Tetrahedron, Vol. 37, Supplement No. 1, pp. 247 to 255, 1981
Printed in Great Britain

0040-4020/81/Suppl. 1-0247-09 $02.00/0
Pergamon Press Ltd.

CATIONIC π-CYCLISATION OF α,β-UNSATURATED CARBONYL COMPOUNDS

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(*Received in Germany* 2 *July* 1980)

Abstract—Several olefinic α,β-unsaturated carbonyl compounds have been cyclized by Lewis acid and the structures of the products determined. In only one case a spirocyclisation with concomitant 1,3-hydride-shift has been observed besides intramolecular cycloaddition. In the other cases there was either no reaction or a 6-endo-trig cyclisation with further rearrangement took place.

Recently[1] we reported about the stereochemical course of a Lewis acid-catalyzed cyclisation on a γ–δ unsaturated vinylic ketone giving two spiro [4.5] decenones in equal amounts. It was shown that after an initial 6-*exo*-trig process[2] of the cationic metalloenolate species a 1,3-hydride shift led to the α,β-unsaturated product ketones (diagram 1). With the present work we intended to use the same principle for building up the spiro [5.5] undecenone skeleton related to the naturally occurring sesquiterpenes α- and β-chamigrene.

Therefore we prepared compound **7** in six steps starting from β-ionone (diagram 6) and subjected it to different protonic and Lewis acids. With stannic chloride in benzene solution at room temperature a very clean reaction ensued furnishing two products **8** and **9** in the ratio 3:7 (80% yield, diagram 2). Chromatographic separation proved to be extremely tedious in the gas phase and practically impossible on columns or thin layer plates. After reduction with LAH in diethyl ether the three alcohols formed could be purified chromatographically on aluminium oxide and

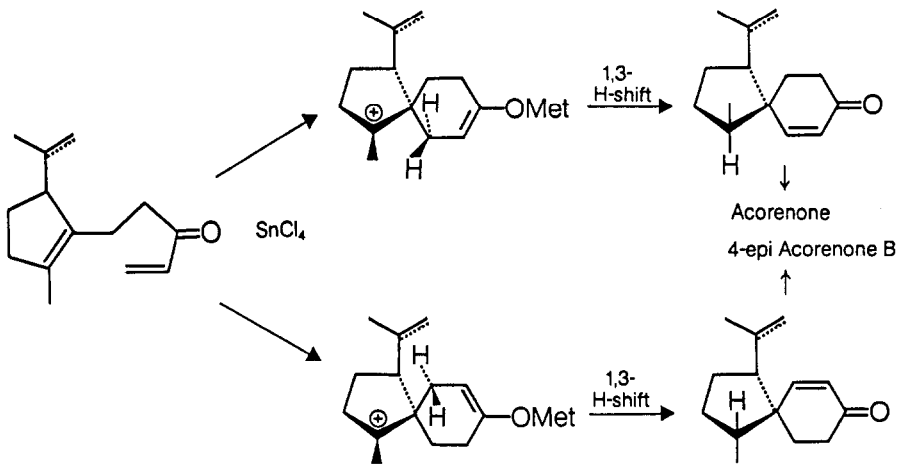
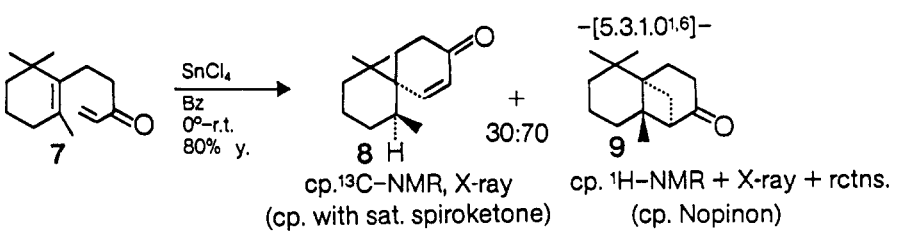
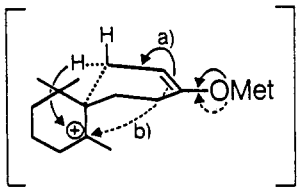


Diagram 1.





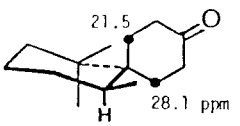
a) 1,3-hydride shift to spiro cpd.
b) cycloaddition

Diagram 2.

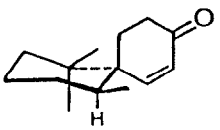
reoxidized by Jones reagent in acetone at $-10°$. Thus the alcohol first eluted gave **9** and the mixture of allylic alcohols gave **8** again (diagram 2).

The overall structure of **8** could be deduced fairly straightforward from its spectra. Besides showing a molecular ion at 206 with a parent peak at 122 *m/e* an UV absorption maximum at 236 nm ($\log \varepsilon = 4$) and a CO band at 1680 cm^{-1} in the IR suggested an isomeric α,β-unsaturated ketone in a 6- or higher membered ring. This was confirmed by the nuclear resonance frequencies of two vinylic protons appearing at $\delta = 6{,}60$ and 6,10 ppm as doublets with coupling constants of 10 c/s. In addition no Me group on a double bond was visible any more but two Me singlets at $\delta = 1{,}05$ and 0,98 ppm still appeared. The decision in favour of a spirocyclohexenone and against an anellated cycloheptenone system was done on grounds of a Me group in the PMR spectrum appearing as a doublet at $\delta = 0{,}81$ ppm with a coupling constant of 7 c/s.

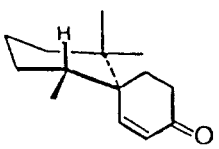
Less clear was the stereochemistry about the spirocentre. We tried to find out by looking at the ^{13}C-chemical shifts of the methylene-C atoms in vicinal position to this centre. As a basis we had to look at the fully saturated spiroketone **8a** in its most stable conformation with only one axial Me group (diagram 3). By europium shift experiments it was possible to place these two triplets at $\delta = 21{,}5$ and 28,1 ppm.



8a



i



ii

Diagram 3.

We believe that the difference in chemical shift of these two C atoms is mainly due to the different number of γ-gauche effects being exerted upon them.[1] In fact in **8a** the pointed C atom in axial position is subjected to four *γ-gauche* effects while the pointed C atom in equatorial position "feels" only three, the difference being 6,6 ppm.[1] Looking now at the original ketone **8** we determined the chemical shift for the single methylene carbon in α-position to the spirocentre to be 20.75 ppm, pointing to the influence of four *γ-gauche* effects. If we consider the two possible spiroconfigurations i and ii of the molecule in its most stable conformations, we can count again 4 *γ-gauche* effects for i and only 3 for ii. Therefore there is a preference to configuration i for ketone **8**. Because this argument gives no proof of the stereochemistry of the molecule we had an X-ray crystallographic structure determination done on the oxime derivative. The structure problem was solved by direct methods and the refinement converged at $R = 7{,}85\%$.[3] This determination confirmed structure **8** as shown in diagram 2 in every detail.

One tends to suggest a simultaneous 1,3-hydride shift during the described cyclisation.[1] A cyclopropane could also be formed first and reprotonated to give exactly the same stereochemistry but in view of the extreme cleanliness of the reaction it would seem to be an elusive compound.

The structure of the main product **9** had to be isomeric (molecular ion at *m/e* 206 with parent peak at 121) and tricyclic because besides a CO carbon at $\delta = 214{,}1$ ppm there was no resonance signal below 56 ppm in the ^{13}C-NMR spectrum. The IR absorption at 1700 cm^{-1} (in $CHCl_3$ soln) suggested a 6 or higher membered ketone. As with compound **8** there were no Me groups on a double bond but three tertiary Me groups visible in the proton NMR spectrum.

Structure **9** having 2 6-membered and one 4-membered ring, was preferred to two cyclopropane alternatives (with or without 1,2-shifted methyl group) because there was no indication of cyclopropane hydrogens in the proton NMR spectrum and no special absorption in the UV spectrum. A comparison with the proton NMR spectrum of nopinone showed striking similarities to **9**. In addition the chemical transformations described below beginning with the insensitivity towards acid would have made an additional structure proof obsolete. All the same an X-ray crystallographic determination of the oxime was done[3] and solved by direct methods, the refinement converging at $R = 9{,}03\%$. This work confirmed structure **9** as shown in diagram 2 in every detail.

