181 (12), 180 (20), 163 (14), 162 (12), 151 (21), 149 (30), 147 (32), 135 (30), 133 (32), 121 (35), 119 (19), 117 (14), 107 (78), 105 (28), 95 (33), 93 (32), 91 (62), 81 (32), 79 (56), 77 (53), 69 (28), 67 (57), 65 (31), 55 (82), 53 (59), 43 (90), 41 (100).

4-Methyl-2-methylene-3(10)-carene (2,3-dimethylene-4,7,7-trimethylbicyclo[4.1.0]heptane) (**8**). Methylenetriphenylphosphorane (30 mmol) was prepared from methyltriphenylphosphonium bromide (10.7 g, 30 mmol) and *n*-butyllithium (32 mmol, 20 ml of 1.6 M solution in hexane) in ether (100 ml).[30] The mixture was stirred for 4 h at room temperature. 5-Methylene-4-caranone (**16**) (5.4 g, 30 mmol) in ether was added dropwise. Stirring at room temperature was continued for 16 h. After usual work-up the residue was 4.2 g. According to GC-MS analysis the product mixture contained 28 % of a compound with *m/z* 162, 7 % of **28**, 44 % of the starting compound **16**, 6 % of **31**, 2 % of triphenylphosphine, 8 % of *n*-butyldiphenylphosphine oxide and 5 % of a compound with *m/z* 326. The compound with *m/z* 162 can be 4-methyl-2-methylene-3(10)-carene (**8**), or 5-vinyl-4-carene: MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 162 (64), 147 (56), 133 (8), 120 (16), 119 (100), 117 (18), 106 (18), 105 (80), 93 (17), 91 (29), 79 (30), 77 (32), 67 (18), 55 (36), 53 (23), 41 (88), 39 (46).[6] The compound with *m/z* 326 can be **33** the adduct of **16** and **8**, or adduct of **16** and 5-vinyl-4-carene: MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 326 (28), 309 (2), 283 (8), 265 (4), 257 (4), 215 (15), 201 (7), 163 (22), 162 (100), 147 (52), 139 (22), 133 (22), 119 (62), 107 (19), 105 (30), 91 (33), 77 (22), 69 (17), 55 (22), 43 (36), 41 (42).

4-Isopropenyl-3-carene (3-(1-methylethenyl)-4,7,7-trimethylbicyclo[4.1.0]hept-3-ene) (**9**). The reaction was performed according to method A.[18a] A mixture of 4-acetyl-3-carene (**21**) and 4α-acetyl-2-carene (**22**) (75:25, respectively) (9.5 g, 53 mmol) reacted at room temperature for 30 h with an excess of methylenetriphenylphosphorane (64 mmol) and yielded 7.0 g of a mixture of 4-isopropenyl-2-carene (**34**) (51 %), 4-isopropenyl-3-carene (**9**) (44 %) and 5 % of an unknown compound with *m/z* 176. The separation of **9** and **34** did not succeed by distillation, or by flash chromatography. Therefore the identification of **9** and **34** was performed for their mixture. 4-Isopropenyl-3-carene (**9**): ^{1}H NMR (400 Mz): δ 4.87 (m_c, 1H, H-12A), 4.54 (m, 1H, H-12B), 2.39-2.30 (m, 1H, H-2A), 2.32-2.23 (m, 1H, H-5A), 2.02-1.93 (m, 1H, H-2B), 1.91-1.83 (m, 1H, H-5B), 1.75 (m_c, 3H, H-13), 1.58 (m_c, 3H, H-10), 1.02 (s, 3H, H-9), 0.93-0.85 (m, 1H, H-6), 0.78 (s, 3H, H-8), 0.73-0.67 (m, 1H, H-1). ^{13}C NMR (100 MHz): δ 148.0 (C-11), 132.1 (C-4), 124.0 (C-3), 112.0 (C-12), 28.2 (C-9), 26.6 & 24.8 (C-5 &-2), 22.2 (C-13), 19.9 (C-10), 18.2 & 17.8 (C-6 & -1), 16.8 (C-7), 12.2 (C-8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 176 (38), 161 (25), 147 (4), 145 (3), 133 (93), 120 (30), 119 (43), 117 (12), 115 (10), 107 (76), 106 (18), 105 (100), 93 (57), 91 (65), 79 (30), 77 (30), 69 (20), 67 (15), 65 (16), 55 (28), 53 (20), 51 (12), 43 (21), 4 (82), 39 (36). 4-Isopropenyl-2-carene (**34**): ^{1}H NMR (400 MHz): δ 5.54 (m_c, 1H, H-2), 4.71 (m_c, 2H, H-12), 2.35 (dd, 1H, H-4), 1.93 (ddd, 1H, H-5A), 1.75 (m_c, 3H, H-13), 1.66 (m_c, 1H, H-5B), 1.60 (m_c, 3H, H-10), 1.05 (s, 3H, H-9), 0.93-0.85 (m, 1H, H-1), 0.86 (s, 3H, H-8), 0.74 (td, 2H, H-6). ^{13}C NMR (100 MHz): δ 147.6 (C-11), 136.7 (C-3), 120.9 (C-2), 110.3 (C-12), 27.8 (C-9), 24.3 (C-5), 23.9 (C-1), 23.6 (C-7), 22.5 (C-10), 20.5 (C-13), 18.0 (C-6), 15.3 (C-8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 176 (10), 161 (22), 147 (3), 145 (2), 133 (100), 131 (8), 119 (51), 117 (10), 115 (7), 107 (62), 106 (39), 105 (83), 93 (93), 91 (64), 79 (25), 77 (35), 69 (15), 67 (10), 65 (15), 55 (26), 53 (18), 51 (10), 43 (42), 41 (69), 39 (33).

