127. Conformationally Controlled Odor Perception in 'Steroid-type' Scent Molecules

by **Günther Ohloff, Wolfgang Giersch, Walter Thommen** and **Bruno Willhalm**

Firmenich SA, Research Laboratories, CH-1211, Geneva 8

Dedicated to Prof. *Edgar Lederer* on the occasion of his 75th birthday

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Summary

A series of compounds possessing a 'steroid-type' scent and related to 4-(4′-*t*-butylcyclohexyl)-4-methyl-2-pentanones (**1** and **2**) has been synthesized. The odor of these compounds has been found to be dependent on their conformation; only when the molecule can assume a steroid-like shape there is an interaction with the odor chemoreceptor.

Structurally unrelated odoriferous compounds can exhibit odor similarities for which no satisfactory explanation on a molecular basis has been offered [1]. A particularly remarkable example is that of the diastereoisomeric 4-(4′-*t*-butylcyclohexyl)-4-methyl-2-pentanones (**1** and **2**) [2]. Namely one of these epimeric ketones exhibits the same penetrating urine-perspiration-type odor as 5*α*-androst-16-en-3-one [3]. The explanation suggested in this case was the similarity of the 'oriented profiles' of the molecular models of these two compounds [2]. A later communication stated that only the *cis*-compound **2** exhibits this specific sensory activity[1]) while the *trans*-compound **1** is odorless [4]. This appears to be in contradiction with the configuration of odoriferous steroids since it is the molecular shape of the odorless *trans*-ketone **1** which can best be compared to the shape of the sensorially active 5*α*-androst-16-en-2-one (**27**) [5]. To clear up this discrepancy we decided to tackle the stereocontrolled synthesis of several 'secosteroids' together with systematic structure modification based on model molecules **1** and **2** (for the syntheses, see *Exper. Part*).

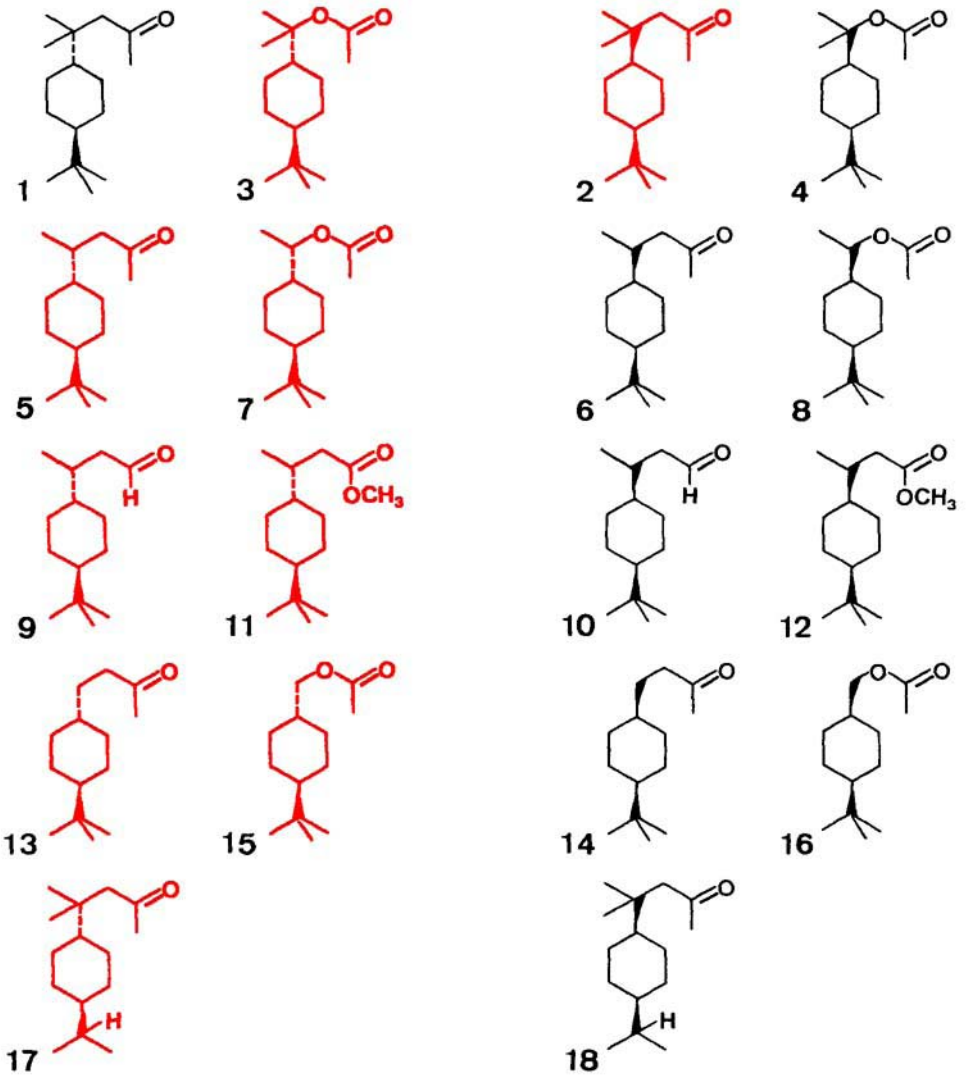
Our results regarding the odor behavior are summarized in *Scheme 1*. Compounds marked in red have a pronounced urine-perspiration odor, which we shall call 'steroid-type'; the other structures represent those diastereoisomers which were either found to be odorless or at the most possessing only a weak and undefinable