Mechanistically the observed cycloaddition of the cationic metalloenolate intermediate is an interesting alternative to the 1,3-hydride shift or cyclopropane formation. The tricyclo-[5.3.1.$0^{1,6}$]-undecane system has been made before by an intramolecular ketene addition to an α,β-unsaturated ketone group to form a cyclobutanone.[4] As a minor product the system with the CO in the 6-membered ring was formed in an intramolecular photo-addition of an olefinic side chain to a cyclohexenone function.[5] It does not seem possible to achieve photocycloaddition of an α,β-unsaturated CO group in a side chain to a double bond in a ring as in **7**.

Ketone **9** was easily brominated in carbon tetrachloride showing a good enolisation tendency which proved a disadvantage in the addition reactions with Grignard reagents or alkyl lithium compounds. Thus the reaction with methyl lithium had to be run five times in consequence in order to get to virtually pure tertiary alcohol **10** (diagram 4). Treatment of **10** with *p*-toluenesulphonic acid in benzene at 55° formed a mixture of hydrocarbons in very good yield. Repeated column chromatography on silicagel impregnated with 15% silver nitrate allowed the separation of all six compounds formed in the dehydration reaction.

Product **13**, **12** + **16**, **17**, **14**, **15** appeared in this order on a UCON glass-capillary glc-column in the ratio indicated in diagram 4. **14** and **15** were identified with the spectra of authentic β- and α-chamigrene. The structure of the main compound **13** was deduced by analysis of its spectra and especially by comparison with the PMR spectrum of α-pinene. For hydrocarbon **12** the same as above holds. But in addition to the close spectral relations with β-pinene it could be synthesized

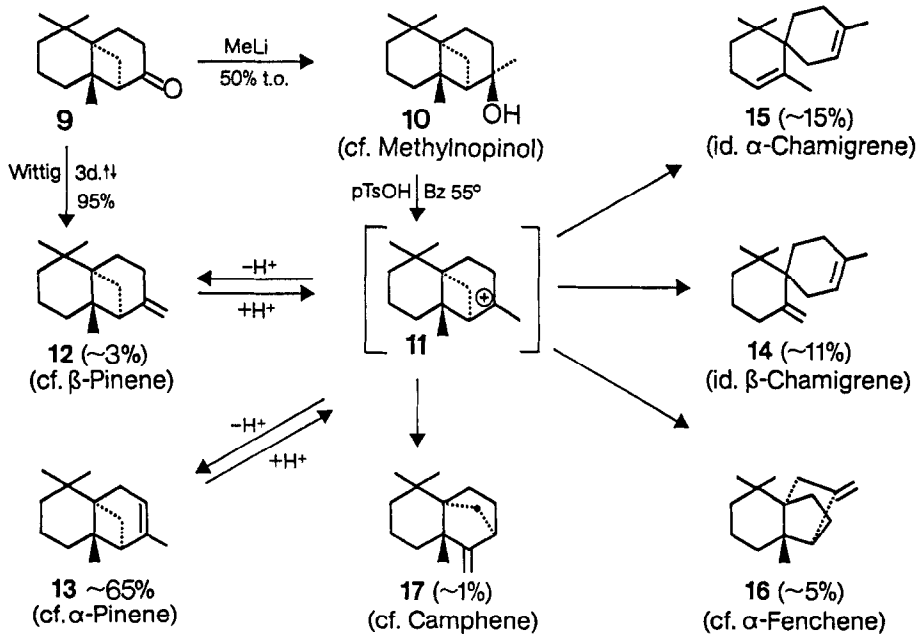


Diagram 4.

by treating tricyclic ketone **9** with methyl triphenyl phosphorane in refluxing THF and identified directly. In addition the treatment of **12** with *p*-toluenesulphonic acid in benzene gave among others **13** as main product.

Structures **16** and **17** are tentative. Because of lack of material there were no further chemical transformations made. According to their NMR-spectral data, they are both containing one methylidene group and three angular Me's. The mass spectra were clearly different from one another and also from anything known. They confirmed only molecular weight 204 and tricyclic structure of the two new hydrocarbons. The structures **16** and **17** in diagram 5 are suggested because they can be derived from cation **11** by two simple and well-known rearrangement steps. Furthermore a comparison of the PMR resonances of the two exomethylene protons of **16** with those of α-fenchene and of **17** with those of camphene showed strikingly close similarities in difference of chemical shift and especially in the coupling pattern.

The same type of cyclisation with stannic chloride was also tried on carbonyl compounds **24**, **30** and **37** (diagrams 6 and 7), hoping for spirocyclisation, in the case of **24** to build up the skeleton of the marine sesquiterpenoid spirolaurenone. We would like to add

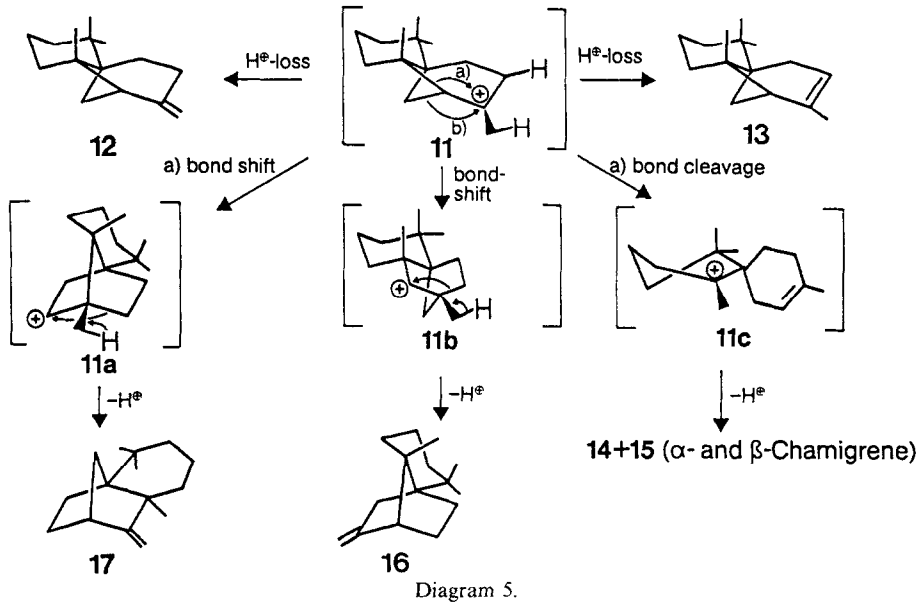


Diagram 5.

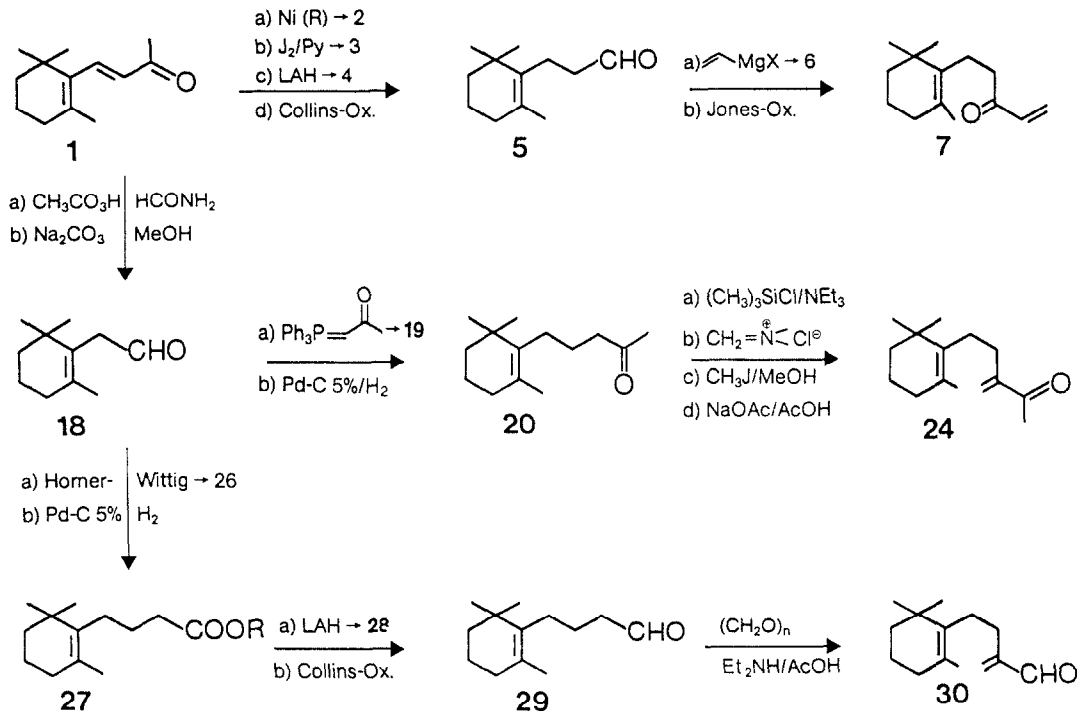


Diagram 6.