The preparation from 4α-acetyl-2-carene. Method A.[18a] 4α-Acetyl-2-carene (**22**) (10.0 g, 56 mmol) reacted with methylenetriphenylphosphorane (56 mmol) in 1 h. The amount of the crude product was 8.0 g. It contained according to GC-MS 54 % of 4-isopropenyl-2-carene (**34**), 20 % of 4-isopropenyl-3-carene (**9**), 9 % of a compound with *m/z* 174, 5 % of 4α-acetyl-2-carene (**22**), 8 % of 4-acetyl-3-carene (**21**), and 4 % of an unknown compound. The product mixture was distilled under reduced pressure. The first fraction, 5.2 g (53 %) b.p. 82 °C/7 Torr, contained 4-isopropenyl-2-carene (**34**), and 4-isopropenyl-3-carene (**9**). The second fraction, 0.3 g (3 %) b.p. 90 - 92 °C/7 Torr, contained the compound with *m/z* 174, and the third fraction, 1.0 g (10 %) b.p. 98 °C/7 Torr, contained 4α-acetyl-2-carene (**22**), and 4-acetyl-3-carene (**21**). The compounds were further purified by flash chromatography (hexane). **21** and **22** were identified by comparison of GC retention times and mass spectra with those of authentic samples. The compound with *m/z* 174 was 2-isopropenyl-*p*-cymene (**35**): ^{1}H NMR (400 MHz): δ 7.03 (d, 1H, H-6, $J_{6,5}$ = 7.7), 6.97 (m_c, 1H, H-5, $J_{5,6}$ = 7.8, $J_{5,3}$ = 1.9), 6.90 (d, 1H, H-3, $J_{3,5}$ = 1.9), 5.11 (m_c, 1H, H-12A, J_{gem} = 2.3, $J_{12A,13}$ = 1.5), 4.77 (m_c, 1H, H-12B, $J_{12B,13}$ = 1.0), 2.78 (sept, 1H, H-8, $J_{8,9}$ = 7.0, $J_{8,10}$ = 7.0), 2.21 (s, 3H, H-13), 1.97 (dd, 3H,

H-7, $J_{7,12}$ = 1.5), 1.17 (d, 6H, H-9 & 10, $J_{9,8}$ = 7.0, $J_{10,8}$ = 7.0). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 174 (38), 160 (15), 159 (100), 144 (8), 133 (7), 131 (10), 128 (10), 119 (17), 117 (9), 115 (12), 105 (10), 91 (12), 77 (7), 71 (4), 65 (5), 51 (4), 41 (15), 39 (8).

Method B.[22] 4α-Acetyl-2-carene (5.0 g, 28 mmol) reacted in 3 h with methylenetriphenylphosphorane (28 mmol). The crude product 4.8 g. According to GC analysis the product mixture contained 76 % of **34**, 7 % of **9**, 5 % of **21**, 4 % of **35**, 4 % of **22**, and 4 % of an unknown compound.