[1]) The odor perception is accompanied by a high percentage of anosmic defect and rapidly ensuing fatigue.

flowery, or slightly woody odor. In all cases there were fundamental differences between the diastereoisomers in odor intensity and quality.

The *trans*-compounds **3**, **5**, **7**, **9**, **11**, **13**, **15**, and **17** are the odoriferous diastereoisomers with the exception of the odorless *trans*-ketone **1** previously described by *Theimer et al.* [4]. In contrast, the 'steroid-type' scent of the corresponding *cis*-diastereoisomer **2** is absent in all the other *cis*-compounds **4**, **6**, **8**, **10**, **12**, **14**, **16**,

Scheme 1. trans- *and* cis-*4-(4'-t-Butylcyclohexyl)-4-methyl-2-pentanones* (**1** *and* **2**), *their congeners and derivatives* (Compounds marked in red have a pronounced 'steroid-type' scent absent in the other compounds shown)



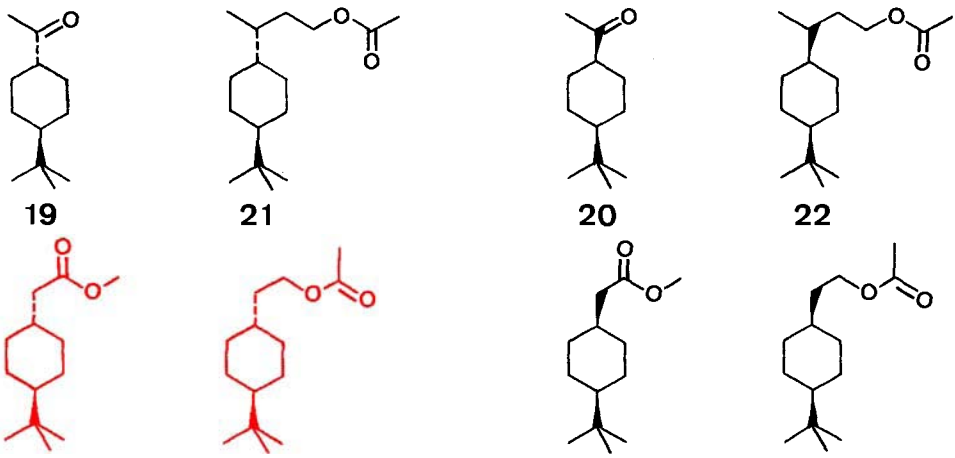
and **18**. Both **1** and **2** thus constitute exceptions to a general rule. It is also remarkable that the sensory properties of **1** and **2** are reversed in their oxa-analogs **3** and **4**.

By extensive structural modification (see *Scheme 1*) it is now possible to elucidate the most important molecular criteria for specific odor release of these 'seco-steroids'. Firstly the molecule should have a non-planar shape: aromatic compounds such as 3-(4′-*t*-butylphenyl)butanal have an odor profile quite different from that of their saturated analogs such as **9** and **10**.

Substitution in the side chain bearing the functional group seems to be of minor importance since the tonality and intensity of the odor of *trans*-4-(4′-*t*-butylcyclohexyl)-2-pentanone (**5**) are practically identical with those of compounds **2** and **3** which are more highly substituted. The odor behavior of the monomethyl derivatives **5** and **6**, however, is inversed with respect to that of the known dimethyl compounds **1** and **2**. Even replacement of the CH_3-group by an H-atom makes little difference; thus ester **15** still exhibits a strong 'steroid-type' scent, whereas for the methyl ketone **13** the urine odor occurs as an undertone to the predominant sandalwood odor. The chemical nature of the carbonyl group does not appear to be decisive because all compounds marked in red in *Scheme 1* have very similar odoriferous properties.