here one remark concerning the preparation of ketone **24**. The only profitable way for the Mannich type synthesis was the smooth reaction of the thermodynamically formed silyl-enol-ether of **20** with dimethyl-methylene-immonium chloride in acetonitrile and subsequent quaternization with methyl iodide and mild β-elimination of trimethylamine with the help of bicarbonate[6] or acetate. In the case of **37** (preparation see Experimental) all our attempts to cyclize this ketone by action of Lewis acids failed. There was no sign of either of the two favoured processes, the 5-*exo*-trig or the 6-*endo*-trig cyclisation[2] but rather if anything happened polymerization took place.

We subjected the aldehyde **30** to the action of stannic chloride in a benzene toluene solvent mixture

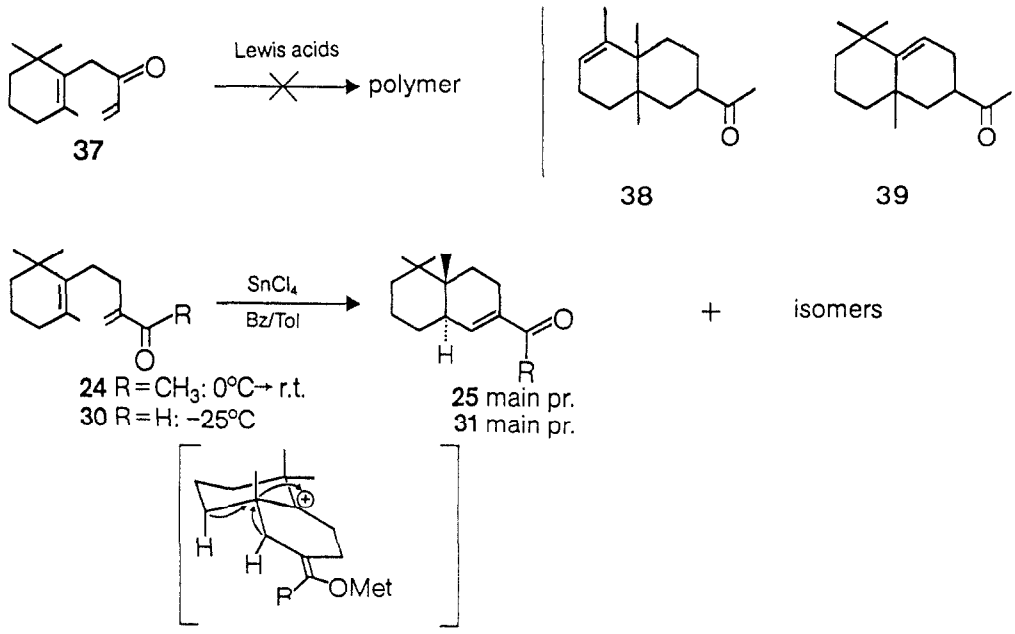


Diagram 7.

at −25 to −20° for about 30 min until the starting material had virtually disappeared. The crude product contained one main product (~60%) that could be well separated by gaschromatographic techniques from a series of 8 to 10 minor products. According to mass, UV and IR spectra it was clearly an isomeric aldehyde with a conjugated trisubstituted double bond. The proton NMR spectrum confirmed these apparent features with resonances at $\delta = 9.40$ (sharp s) and $\delta = 6.46$ ppm (small q) each accounting for 1 proton.

Furthermore three singlets, each for three H atoms at $\delta = 0.985$ and 0.850 and 0.786 ppm accounted for three tertiary Me groups. Downfield from $\delta = 1.8$ ppm there were only three more protons accounting for the allylic positions 5 and 8. Analysis of the couplings spoke in favour of an axial proton in 5 *trans* configurated to the angular Me group in 10 as depicted in formula **31**. No evidence for a 5-*exo*-trig cyclisation to a spiro compound could be gained from spectral analysis of the more prominent minor reaction products.

The analogous cyclisation reaction of ketone **24** was slower and gave a more complex product mixture. The main product and the major by-products were separated through column-chromatography on silicagel and purified by preparative gas-chromatography.

The main cyclisation product could be assigned structure **25** on grounds of IR, UV, mass and PMR spectra being analogous to those of aldehyde **31** (Experimental). There was again no evidence whatsoever for the 5-*exo*-trig process to spiro compounds nor were there products suggesting a 1,3-hydride shift during the multistep reaction. The dominant feature in these two cases seems to be a 6-*endo*-trig-cyclisation with further rearrangements (Me shifts, proton loss and double bond isomerization). The major by-products in the above reaction were two non-conjugated methyl ketones. Both of them, according to their PMR absorptions especially, are also logic derivatives of the primarily formed cationic metal enolate i.e. either Me migration from position 1 with subsequent proton loss from carbon 2 to give **38** or simply proton loss from carbon 9 to form **39** (diagram 7).

EXPERIMENTAL

Preparation of **2**. Although being a known compound we describe a procedure that will consistently yield **2** of 90% purity in almost quantitative yield, the tetrahydroionone being the main by-product. Through careful fractional distillation under vacuum (~0.1 Torr) the crude **2** can be purified to a higher degree (95% or better). The catalyst after two initial hydrogenation batches not giving good quality hydrogenation, can be reused for the same purpose at least ten times. For a one-mole batch by hydrogenation at room temp and normal pressure one takes 30 ml Raney–Ni sedimented in EtOH (Fluka puriss, Buchs, Switzerland) which corresponds to about 18 g metal catalyst. After washing it with EtOAc it is combined with a soln of 200 mg 1,2-Bis(2-hydroxy-ethylthio)-ethane in 30 ml MeOH. Then this preparation is added to a soln of 192 g (1 mole) β-ionone in 1200 ml EtOAc. The hydrogen take-up is monitored and after 25 l the reaction can be stopped although the hydrogenation curve is not completely horizontal. H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): s(3 H) at $\delta = 2.143$; s(3 H) at $\delta = 1.568$; s(6 H) at $\delta = 0.98$; (dd(2 H, J = 8 and 8 c/s) at $\delta = 2.5$; dd(2 H, J = 8 and 8 c/s) at $\delta = 2.255$; pseudo t(2 H) at $\delta = 2.40$ (J = 6 c/s); m(2 H) at $\delta = 1.568$ and m(2 H) at $\delta = 1.416$ ppm.

Preparation of **3** was done according to lit.[7] reaching 60% crystalline acid after distillation at 0.06 Torr, 102°. Similarly **4**[7] and **5**[8] were prepared according to lit.

Preparation of **6**. 16 g (667 mmoles) Mg turnings were covered by 100 ml dry THF and a small amount of vinyl bromide added. After the reaction started the remaining 51 ml (690 mmoles) of vinyl bromide and 900 ml of THF were added in order to keep the soln at 60–65°. After additional 30 min stirring at the same temp the grey soln was kept at 35° while 41.6 g aldehyde **5** (230 mmoles) was added dropwise. The mixture was stirred at 35° for 2 more hr before it was diluted with sat NH_4Cl, extracted with ether, washed and dried in the usual way. After evaporation of the solvent the crude product was short path distilled at ~75°/0,001 Torr to give 45,5 g (94%) **6** (Found: C, 80.54; H, 11.62; $C_{14}H_{24}O$ requires: C, 80.71; H, 11.61%). ν_{max} (neat) 3350, 3090, 1640, 920 cm^{-1}. MS (CEC 21–110 B): M^+ 208 (16) *m/e* = 193 (5), 175 (19), 147 (4), 136 (17), 123 (100), 109 (19), 95 (41), 81 (29), 69 (25), 55 (18), 41 (16); H-NMR ($CDCl_3$ plus TMS on Varian EM 360): dq (1 H, J = 17, 10, 6 *c/s*) at $\delta = 5.92$; broad d (1 H, J = 17 c/s) at $\delta = 5.19$; broad d (1 H, J = 10 c/s) at $\delta = 5.10$; broad q (1 H, J = 6 c/s) at $\delta = 4.1$; s (3 H) at $\delta = 1.56$; s (6 H) at $\delta = 0.95$ ppm.