Isomerization of 4-isopropenyl-2-carene (**34**).The mixture containing 4-isopropenyl-2-carene (**34**), and 4-isopropenyl-3-carene (**9**) (9:1) (0.50 g, 2.8 mmol) in 2 ml of dry DMSO was quickly added into 3 ml of DMSO solution of K-*tert*-butoxide (0.31 g, 2.8 mmol). The reaction mixture was stirred at 70 °C. After 2 h no more change was observed in the product composition (GC). After the usual work-up the residue was 0.43 g and the composition 3 % of the unreacted 4-isopropenyl-2-carene (**34**), 42 % of 4-isopropenyl-3-carene (**9**), 53 % of the isomerized product, and 2 % of an impurity from the starting material. After purification (flash chromatography, heptane) the isomerized product and was identified as 4-isopropylidene-2-carene (4-methylethylidene-3,7,7-trimethylbicyclo[4.1.0]hept-2-ene) (**36**): ^{1}H NMR (200 MHz,): δ 5.67 (m_c, 1H, H-2), 2.53-2.13 (m, 2H, H-5, J_{gem} = 14.4), 1.94 (m_c, 3H, H-10), 1.78 (s, 3H, H-13), 1.73 (s, 3H, H-12), 1.14-1.00 (m, 1H, H-1), 1.08-0.92 (m, 1H, H-6), 1.04 (s, 3H, H-9), 0.83 (s, 3H, H-8). ^{13}C NMR (50 MHz): δ 134.1 (C-3), 130.8 (C-4), 126.1 (C-2), 125.6 (C-11), 28.5 (C-9), 25.0 (C-5), 24.7 (C-7), 24.3 & 24.2 (C-1 & -6), 23.9 (C-10), 23.6 (C-13), 22.0 (C-12), 14.5 (C-8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 176 (22), 161 (60), 146 (4), 133 (100), 119 (46),117 (9), 115 (9), 105 (85), 93 (21), 91 (43), 79 (11), 77 (18), 65 (12), 55 (10), 53 (10), 51 (8), 43 (20), 41 (46), 39 (18).

4-isopropenyl-3-caren-2α-ol (2-hydroxy-4-(1-methylethenyl)-3,7,7-trimethylbicyclo[4.1.0]hept-3-ene) (**11**) Method A.[18a] 4-Acetyl-3-caren-2α-ol (**23**) (10.0 g, 52 mmol) reacted with methylene triphenylphosphorane (52 mmol) at room temperature for two hours. The product mixture (8.7 g) contained the desired product 4-isopropenyl-3-caren-2α-ol (**11**) (51 %), **38** (10 %), the unreacted 4-acetyl-3-caren-2α-ol (**23**) (5 %), **37** (2 %), **35** (7 %), **9** (7 %), **34** (4 %) and 14 % of unknown products. All attempts to obtain **11** as a pure compound isomerized it to a compound with *m/z* 192. After purification by flash chromatography (hexane/diethyl ether, 1:1) the compound was identified as 2-isopropenyl-1,5-*p*-menthadien-8-ol (**39**). ^{1}H NMR (200 MHz): δ 5.90 (dd, 1H, H-6, $J_{6,5}$ = 9.9, $J_{6,4}$ = 2.1), 5.72 (dd, 1H, H-5, $J_{5,6}$ = 9.9, $J_{5,4}$ = 9.6), 4.96 (m_c, 1H, H-12A, J_{gem} = 2.5, $J_{12B,7}$ = 1.5), 4.69 (m_c, 1H, H-12B, $J_{12B,13}$ = 0.9), 2.34-2.24 (m, 1H, H-4), 2.40-2.14 (m, 2H, H-3), 1.81 (m_c, 3H, H-13, $J_{13,12}$ = 0.9), 1.74 (m_c, 3H, H-7, $J_{7,12}$ = 1.5), 1.20 (s, 6H, H-9 & 10). ^{13}C NMR (50 MHz): δ 145.6 (C-11), 133.9 (C-2), 131.2 (C-6), 125.4 (C-5), 124.3 (C-1), 113.0 (C-12), 73.0 (C-8), 45.6 (C-4), 28.8 (C-3), 27.2 & 27.1 (C-9 & C-10), 21.6 (C-13), 18.2 (C-7). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 192 (1), 177 (1), 174 (1), 159 (2), 134 (55), 119 (72), 117 (12), 115 (9), 105 (28), 93 (25), 91 (31), 77 (12), 65 (8), 59 (100), 43 (21), 41 (37), 39 (15). MS (CI, ammonia): *m/z* 193 (MH^+). Isomerization also occurred during storage in a refrigerator. The GC-MS analysis of the crude product showed for 4-isopropenyl-3-caren-2α-ol (**11**) MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 192 (2), 175 (6), 174 (32), 172 (4), 160 (15), 159 (100), 149 (5), 145 (10), 144 (15), 134 (11), 133 (28), 131 (29), 130 (12), 129 (17), 119 (34), 117 (28), 115 (22), 105 (38), 96 (13), 93 (19), 91 (38), 79 (9), 77 (16), 65 (7), 59 (5), 41 (4). *p*-Nitrobenzoate derivative of **11** (prepared by the pyridine method) had after recrystallization from methanol m.p. of 203 - 204 °C. The derivative decomposed in GC, TLC, and on standing to 2-isopropenyl-*p*-cymene (**35**).[40]