Another important factor is the number of atoms – in all relevant cases 7 – which are located between the carbonyl and the CH_3-groups of the *t*-butyl residue in position 4′. Thus, in the C_{12}-methyl ketones **19** and **20** this number (5) is insufficient, and for esters **21** and **22** it is too large (9): both pairs of stereoisomers have no 'steroid-type' scent[2]), and the molecular limits, thus, lie between structures **23** and **25**, which both possess the typical steroid odor[3]).

A possible explanation for the divergent odor behavior of methyl ketones **1** and **2** in relation to the other compounds shown in *Scheme 1* is apparent from detailed conformational analysis. Here, ^{13}C-NMR. spectroscopy is of great assis-

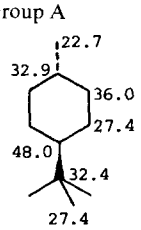


[2]) A sandalwood note is also absent in the odor of the stereoisomers **19** and **20** [7].

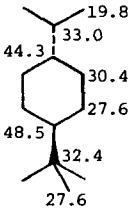
[3]) For completeness it should be pointed out that the methyl ester **24** and the acetate **26** both belong to the odorless category of *cis*-derivatives.

Scheme 2. *Chemical shifts of the ^{13}C-NMR. signals of 4-t-butylcyclohexyl derivatives*

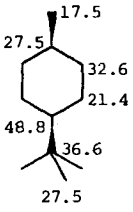
Group A



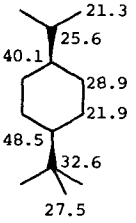
[8]

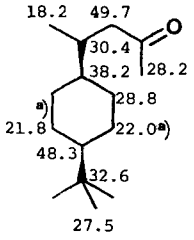


Group B



[8]





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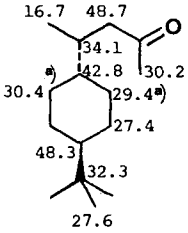
Group C



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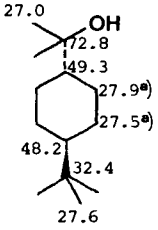
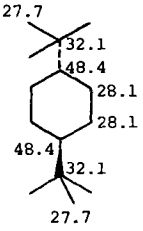
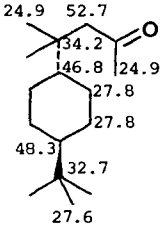
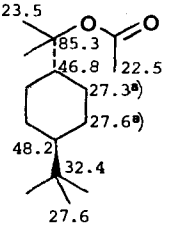




[9]

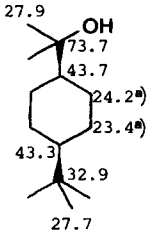


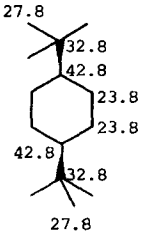
1



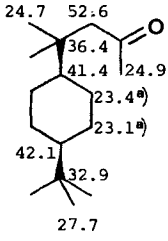
3

Group D





[9]



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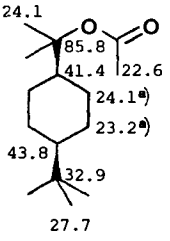


4

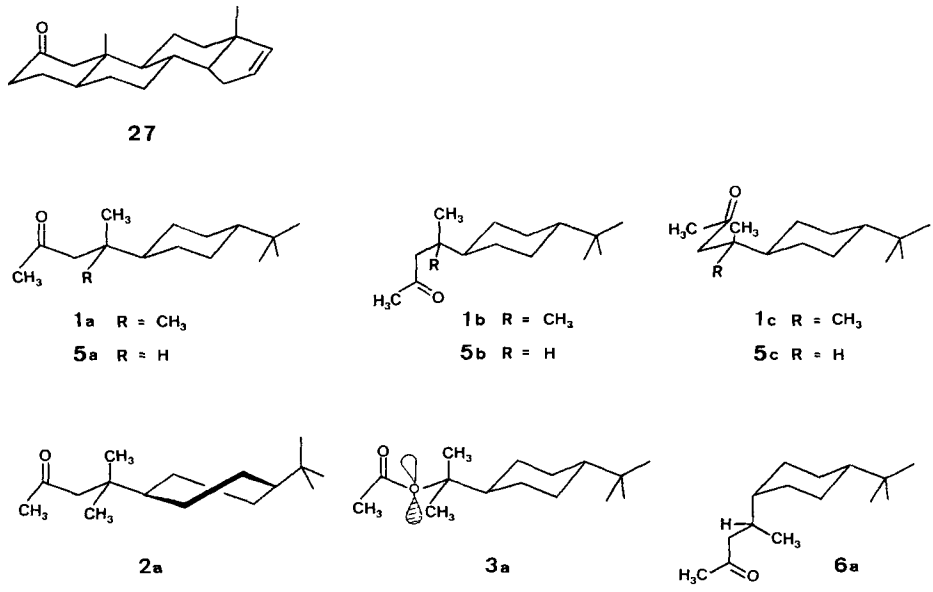
a) Not unambiguously assigned.

tance, and the data obtained for compounds **1–6** as well as for suitable reference compounds are outlined in *Scheme 2*. In accordance with known data [6], all *trans*-substituted compounds of groups A and C exist in a chair conformation with both substituents in an equatorial position. The chemical shifts of the ring C-atom bearing the *t*-butyl substituent are remarkably constant (48.0–48.5 ppm).