Preparation of **7**. 20.8 g (0,1 mole) **6** was dissolved in 700 ml acetone and kept at −10°. Under vigorous stirring 40 ml Jones reagent (0,106 mole CrO_3) was added dropwise and the temp finally reached 0°. After five more min further stirring the mixture was worked up with ether–water, washed to neutrality, dried and evaporated. Short path distillation at 50°/0.06 Torr gave 18.1 g pure **7** (88%); (Found: C, 81.18; H, 10.94; $C_{14}H_{22}O$ requires: C, 81.50; H, 10.75%). λ_{max} 213 nm (ε = 9500 in EtOH). ν_{max} (neat) 1695/1685, 1615, 1092, 985, 960 cm^{-1}. MS (CEC 21–110 B): M^+ 206 (14) *m/e* = 191 (24), 188 (27), 173 (28), 163 (3), 145 (5), 136 (55), 121 (100), 107 (19), 93 (30), 79/81 (16), 69 (14), 55 (33), 41 (19). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): $\delta = 6.36$ (1 H, dd, J = 18/10 c/s); $\delta = 6.22$ (1 H, split d, J = 18/1 c/s); $\delta = 5.82$ (1 H, split, J = 10/1 c/s); $\delta = 2.650$ (2 H, m, J = 8 c/s + +); $\delta = 2.310$ (2 H, m, J = 8 c/s + +); $\delta = 1.920$ (2 H, broad pseudo t, J = 6 c/s); $\delta = 1.590$ (3 H, s); $\delta = 1.575$ (2 H, m); $\delta = 1.428$ (2 H, m); $\delta = 0.990$ ppm (3 H, s).

Preparation of **8** *and* **9**. To 25.8 g (125 mmoles) of **7**, dissolved in 1250 ml dry benzene plus 250 ml dry ether, 275 ml of a soln of stannic chloride in benzene (0.5 molar) were added at −5°. After addition the soln was stirred and slowly (3–4 hr) brought to room temp and left overnight. The mixture was then poured into an excess of sat bicarbonate–ice mixture and extracted thoroughly with ether. After washing to neutral and drying, the solvent was evaporated to give 28 g of a viscous yellow oil which was short path distilled at 70–78°/0.01 Torr (~10% residue). The distillate was semicrystalline and consisted of **8** and **9** in a ratio of roughly 1:2. This distillate was dissolved in 100 ml ether and added dropwise to a stirred suspension of 1.64 g (43.3 mmoles) LAH in 1 l ether at room temp. After 3 hr stirring sat NH_4Cl was carefully added. A sandy ppt formed which was separated by decantation and twice washed with ether. After washing the combined organic layer to neutrality, drying with $MgSO_4$ and evaporation 25.1 g semicrystalline product was obtained. Chromatography on the 65-fold weight silicagel (0.06–0.2 mm particle size) using hexane–ether eluted the tricyclic alcohol first (m.p. 96–98.5°) and then the spiroalcohols (with hexane ÷ ether = 50 ÷ 50). They were individually re-oxidized with Jones reagent in acetone soln at −10° to give **8** and **9** again in pure state after Kugelrohr-distillation.

Data of **8**. λ_{max} 236 nm (ε = 10000 in EtOH). ν_{max} (neat) 1680, 1620, 1380, 1365, 970/960/940, 865, 795, 750 cm^{-1}; MS (Varian-MAT CH5): M^+ 206 (85), *m/e* = 191 (16), 171 (4), 163 (17), 149 (12), 136 (20), 122 (100), 107 (40), 94 (69), 79 (80), 69 (40), 55 (38), 41 (50), 29 (12). H-NMR ($CDCl_3$ plus TMS on Varian XL-100): d (1 H, J = 10 c/s) at $\delta = 6.60$; d (1 H, J = 10 c/s) at $\delta = 6.10$; sharply split group (2 H) at

δ = 2.6–2.4; s (3 H) at δ = 1.05; s (3 H) at δ = 0.98; d (3 H, J = 7 c/s) at δ = 0.81 ppm. ^{13}C-NMR ($CDCl_3$ plus TMS on Varian XL-100; shift experiment with Eu(fod)$_3$-d_{27}): singlets at δ = 199.2/44.1/38.7 ppm; doublets at δ = 156.6/129.8/36.2 ppm; triplets at δ = 36.7/35.8/29.6/21.8/20.75 ppm; quartets at δ = 28.5/23.2/17.95 ppm. The oxime of **8** was made with freshly prepared hydroxylamine acetate in refluxing ethanolic soln and extracted from the diluted reaction mixture with ether. Recrystallization from ether–hexane or methylene chloride–hexane mixtures gives needles having a m.p. 176–177° (Found: C, 75.91; H, 10.27; N, 6.29%; $C_{14}H_{23}ON$ requires: C, 75.97; H, 10.47; N, 6.33%).

Data of **9** (Found: C, 81.50; H, 10.98%; $C_{14}H_{22}O$ requires: C, 81.50; H, 10.75%) m.p. 145–150° (waxy crystals). ν_{max} ($CHCl_3$) 1700, 1450, 1408, 1375, 1360, 1295, 1045, 970 cm^{-1}. MS (Varian MAT CH5): M$^+$ 206 (26), *m/e* = 191 (30), 188 (77), 173 (35), 163 (16), 149 (18), 136 (78), 121 (100), 109 (55), 93 (83), 79 (74), 69 (50), 55 (64), 41 (76), 39 (36), 27 (19). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 2.545 (1 H, dq, J = 18/10/7 c/s); δ = 2.415 (1 H, broad dd, J = 10/6 c/s); δ = 2.365 (1 H, d, J = 6 c/s); δ = 2.348 (1 H, dd, J = 18/9/1.5 c/s); δ = 1.962 (1 H, broad dd, J = 14/10 c/s); δ = 1.860–1.660 (2 H, m); δ = 1.545 (1 H, sharp d, J = 10 c/s belonging to hydrogen on cyclobutane bridge, coupling only with its geminal partner and pointing towards carbonyl side of the molecule); δ = 1.318 (1 H, dm with J_1 = 13 c/s); δ = 0.91 (3 H, s); δ = 0.845 (3 H, s); δ = 0.785 ppm (3 H, s). The best substance for spectral comparison in this case is nopinone. ^{13}C-NMR ($CDCl_3$ plus TMS on Varian XL-100; shift experiment with Eu(fod)$_3$-d_{27}): singlets at δ = 214.1/48.0/42.4/32.4 ppm; doublet at δ = 55.8 ppm; triplets at δ = 38.8/36.2/33.3/25.6/22.5/18.1 ppm; quartets at δ = 25.2/23.5/20.7 ppm. The oxime of **9** was prepared as described above and recrystallized from ether–hexane, m.p. 159–160°.