Method B.[22] A slightly exothermic reaction of 4-acetyl-3-caren-2α-ol (**23**) (5.4 g, 28 mmol) with methylene triphenylphosphorane (28 mmol) occurred in one hour. After the usual work-up the residue was 4.9 g. The product mixture analyzed by GC-MS contained 25 % of 4-isopropenyl-3-caren-2α-ol (**11**), 12 % of **38**, 22 % of 2-isopropenyl-1,5-*p*-menthadien-8-ol (**39**), 13 % of 2-isopropenyl-*p*-cymene (**35**), 6 % of 4-isopropenyl-3-carene (**9**), 4 % of 4-isopropenyl-2-carene (**34**), 7 % of an aromatic compound with *m/z* 190 which is presumably a derivative of acetophenone, and 11 % of unknown compounds.

Diels-Alder reaction with maleic anhydride. 3-Vinyl-3-apocarene (**6**). The diene synthesis between **6** (1.50 g, 10.1 mmol) and maleic anhydride (0.99 g, 10.1 mmol) in dry benzene occured under reflux in 3h. The reaction was quenched by pouring into water. The organic phase was washed several times with water. Evaporation of benzene yielded the anhydride (2.2 g) which was hydrolyzed by boiling for 1 h with 5 % NaOH solution (12 ml). Impurities were extracted off with ether. The alkaline solution was acidified with 6 M HCl. The crystalline product was filtered and washed with ice-water. Repeated crystallizations from the absolute ethanol-petroleum ether mixture yielded 1.5 g (56 %) of dicarboxylic acid **40**, decomposed at 180 - 185

°C. ^{1}H NMR (400 MHz, CD_3OD): δ 5.40 (m_c, 1H, H-8), 3.02 (dd, 1H, H-11, $J_{11,10}$ = 5.9, $J_{11,1}$ = 6.0), 2.92 (m_c, 1H, H-10), 2.54 (m_c, 1H, H-9A, J_{gem} = 17.0), 2.43 (dd, 1H, H-6A J_{gem} = 14.9, $J_{6,5}$ = 9.9), 2.39 (m_c, 1H, H-1), 1.99 (m_c, 1H, H-9B), 1.92-1.75 (m, 3H, H-6B, & H-2:s), 1.05 (s, 3H, H-13), 0.95 (s, 3H, H-12), 0.77 (td, 1H, H-5, $J_{5,3}$ = 9.6), 0.48 (m_c, 1H, H-3). ^{13}C NMR (100 MHz, CD_3OD): δ 182.5 & 180.8 (COOH:s), 139.5 (C-7), 119.6 (C-8), 50.8 (C-11), 40.4 (C-10), 37.0 (C-1), 31.0 (C-6), 30.4 (C-12), 29.5 (C-9), 25.6 (C-2), 24.5 (C-5), 22.0 (C-3), 19.2 (C-4), 16.4 (C-13). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 264 (2), 246 (22), 218 (43), 203 (18), 175 (19), 173 (20), 157 (15), 147 (83), 133 (40), 131 (46), 129 (61), 117 (43), 115 (16), 105 (87), 100 (16), 99 (22), 91 (100), 79 (20), 77 (26), 67 (19), 65 (21), 55 (20), 53 (22), 44 (31), 43 (60), 41 (85), 39 (54).