Preparation of **8a**. 618 mg (3 mmoles) of **8**, dissolved in 25 ml dry EtOAc were hydrogenated completely in presence of 0.5 g pre-hydrogenated platinum oxide (Adams catalyst) at room temp and normal pressure. After filtration over Celite and evaporation of the solvent, 610 mg fully saturated alcohol-mixture, m.p. ~65–75° was obtained. Jones oxidation in acetone at −10° gave after normal work-up 590 mg **8a** m.p. 60–62° (~95% purity). ν_{max} ($CHCl_3$) 1710, 1475/1465, 1405, 1390, 1330, 1150, 975, 960/950, 925, 895, 850, 830 cm^{-1}. MS (Varian MAT CH5): M$^+$ 208 (55), *m/e* = 193 (2), 175 (2), 165 (2), 161 (2), 150 (4), 137 (10), 123 (100), 109 (24), 95 (17), 82 (22), 69 (19), 55 (22), 41 (21), 29 (6). H-NMR ($CDCl_3$ plus TMS on Varian XL-100): δ = 2.48–2.15 (4 H, m); δ = 0.96 (6 H, s); δ = 0.99 ppm (3 H, d, J = 7 c/s). ^{13}C-NMR ($CDCl_3$ plus TMS on Varian XL-100; shift experiment with Eu(fod)$_3$-d_{27}): singlets at δ = 214/38.3/38.1 ppm; doublet at δ = 38.1 ppm; triplets at δ = 38.9/38.7/37.3/31.0/28.1/21.8/21.5 ppm; quartets at δ = 27.0/22.6/18.2 ppm.

Preparation of **10**. 3.1 g (15 mmoles) of **9** were dissolved in 150 ml dry ether and a soln of 10 ml MeLi in ether (18 mmoles) was added at room temp. Stirring was continued for 30 min and then the mixture was poured into crushed ice–hexane (pH 10–11), washed to neutrality, dried and the solvents evaporated. The crude product showed 50% starting material. Therefore the same procedure was repeated five times. 2.9 g crystalline **10** resulted. (Found: C, 81.12; H, 11.89%; $C_{15}H_{26}O$ requires: C, 81.02; H, 11.79%). After recrystallization from hexane the m.p. was 110–111°. ν_{max} ($CHCl_3$) 3650, 3480, 1370/1360, 1130, 1102, 1090, 1035, 990, 975, 935, 905/900, 885/880 cm^{-1}. MS (Varian MAT CH5): M$^+$ 222 (4), *m/e* = 207 (7), 204 (100), 189 (56), 161 (35), 147/148/151 (22), 133 (43), 119 (98), 109 (65), 95 (99), 81 (55), 69 (43), 55 (41), 43 (60). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 2.135 (1 H, split dd, J = 10/7/1 c/s); δ = 1.680 (1 H, d, J = 7 c/s); δ = 0.985 (1 H, d, J = 10 c/s); δ = 1.223 (3 H, s); δ = 1.167 (3 H, s); δ = 0.780 (3 H, s); δ = 0.660 ppm (3 H, s). ^{13}C-NMR ($CDCl_3$ plus TMS on Varian XL-100); singlets at δ = 74.55/47.8/39.5/32.2 ppm; doublet at δ = 51.7 ppm; triplets at δ = 38.8/36.8/33.0/28.2/24.4/18.1 ppm; quartets at δ = 31.7/25.4/23.5/21.8 ppm.

Preparation of **12**. 8.1 g (20 mmoles) triphenylphosphonium–iodide, suspended in 200 ml THF, was brought into contact with 10 ml (~20 mmoles) n-BuLi in hexane. The orange soln was stirred 1 hr at room temp before 4.12 g (20 mmoles) of **9** in 30 ml THF were added at −20°. Shortly after addition a ppt formed. After 24 hr at room temp analysis still showed 90% starting ketone present. Therefore the mixture was kept under reflux for another 2 days after which time the turnover was more than 90%. Pouring on ice, extraction with hexane and usual work-up gave 5 g crude oily product. This was chromatographed on 30 g silicagel. Hexane eluted 3.6 g (88%); pure **12** (Found: C, 87.81; H, 11.91%; $C_{15}H_{24}$ requires: C, 88.16; H, 11.84%); ν_{max} (neat) 3080, 1645, 1450, 1380/1370/1360, 1190, 1090, 1065, 980, 965, 875 cm^{-1}. MS (Varian MAT CH5): M$^+$ 204 (51), *m/e* = 189 (53), 175 (15), 161 (22), 148 (24), 137 (48), 133 (53), 123 (31), 119 (43), 111 (94), 105 (37), 95 (78), 93 (62), 91 (58), 81 (64), 69 (100), 55 (48), 41 (61). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 4.633 (1 H, narrow m); δ = 4.566 (1 H, narrow m); δ = 2.50 (1 H, allyl, coupled dt, J = 17/9/2.5 c/s); δ = 2.27 (1 H, ddd, J = 17/7/4 c/s); δ = 2.25 (1 H, d, J = 6 c/s); δ = 2.20 (1 H, dd, J = 9/6 c/s); δ = 1.375 (1 H, d, J = 9 c/s); δ = 1.23 (1 H, dm, J = 12 c/s); δ = 0.77 (3 H, s); δ = 0.76 (3 H, s); δ = 0.69 ppm (3 H, s). (The best information for comparison is gained from β-pinene). ^{13}C-NMR ($CDCl_3$ plus TMS on Bruker WH 360); singlets at δ = 150.5/47.6/41.7/32.5 ppm; doublet at δ = 49.7 ppm; triplets at δ = 105.6/39.1/36.4/26.8/25.0/24.1/18.9 ppm; quartets at δ = 25.5/23.4/20.6 ppm.

Preparation of **13**, **16**, **17** (besides **12**, **14**, **15**). 2.45 g (11 mmoles) of **10** and 200 mg *p*-toluenesulfonic acid hydrate were dissolved in 65 ml dry benzene and kept at 55° bath temp for 5 hr (until no starting material was visible on glc). The water formed was pipetted out. After diluting with hexane the soln was washed to neutrality. The crude oily product was pre-purified on 8 thick layer plates (Merck) with the solvent system 25 pentane ÷ 25 hexane ÷ 50 $CHCl_3$ ÷ 5 EtOAc to yield 1.9 g (85%) of water-clear hydrocarbon mixture. Column chromatography on silicagel impregnated with 15% $AgNO_3$ (first on 100-fold weight, then again on 200-fold weight, particle size 0.06–0.2 mm) using hexane and 99 hexane ÷ 1 ether mixture and for a third column using hexane and 99 hexane ÷ 1 benzene mixture as eluant, allowed the separation in the following order: **13**, **15**, **16**, **17**, **12**, **14**.

Data of **13** (Found: C, 87.82; H, 12.07%; $C_{15}H_{24}$ requires: C, 88.16; H, 11.84%). ν_{max} (neat) 1470/1460/1455, 1380/1370/1360, 1330, 1190, 1165/1155, 1130, 1060, 1020, 980, 965, 895, 795, 785 cm^{-1}. MS (Varian MAT CH5): M$^+$ 204 (20), *m/e* = 189 (10), 175 (2), 161 (9), 147 (11), 133 (32), 119 (100), 111 (31), 105 (25), 93 (27), 81 (12), 77 (11), 69 (18), 55 (12), 41 (16), 29 (7). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 5.25 (1 H, narrow m); δ = 2.27 (1 H, dd, J = 8/6 c/s); δ = 2.09 (1 H, dm, J = 16/~1 c/s); δ = 1.995 (1 H, dm, J = 16/~1 c/s); δ = 1.756 (1 H, dd, J = 6/~1 c/s); δ = 1.672 (3 H, narrow m); δ = 1.215 (1 H, dm, J = 12 c/s); δ = 1.044 (1 H, d, J = 8 c/s); δ = 0.822 (3 H, s); δ = 0.803 (3 H, s); δ = 0.680 ppm (3 H, s). ^{13}C-NMR ($CDCl_3$ plus TMS on Bruker WH 360): singlets at δ = 142.6/47.9/32.2 ppm; doublets at δ = 117.3/45.1 ppm; triplets at δ = 38.9/35.7/32.2/31.4/18.9 ppm; quartets at δ = 24.9/23.3/22.6/19.5 ppm. (The best information for comparison is gained from α-pinene).

Data of **16** (tentative structure, comparison in certain features with α-fenchene). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 4.712 (1 H, narrow q); δ = 4.528 (1 H, narrow q); δ = 2.545 (1 H, broad d, J = 16 c/s); δ = 1.84 (1 H, broad d, J = 16/~2 c/s); δ = 1.945 (1 H, tm, allylic cpl); δ = 1.008 (3 H, s); δ = 0.969 (3 H, s); δ = 0.808 ppm (3 H, s). MS (glc-coupling to Varian MAT 212, Finnigan–Incos data system): M$^+$ 204 (10), *m/e* = 189 (20), 175 (4), 161 (18), 148

(15), 133 (26), 119 (50), 108 (100), 93 (97), 79 (58), 69 (40), 55 (32), 41 (50).

Data of **17** (tentative structure, comparison in certain features with camphene: H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): $\delta = 4.631$ (1 H, s); $\delta = 4.392$ (1 H, s); $\delta = 2.581$ (1 H, broad t, J ~ 5 c/s); $\delta = 2.072$ (2 H, d, J ~ 5 c/s) ?; $\delta = 0.969$ (3 H, s); $\delta = 0.900$ (3 H, s); $\delta = 0.883$ ppm (3 H, s). MS (glc-coupling to Varian MAT 212, Finnigan–Incos data system): M^+ 204 (55), *m/e* = 189 (36), 175 (14), 161 (36), 147 (40), 133 (100), 119 (62), 106 (87), 107 (90), 91 (95), 93 (66), 79 (63), 67 (32), 69 (28), 55 (38), 41 (57).

Preparation of **18**. This was done according to lit.[9]

Preparation of **37**.[10] 6.96 g (290 mmoles) magnesium turnings were covered with 60 ml dry THF and 1 ml vinyl bromide was added while heating the turnings in order to induce reaction. Then 600 ml THF and 21.3 ml (totally 300 mmoles) vinyl bromide was added within 15 min to keep the reaction going. After additional stirring for 30 min the grey-brownish soln was cooled to 20° and 16.63 g (100 mmoles) of **18** in 100 ml THF was added within 35 min at 30–35°. After 2 hr at 35–40° the reaction was complete and the work-up done with ice-cooled sat NH_4Cl and ether extraction. After drying and evaporating the solvent, 17.9 g (92%) of a yellowish oil was obtained which according to IR neat (3450, 3100, 1645, 920 cm^{-1}) and H-NMR in $CDCl_3$ ($\delta = 5.98$, 1 H, dq with J = 17/10/5.5 c/s; $\delta = 4.28$, 1 H, broad q, J = 6.5 c/s; $\delta = 2.36$, 2 H, broad d, J = 7 c/s; $\delta = 1.7$, 3 H, s; $\delta = 1.07$ ppm, 6 H, s) has the structure of the expected **36**. To 15.5 g (80 mmoles) of **36**, dissolved in acetone, 32 ml Jones reagent (84.8 mmoles CrO_3) were added at −20°. After dilution with water and extraction with hexane, drying and evaporation of solvent 15 g (~90%) of **37** remained ν_{max} (neat): 1695, 1620, 1470, 1400, 1325, 1190, 1080, 990, 965 cm^{-1}. MS (CEC21-110B): M^+ 192 (64), *m/e* = 177 (36), 159 (7), 149 (7), 137 (93), 122 (36), 107 (93), 95 (100), 81 (57), 69 (21), 55 (61), 41 (39). H-NMR ($CDCl_3$ plus TMS on Varian XL-100); $\delta = 6.40$ (2 H, m); $\delta = 5.75$ (1 H, dd, J = 8.5/2.5 c/s); $\delta = 3.32$ (2 H, s); $\delta = 2.02$ (2 H, broad dd, J = 5 c/s); $\delta = 1.52$ (3 H, s); $\delta = 0.93$ ppm (6 H, s).

Preparation of **19**[11]. To 49.8 g (0.3 mole) **18** in 750 ml benzene 96 g (0.3 mole) triphenylphosphorylidene acetone was added and the mixture stirred for 24 hr at 90° bath temp (70% starting material still present). After addition of 500 mg benzoic acid and 24 hr stirring at the same temp a probe still showed about 20% starting material. After addition of 66 g (210 mmoles) of the phosphorane the reaction was virtually complete after 24 hr under reflux temp. The brown soln was diluted with 3 l hexane and the ppt filtered off and re-washed with hexane and the hexane extract evaporated on a rotary evaporator (water pump) at 40°. The brown crystalline residue was dissolved in 100 ml 90% MeOH and extracted three times with 500 ml hexane. The combined hexane extracts were again washed three times with 50 ml 90% MeOH. All the MeOH extracts and the ppt were combined and twice extracted with hexane. After drying the total hexane soln and evaporating the solvent the yield was 54.3 g (88%). This product had to be filtered as a hexane-soln through a layer of 55 g silicagel (0.06–0.2 mm) to assure a smooth hydrogenation. λ_{max} 227 nm (ε = 13000 EtOH). ν_{max} (neat): 1695/1680, 1625, 1360, 1258, 985 cm^{-1}. MS (CEC21-110B): M^+ 206 (60), *m/e* = 191 (54), 177 (14), 163 (12), 147 (25), 133 (58), 123 (92), 107 (98), 91 (54), 81 (40), 69 (18), 67 (17), 55 (25), 43 (100). H-NMR ($CDCl_3$ plus TMS on Varian EM 360): $\delta = 6.85$ (1 H, dt, J = 16/7 c/s); $\delta = 6.07$ (1 H, d of narrow m, J = 16 c/s); $\delta = 3.02$ (2 H, broad d, J = 5.5 c/s); $\delta = 2.28$ (3 H, s); $\delta = 1.60$ (3 H, s); $\delta = 1.02$ ppm (6 H, s).

Preparation of **20**. 12.5 g (60 mmoles) of **19** in 500 ml pentane were hydrogenated in the presence of 1.8 g 5% Pd–C at room temp, strong stirring and normal pressure. As soon as the hydrogenation curve flattened out the soln was freed from the catalyst by filtration over Celite and evaporated to leave 12.2 g (97%) colourless oil (b.p. 90°/0.005 Torr). ν_{max} (neat) 1710, 1358, 1170 cm^{-1}. MS (CEC21-110B): M^+ 208 (22), *m/e* = 193 (22), 175 (21), 150 (33), 135 (100), 123 (75), 107 (33), 94 (44), 81 (39), 71 (17), 67 (18), 55 (24), 43 (93). H-NMR ($CDCl_3$ plus TMS on Varian EM 360): $\delta = 2.32$ (2 H, broad t, J = 7.5 c/s); $\delta = 2.12$ (3 H, s); $\delta = 1.58$ (3 H, s); $\delta = 0.97$ ppm (6 H, s).