4-Methylene-3(10)-carene (7). Maleic anhydride (0.50 g, 5.1 mmol) and a mixture containing 36 % of 4-methylene-3(10)-carene (7) (0.50 g, 3.4 mmol) in dry benzene were stirred at room temperature for 18 h. The work-up as before precipitated the dicarboxylic acid. Recrystallized from dilute ethanol, yielded the acid with m.p. 186 - 188 °C. Yield 0.70 g (78 %). 4,4-Dimethyltricyclo[5.4.0.0^{3,5}]undec-1(7)-en-9,10-dicarboxylic acid (**42**): ^{1}H NMR (400 MHz, CD_3OD): δ 2.96 (m_c, 2H, H-9 & -10), 2.39 (m_c, 2H, H-8A & -11A, J_{gem} = 15.7), 2.25-2.15 (m, 2H, H-2A & -6A), 2.15-2.06 (m_c, 2H, H-8 & -11, J_{gem} = 16.7), 1.87-1.77 (m, 2H, H-2B & -6B), 1.00 (s, 3H, H-13), 0.75 (s, 3H, H-12), 0.73-0.66 (m, 2H, H-3 & -5). ^{13}C NMR (100 MHz, CD_3OD): δ 178.0 (COOH:s), 126.3 (C-1 & -7), 42.3 (C-9 & -10), 32.7 (C-8 & -11), 29.4 (C-13), 27.3 (C-2 & -6), 20.0 (C-3 & -5), 18.2 (C-4), 14.3 (C-12). Ref.[6] MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 264 (2), 246 (9), 218 (35), 203 (24), 175 (23), 173 (13), 157 (13), 147 (29), 133 (40), 131 (37), 129 (100), 117 (38), 105 (36), 91 (67), 79 (19), 77 (22), 67 (16), 65 (21), 55 (20), 53 (18), 51 (12), 43 (38), 41 (77), 39 (53).

Diels-Alder reaction with tetracyanoethylene. Mixture of 4-isopropenyl-3-carene (**9**) (41 %) and 4-isopropenyl-2-carene (**34**) (57 %) (2.7 g, 15.3 mmol) was refluxed with tetracyanoethylene (0.9 g, 7.8 mmol) in dry benzene (25 ml). In 30 min **9** had completely reacted but **34** remained unchanged (TLC). Benzene was evaporated and replaced with ether to precipitate excess of tetracyanoethylene. The filtrate was evaporated to dryness under reduced pressure. Addition of absolute ethanol precipitated the crystalline adduct. The compound, m.p. 228 °C (purified by sublimation (160 - 170 °C/10 Torr) was inferred to 10,10,11,11-tetracyano-1,4,4,8-tetramethyltricyclo[5.4.0.0^{3,5}]undec-3-ene (**43**): ^{1}H NMR (200 MHz): δ 3.03 (br s, 2H, H-5), 2.74 (dd, 1H, H-2A, J_{gem} = 14.3), 2.41 (dd, 1H, H-9A, J_{gem} = 16.9), 1.75 (s, 3H, H-12), 1.49 (s, 3H, H-13), 1.24 (dd, 1H, H-9B), 1.19-1.08 (m, 1H, H-2B), 0.98 (s, 3H, H-14 or -15), 0.97 (s, 3H, H-15 or -14), 0.89-0.82 (m, 1H, H-1), 0.85-0.77 (m, 1H, H-10). ^{13}C NMR (50 MHz): δ 133.9 (C-4), 117.9 (C-3), 112.7, 112.6, 111.3, 111.2 (4xCN), 49.2 & 44.1 (C-6 & -7), 38.1 (C-2), 37.0 (C-8), 35.3 (C-9), 27.5 (C-15), 25.7 (C-12), 25.3 (C-1), 22.7 (C-5), 19.2 (C-11), 18.6 (C-13), 18.6 (C-10), 14.5 (C-14).