Preparation of **24**. 6.5 g = 7.6 ml (60 mmoles) of trimethylchlorosilane and 12.1 g = 16.6 ml (120 mmoles) Et_3N were dissolved in 20 ml DMF and 10.4 g (50 mmoles) of **20** added. A spontaneous ppt formed. The mixture was stirred at 96° for 4 days. Then it was diluted with hexane, washed with cold bicarbonate then with cold 1 N HCl and water. After drying and evaporating the solvent, 15.5 g crude material was obtained. After distillation with a Vigreux column in the presence of a little dry K_2CO_3 to yield 7.5 g (54%) of **21**. In a 6-fold run the yield was 68% (b.p. 70°/0.005 Torr or 96°/0.01 Torr). ν_{max} (neat): 1678, 1380, 1360/1345/1320, 1258, 1200, 1150, 1100, 1060, 1010, 850, 760 cm^{-1}. MS (CEC21-110B): M^+ 280 (tr), *m/e* = 265 (~1), 253 (tr), 190 (7), 163 (~1), 150 (4), 143 (100), 135 (6), 105 (3), 93 (~2), 73 (31), 55 (2), 41 (3). H-NMR ($CDCl_3$ plus TMS on Varian EM 360): $\delta = 4.7$ and 4.48 (~1 H total, broad m); $\delta = 4.04$ (≪1 H, narrow m); $\delta = 1.62$ (3 H, s); $\delta = 1.0$ (6 H, s); $\delta = 0.20$ ppm (9 H, s). It was evident that there was always about 15–20% kinetically formed enolether present. 18.7 g (0.2 mole) dimethyl-methyleneimmonium chloride[12] was dissolved in 180 ml dry acetonitrile and 50.4 g (0.18 mole) of **21** added. After a slight exothermic reaction the soln became homogenous after 20 min. After 2 to 3 hr at room temp it was diluted with ether and extracted with cold 2 N Na_2CO_3. Then the ether phase was extracted with 2 N HCl. The ether phase after normal treatment left 7.6 g neutral part, mainly unreacted silylenolether. The acid aqueous phase was made alkaline with 2 N NaOH and extracted with ether to furnish 39.5 g (83%) Mannich-base **22** after normal washing, drying and evaporating the organic solvent. ν_{max} (neat) 2800, 1715, 1465, 1380/1365, 1270, 1050, 850 cm^{-1}. H-NMR ($CDCl_3$ plus TMS on Varian EM 360): $\delta = 2.20$ (9 H, s); $\delta = 1.55$ (3 H, s); $\delta = 0.96$ ppm (6 H, s). This material is directly dissolved in 180 ml dry MeOH and 90 ml = 205 g (1.444 mole) methyl iodide are added and the mixture stirred overnight at room temp. A ppt forms. The whole mixture was evaporated to dryness and then the residue triturated with 1 l hexane for 1 hr. The mother liquor was filtered off through a sintered glass funnel or centrifuged leaving 51.2 g (84–85%) quaternary iodide **23**/m.p. 164–167° (beginning 155°). The evaporated mother liquor contained all the substitution product (with MeOH) of the Mannich base stemming from the kinetically formed trimethylsilylenolether. All the crystalline product **23** was dissolved in 1.9 l AcOH, 44 g (~540 mmoles) anhyd NaOAc added and the mixture stirred well for 5 hr at 95° bath temp. After cooling and diluting with a large amount of water, it was extracted with hexane. Normal work-up yielded 25 g (90%) bright yellowish oily **24**. λ_{max} 221 nm (ε = 7800 cyclohexane). ν_{max} (neat) 1682, 1630, 1368, 1170, 1130, 940 cm^{-1}. MS (CEC21-110B): M^+ 220 (40), *m/e* = 205 (13), 187 (5), 177 (15), 164 (5), 151 (15), 137 (100), 123 (50), 109 (5), 95 (40), 81 (32), 69 (20), 55 (25), 43 (65). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): $\delta = 6.00$ (1 H, s); $\delta = 5.80$ (1 H, s); $\delta = 2.34$ (3 H, s); $\delta = 2.305$ (2 H, m); $\delta = 2.055$ (2 H, m); $\delta = 1.91$ (2 H, pseudo t); $\delta = 1.633$ (3 H, s); $\delta = 1.567$ (2 H, m); $\delta = 1.422$ (2 H, m); $\delta = 1.01$ ppm (6 H, s).

Preparation of **26**. 10.5 g (240 mmoles) NaH (55% dispersion) was washed with benzene by decantation. 1 l dry benzene and 52 ml (260 mmoles) ethyl-diethylphosphono-acetate were added and then to this mixture 33.3 g (200 mmoles) of **18** was added dropwise at 10–15°. The mixture was stirred overnight at room temp before it was poured into excess cold sat NH_4Cl. Extraction with ether, washing with water, drying and evaporating the solvent yielded 48.1 g (quantit.) of **26** which should not be distilled in larger amounts because of isomerization of the double bond. ν_{max} (neat) 1720, 1650, 1370, 1325, 1270, 1160–1190, 1050, 985 cm^{-1}. MS (CEC21-110B): M^+ 235 (28), *m/e* = 221 (38), 191 (15), 175 (18), 163 (4), 147 (49), 133 (8), 123 (100), 107 (43),

91 (23), 81 (15), 79 (15), 69 (7), 55 (12), 41 (28). H-NMR ($CDCl_3$ plus TMS on Varian EM 360): δ = 6.91 (1 H, dt, J = 15/6 c/s); δ = 5.70 (1 H, dm, J = 15 c/s); δ = 4.18 (2 H, q, J = 7 c/s); δ = 2.92 (2 H, broad d, J = 6 c/s); δ = 1.52 (3 H, s); δ = 1.26 (3 H, t, J = 7 c/s); δ = 0.94 ppm (6 H, s).

Preparation of **27**. 23.6 g (100 mmoles) of **26** in 1 l pentane were hydrogenated at room temp and under normal pressure in the presence of 500 mg 5% Pd–C. The reaction was monitored and stopped accordingly when the hydrogenation curve flattened out (~2.5 l H_2). The product was filtered over Celite, evaporated and short path distilled under vacuum to furnish a quantitative yield of **27** b.p. 74°/0.001 Torr; also ~80°/0.04 Torr. (Found: C, 75.27; H, 10.98%; $C_{15}H_{26}O_2$ requires: C, 75.58; H, 10.99%). ν_{max} (neat) 1738, 1376, 1250, 1190, 1150, 1080, 1040 cm^{-1}. MS (Varian MAT CH5): M^+ 238 (18), *m/e* = 223 (38), 193 (6), 182 (40), 177 (31), 159 (16), 149 (18), 135 (75), 123 (100), 108 (46), 95 (77), 81 (62), 69 (35), 55 (43), 41 (45), 29 (38). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 4.136 (2 H, q, J = 7 c/s); δ = 2.311 (2 H, t, J = 7 c/s); δ = 1.986 (2 H, m); δ = 1.90 (2 H, pseudo t, J = 6 c/s); δ = 1.683 (2 H, m); δ = 1.60 (3 H, s); δ ~ 1.56 (2 H, m); δ = 1.41 (2 H, m); δ = 1.264 (3 H, t, J = 7 c/s); δ = 0.981 ppm (6 H, s).

Preparation of **28**. 64.2 g (0.27 mole) of **27** dissolved in 400 ml dry ether were added to 10.2 g (0.27 mole) of LAH in 1.8 l ether such as to have a weak reflux. After addition the mixture was stirred for 2 hr under reflux. Then the excess reagent was destroyed carefully with sat NH_4Cl (cooling with an ice bath) in excess. The ether extract was washed to neutral, dried and the solvent evaporated to furnish 51 g crude oily product which was fractionated to give 44.5 g (84% yield) pure **28** b.p. 92/0.04 Torr. (Found: C, 79.23; H, 12.45%; $C_{13}H_{24}O$ requires: C, 79.53; H, 12.32%). ν_{max} (neat) 3350, 1480–1440, 1380, 1360, 1205, 1070, 1040, 988, 945 cm^{-1}. MS (CEC21–110B): M^+ 196 (37), *m/e* = 181 (45), 163 (16), 153 (1), 147 (1), 137 (8), 123 (100), 107 (25), 95 (41), 81 (40), 71 (24), 69 (20), 55 (27), 41 (29), 31 (11), 27 (10). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 3.661 (2 H, t, J = 6.5 c/s); δ = 1.989 (2 H, m); δ = 1.90 (2 H, pseudo t, J = 6 c/s); δ = 1.583 (3 H, s); δ = 0.983 ppm (6 H, s).

Preparation of **29**. 35 ml (451 mmoles) dry pyridine and 310 ml dry CH_2Cl_2 were placed in a predried flask. 21.69 g (217 mmoles) CrO_3 (predried over P_2O_5 under vacuum) were added portionwise through a closed system. A red-brown soln formed with a dark brown ppt which was stirred at 20° for 35 min. To this was added at 0° quickly a soln of 7.09 g (36.1 mmoles) of **28** in 90 ml dry CH_2Cl_2. Additional stirring for 25 min at 0–22° was necessary before the organic soln was decanted from a dark tar-like residue. The latter was rewashed with CH_2Cl_2 three times. The combined organic phase was consecutively washed with cold 2 N NaOH, 2 N H_2SO_4, sat $NaHCO_3$ and water. Drying and evaporating the CH_2Cl_2 yielded 5.55 g (79%) golden-brown liquid which was short path distilled →5 g **29** (70%); b.p. 120°/0.06 Torr. ν_{max} (neat 2730, 1730, 1450–1480, 1418/1392/1365 cm^{-1}. MS (CEC21–110B): M^+ 194 (41), *m/e* = 179 (38), 161 (45), 150 (21), 135 (9), 123 (100), 107 (38), 100 (34), 95 (66), 81 (51), 69 (28), 67 (24), 55 (31), 41 (41), 29 (10). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 9.786 (1 H, t, J = 1.5 c/s); δ = 2.444 (2 H, td, J = 7/2 c/s); δ = 1.983 (2 H, m); δ = 1.901 (2 H, pseudo t, J = 6 c/s); δ = 1.689 (2 H, m); δ = 1.60 (3 H, s); δ = 1.569 (2 H, m); δ = 1.417 (2 H, m); δ = 0.983 ppm (6 H, s).