Decarboxylation.[34] $K_3[Fe(CN)_6]$ (6.0 g, 18.2 mmol) in 15 ml of 5 % NaOH solution was added dropwise to the hot alkaline solution (15 ml of 5 % NaOH) of 4,4-dimethyltricyclo[5.4.0.0^{3,5}]undec-7-en-10,11-dicarboxylic acid (**40**) (1.50 g, 5.7 mmol), and heated overnight with stirring in a water bath (90 °C). After cooling the reaction mixture was extracted with ether. The combined extracts were washed with brine and dried over $MgSO_4$. Yield 0.21 g. The residue purified with flash chromatography (hexane/ethyl acetate, 40:1) was benz-3-apocarene (**41**): ^{1}H NMR (400 MHz): δ 7.06 (m_c, 4H, H-8, -9, -10, & -11), 3.10 (m_c, 2H, H-2e & -6e, J_{gem} = 17, $J_{2e,3}$ = 8, $J_{6e,5}$ = 8), 2.63 (d, 2H, H-2a & -6a, J_{gem} = 17, $J_{2a,3}$ = 5, $J_{6a,5}$ = 5), 1.11 (s, 3H, H-13), 0.94 (m_c, 2H, H-3 & -5, $J_{3,2e}$ = 8, $J_{3,2a}$ = 5, $J_{5,6e}$ = 8, $J_{5,6a}$ = 5), 0.81 (s, 3H, H-12). ^{13}C NMR (100 MHz): δ 136.4 (C-1 & -7), 128.6 (C-8 & -11), 125.3 (C-9 & -10), 28.6 (C-13), 24.9 (C-2 & -6), 20.1 (C-3 & -5), 17.7 (C-4), 14.6 (C-12). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 172 (10), 157 (12), 142 (8), 141 (5), 130 (12), 129 (100), 128 (42), 127 (11), 116 (20), 115 (20), 91 (7), 77 (9), 65 (5), 63 (5), 51 (8), 41 (18), 39 (19).

Decarboxylation of 4,4-dimethyltricyclo[5.4.0.0^{3,5}]undec-1(7)-en-9,10-dicarboxylic acid (**42**) (1.00 g, 3.8 mmol) with $K_3[Fe(CN)_6]$ (4.00 g, 12.2 mmol) in 20 ml of 5 % NaOH yielded 0.12 g of the product. ^{1}H and ^{13}C NMR spectra as well as the mass spectrum of the decarboxylation product were identical with those presented for **41**.

*The preparation of starting materials.*The mixture of 3(10)-caren-4-ols (**13**) (*trans:cis*, 63:37, respectively) was oxidized according to Gollnick and Schade.[7] A mixture of $K_2Cr_2O_7$ (22.0 g, 75 mmol), conc. H_2SO_4 (14.2 g), and water (33 ml) was added to a stirred solution of **13** (9.2 g, 61 mmol) in dry benzene (50 ml) keeping the temperature of the reaction mixture at 50 - 60 °C. Stirring was continued at 40 °C until TLC showed that all 3(10)-caren-4-ols had reacted (4 h). After the usual work-up the residue was 6.8 g. GC analysis showed that the product mixture contained four components in the ratio 8:39:50:3 at retention times of

5.0, 8.5, 9.6, and 9.8 min., respectively. Distillation under reduced pressure yielded two fractions: the compound with retention time 5.0 distilled at 85 - 87 °C/10 Torr, and the remaining products at 103 °C/11 Torr. The component with retention time 8.5 dimerized during distillation and the second fraction contained only 14 % of it. The dimerized product remained in the distillation residue. The final separation and purification were performed with flash chromatography (hexane/diethyl ether, 5:1 and 1:1). Compounds with the RT 5.0, 8.5, and 9.6 min. were identified according to their MS, 1D and 2D ^1H and ^{13}C NMR spectra as 3,6,6-trimethylbicyclo[3.1.0]hexane-3-carboxaldehyde (**25**), 3(10)-caren-4-one (**14**), and 3-caren-10-al (**12**), respectively. (**25**): b.p. 85 - 87 °C/10 Torr. Ref.[41a] b.p. 70 - 72°C/9 Torr. ^1H NMR (400 MHz): δ 9.45 (s,1H, H-10), 2.19 (m_c, 2H, H-2A & -4A), 1.23-1.16 (m, 2H, H-2B & -4B), 1.19-1.11 (m, 2H, H-1 & -5), 1.01 (s, 3H, H-9), 0.99 (s, 3H, H-8 or -7), 0.95 (s, 3H, H-7 or -8). Ref.[41b] ^{13}C NMR (100 MHz): δ 204.2 (C-10), 64.0 (C-3), 33.2 (C-2 & -4), 31.8 (C-1 & -5), 27.2 (C-8 or -7), 23.3 (C-6), 18.7 (C-9), 14.6 (C-7 or -8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 152 (11), 137 (49), 123 (37), 119 (11), 109 (100), 107 (10), 95 (22), 93 (21), 91 (20), 81 (64), 79 (22), 77 (14), 69 (22), 67 (40), 55 (18), 53 (15), 43 (30), 41 (35), 39 (18). Ref.[41b] **14**: ^1H NMR (200 MHz): δ 5.93 (td, 1H, H-10*c*, J_{gem} = 2.1, $J_{10c,2}$ = 0.8), 5.12 (tdd, 1H, H-10*t*, J_{gem} = 1.9, $J_{10t,2}$ = 0.6), 2.77 (m_c, 1H, H-2A, J_{gem} = 16.5), 2.57 (m_c, 1H, H-5A, J_{gem} = 17.6), 2.16 (m_c, 1H, H-2B, J_{gem} = 16.5), 2.02 (m_c, 1H, H-5B, J_{gem} = 17.7), 1.02 (s, 3H, H-8 or -9), 0.99 (s, 3H, H-9 or -8), 0.85-0.75 (m, 2H, H-1 & 6). Ref.[41] ^{13}C NMR (50 MHz): δ 200.9 (C-4), 142.0 (C-3), 120.7 (C-10), 35.5 (C-5), 28.2 (C-9), 28.0 (C-2), 20.6 & 19.8 (C-1 & -6), 19.6 (C-7), 14.5 (C-8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 150 (62), 135 (46), 122 (11), 119 (8), 117 (5), 108 (78), 107 (100), 105 (21), 95 (18), 93 (28), 91 (56), 81 (44), 79 (94), 77 (39), 69 (25), 68 (93), 67 (50), 65 (17), 55 (28), 53 (51), 51 (16), 43 (21), 41 (66), 40 (72), 39 (49). Ref.[42] **12**: ^1H NMR (200 MHz): δ 9.37 (s, 1H, H-10), 6.68 (m_c, 1H, H-4), 2.73 (m_c, 1H, H-5A, J_{gem} = 21.8), 2.46 (m_c, 1H, H-2, J_{gem} = 19.0), 2.27 (m_c, 1H, H-5B, J_{gem} = 21.8), 2.10 (m_c, 1H, H-2B, J_{gem} = 19.1), 1.04 (s, 3H, H-9), 0.79 (m_c, 2H, H-1 & 6), 0.67 (s, 3H, H-8). Ref.[7,8,37,41b] ^{13}C NMR (50 MHz): δ 193.6 (C-10), 149.8 (C-4), 140.0 (C-3), 28.2 (C-9), 22.4 (C-5), 17.7 (C-6), 17.6 (C-7), 17.2 (C-1), 16.6 (C-2), 13.4 (C-8). MS [*m/z* (relative intensity %)]: $M^{+\cdot}$ 150 (5), 135 (9), 121 (21), 117 (4), 108 (19), 107 (100), 105 (19), 93 (13), 91 (25), 79 (72), 77 (31), 67 (10), 66 (9), 65 (7), 55 (5), 53 (11), 51 (9), 43 (18), 41 (20), 39 (15). Ref.[8] The minor component (retention time 9.8) had a weak M+. with *m/z* 166. The presence of $(M - 1)^{+\cdot}$, $(M - 29)^+$ and $(M - 18)^+$ indicates a hydroxylated carenaldehyde.

Oxidation by the method of Corey and Fleet.[14] CrO_3 (18.2 g, 0.180 mol) and 3,5-dimethylpyrazole (17.6 g, 0.180 mol) were stirred in dry CH_2Cl_2 (450 ml) for 20 min at room temperature. 3(10)-caren-4-ols (*cis:trans*, 55:45, 9.2 g, 61 mmol) in CH_2Cl_2 (50 ml) was added into the ice-cold mixture of the oxidant. After stirring for 1.5 h the solvent was evaporated and the residue extracted with anhydrous ether and petroleum ether (40 - 60 °C). The combined extracts were purified with chromatography using a silica gel column. Removal of solvent gave 8.0 g of the crude product which contained (through GC) 3(10)-caren-4-one (**14**) (89 %), 3-caren-10-al (**12**) (7 %), and unidentified products (4 %). **14** and **12** were identified by comparison of GC retention times and mass spectra of those of authentic samples.

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