Preparation of **30**. 13.8 g (71 mmoles) of **29** and 2.8 g (94.7 mmoles) paraformaldehyde were dissolved in a mixture of 14.3 ml (137.3 mmoles), diethylamine and 13.5 ml (236.7 mmoles) glacial AcOH. As a polymerization inhibitor 100 mg BHT were added. The mixture was stirred for 3 hr at 60°. The mixture was cooled, diluted with ether, washed with water to neutral pH and dried. Evaporation of the solvent furnished 16.3 g yellow liquid. Short path distillation (twice!) at 70°/0.05 Torr left 8.8 g distillate which was chromatographed on 100 g silicagel with pentane as eluant. 6.5 g (43%) pure **30** resulted. λ_{max} 219 nm (ε = 9500 in cyclohexane). ν_{max} (neat) 2700, 1695, 1625, 1480–1440, 1380, 1360, 1340, 1325, 1230, 1210, 1155, 945, 882, 840. MS (Varian MAT CH5): M^+ 206 (13), *m/e* = 191 (8), 188 (2), 173 (21), 163 (7), 150 (9), 137 (84), 123 (52), 107 (27), 95 (100), 81 (84), 69 (25), 67 (24), 55 (31), 41 (54), 29 (16). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 9.556 (1 H, s); δ = 6.286 (1 H, broad s); δ = 5.896 (1 H, s); δ = 2.292 (2 H, m = A_2) and δ = 2.097 (2 H, m = B_2); δ = 1.914 (2 H, pseudo t, J = 6 c/s); δ = 1.636 (3 H, s); δ = 1.569 (2 H, m); δ = 1.428 (2 H, m); δ = 1.011 ppm (6 H, s).

Preparation of **31**. To 2 g (9.7 mmoles) of **30** in 50 ml toluene and 60 ml benzene, 21.4 ml (10.7 mmoles) 0.5 M stannic chloride in benzene was added dropwise within 15 min at −25° to −18°. After 40 min stirring at −25° no starting material could be observed. The soln was poured into excess icecold bicarbonate (pH → 7) and the whole extracted with hexane. After normal procedure 1.9 g bright yellow oil (ν_{max} (neat) 2720, 1690, 1645 cm^{-1}) was obtained which consisted of one big peak on glc with a series of minor impurities. Preparative gas-chromatographic purification on CW-20M furnished pure **31** (500 mg). λ_{max} 228 nm (ε = 11000 in cyclohexane). ν_{max} (neat) 2720, 1695, 1645, 1475, 1450, 1400, 1380, 1305, 1220/1210, 1195, 1170, 1125, 1095, 1085, 1060, 1045, 1020, 1000, 940, 900, 875, 855, 830, 790, 770, 730 cm^{-1}. MS (CEC21–110B); shows that the aldehyde quite easily oxidizes): M^+ 206 (52), *m/e* = 191 (11), 173 (9), 163 (13), 150 (19), 137 (100), 123 (56), 107 (41), 91 (44), 79 (44), 77 (48), 69 (30), 67 (26), 55 (41), 41 (56). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 9.402 (1 H, s); δ = 6.462 (1 H, narrow q, J ~ 1 c/s); δ = 2.511 (1 H, dm, J = 13 c/s, axial angular proton); δ = 2.355 (1 H, d of broad d, J = 18/6 c/s, equat. allylic proton); δ = 2.085 (1 H, m with J = 18/13/6 c/s axial allyl. proton); δ = 1.19 (1 H, dm, J = 13 c/s); δ = 0.965 (3 H, s); δ = 0.85 (3 H, s); δ = 0.786 ppm (3 H, s).

Preparation of **25**. 15.4 g (70 mmoles) of **24** in 1.5 l benzene and 300 ml dry ether was subjected to the slow addition (30 min) of 182 ml (91 mmoles) 0.5 M stannic chloride in benzene at −5°. After 27 hr at room temp (25°) the conversion was ≈95%, and the bright yellow soln was poured into excess icecold bicarbonate soln (pH 8) and extracted with hexane. Normal washing, drying and evaporation of solvent furnished 15.6 g crude cyclization mixture, consisting according to glc of many ketones, but mainly of three dominant peaks. After column chromatography over 65 g silicagel (0.06–0.2 mm particle size) using hexane, hexane–ether mixtures, the elution of the different ketones took place with hexane ÷ ether = 9 ÷ 1. One fraction of 3.8 g mixture of the dominant peaks was separated further by preparative glc technique on Carbowax to yield the pure **25** as the last peak. (Found: C, 81.27; H, 10.95%; $C_{15}H_{24}O$ requires: C, 81.76; H, 10.98%). λ_{max} 230 nm (ε = 13900 in cyclohexane). ν_{max} (neat) 1670, 1645, 1480, 1455/1440, 1390/1380, 1360, 1312, 1280/1260, 1130, 1115, 1075, 1015, 948, 910/900, 880, 855 cm^{-1}. MS (CEC21–110B): M^+ 220 (77), *m/e* = 205 (26), 202 (5), 192 (3), 187 (7), 177 (24), 163 (16), 151 (100), 137 (49), 123 (33), 107 (26), 95 (26), 83 (16), 69 (12), 55 (12), 43 (58). ^{13}C–NMR ($CDCl_3$ plus TMS on Varian XL 100): singlets at δ = 197.64/137.84/36.98/35.67 ppm; doublets at δ = 145.24/-40.23 ppm; triplets at δ = 37.14/28.74/27.66/22.84/21.63 ppm; quartets at δ = 2 × 24.98/22.03/13.82 ppm. H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 6.531 (1 H, narrow m); δ = 2.439 (1 H, d of broad m, J = 13 c/s, axial angular proton); δ = 2.392 (1 H, dd of broad m, J = 18/6 c/s, equat. allylic proton); δ = 2.278 (3 H, s); δ = 2.117 (1 H, very broad m, axial allyl, proton); δ = 1.172 (1 H, dm, J = 13 c/s); δ = 0.944 (3 H, s); δ = 0.839 (3 H, s); δ = 0.772 ppm (3 H, s). The second last peak from glc preparation (tentative structure **38**); ν_{max} (neat) 1710, 1470–1440, 1390/1375/1358, 1290/1275, 1210, 1182, 1170, 1090/1080, 1010, 950, 815 cm^{-1}. MS (CEC21–110B): M^+ 220 (100), *m/e* = 205 (36), 202 (10), 187 (24), 177 (48), 159 (17), 152 (21), 151 (33), 135 (19), 123 (67), 121 (76), 107 (71), 93 (45), 81 (24), 67 (17), 55 (19), 43 (57). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360): δ = 5.267 (1 H, unsplit m); δ = 2.608 (1 H, tt, J = 12/4 c/s, axial α-proton to carbonyl); δ = 2.142 (3 H, s); δ = 1.614 (3 H, narrow m); δ = 0.908 (3 H, s); δ = 0.844 ppm (3 H, s). The third last main peak from glc

preparation (tentative structure **39**); ν_{max} (neat) 1712, 1465, 1375, 1358, 1305, 1270, 1175 cm^{-1}. MS (CEC21–110B): M^+ 220 (100), *m/e* = 205 (47), 202 (6), 187 (18), 177 (41), 164 (29), 161 (53), 149 (26), 137 (41), 135 (38), 121 (56), 107 (59), 105 (82), 91 (79), 85 (15), 81 (29), 69 (18), 55 (21), 43 (79). H-NMR ($CDCl_3$ plus TMS on Bruker WH 360); δ = 5.539 (1 H, dd, J = 6/3 c/s); δ = 2.528 (1 H, m, axial α-proton to carbonyl); δ = 2.178 (3 H, s); δ = 1.133 (3 H, s); δ = 1.117 (3 H, s); δ = 1.056 ppm (3 H, s).

All IR-spectra were taken on a PE-157 model and the UV-spectra measured on a Beckman DB-G instrument.

Acknowledgements—Our thanks go to Dr. E. Billeter and Mr. J. Maerki for their help in the NMR-field.

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