The *cis*-substituted compounds, however, are clearly split into two groups B and D. The compounds of group B are predominantly in a chair conformation with the *t*-butyl group in the equatorial and the other substituent in the axial position. This is indicated by the chemical shifts of the *t*-butyl-substituted ring C-atom (48.3–48.8 ppm) and the very pronounced γ-gauche effect [6] of the axial substituents (-5.4 to -6.0 ppm). In contrast, the *cis*-substituted compounds of group D exhibit predominant contributions of twist conformers [9] which are indicated by the absence of the γ-gauche effect and the significant decrease in the chemical shifts of the *t*-butyl-substituted ring C-atom (42.1–43.8 ppm).

Based on the spectroscopic data, a common molecular basis for receptor activity of the methyl ketones **2** and **5** can be invoked. Apparently, the only difference between these two ketones of opposite configuration is that **2** seems to be sensorially active in the twist conformation **2a**, while the same type of activity in compound **5** could arise from its chair conformation **5a**. However, a satisfactory explanation is still required for the deviating behavior of compound **1** with respect to compounds **5** and **3**. In solution, the side chain of **1** can adopt three different conformations (**1a–1c**). In conformation **1a**, possessing the steroidal shape of **27**, the acetyl CH_3-group and one of the geminal CH_3-groups are unfavorably close

Scheme 3. *5α-Androst-16-en-2-one* (**27**) *and conformational isomers of the structurally related carbonyl compounds* **1–3**, **5** *and* **6**



to each other. Computer calculations using CASP-system confirm **1b** and **1c** to be the most favored conformations and at the same time discount a stretched shape for the side chain as in **1a**[4]). Thus, compound **1** in solution should adopt the non-steroidal shape conformations **1b** and **1c** and hence should not interact with a 'steroid-type' receptor.

For ester **3**, on the other hand, a stretched conformation **3a** analogous to **1a** is likely, because of the energetically favored antiperiplanarity of the sp^3-orbitals of the ether O-atom with the π-bond of the carbonyl group as well as with one of the geminal CH_3-groups. This ester therefore exhibits a 'steroid-type' scent in contrast with the C-analog **1**. Although the population of twist conformers of the diastereoisomeric ester **4** in solution is high, the shape of these molecules apparently does not fit into the steroid receptor system, because **4** is odorless. The situation for the remaining esters **7/8** and **15/16** is much clearer, because of the predominant chair conformation of all stereoisomers.

In ketone **5**, as well as in related compounds **9**, **11** and **13**, there are no unfavorable interactions of the type discussed above, and thus compound **5** should assume conformation **5a** rather than **5b** or **5c**. Thus conformational differences between compounds **1** and **5** seem to be the principal reason for their different action at the receptor site. In addition, the odorless diastereoisomer **6**, and similarly the related carbonyl compounds **10**, **12** and **14**, presumably adopt the non-steroidal conformation **6a**.

A remaining problem is an explanation for why the diastereoisomers **17** and **18** which, although isopropyl analogs of methyl ketones **1** and **2**, exhibit the normal receptor activity. From steric considerations, ^{13}C-NMR. data and CASP-calculations[4]) it is evident that ketone **18** assumes a chair conformation with the isopropyl group in axial position. Therefore **18** prefers a nonsteroidal shape and is odorless. The sensory activity of its diastereoisomer **17** is not yet fully understood and will be the subject of further investigation.

We are grateful to Prof. *A. Eschenmoser* and Dr. *R.L. Snowden* for valuable discussions, Dr. *A. F. Thomas* for corrections and Miss *G. Lingesleben* for the layout of the manuscript.

Experimental Part

(with the valuable collaboration of Miss *Beatrice Frei*)

General remarks. For bulb-to-bulb distillation, a *Büchi* apparatus with external temperature reading was used. Gas chromatography (GC.) was carried out on a *Carlo Erba Fractovap 4200* and on *Varian Aerograph* instruments (models *1700* and *2700*); carrier gas: He (*ca.* 40 ml/min), using *Carbowax 20 M* or *SE 30* or 10% *SOMB* on *Chromosorb W 95*, 60–80 mesh (4 mm × 3 m). Prep. GC. separations were performed on a *Wilkens A 700 Autoprep* instrument (10% *Carbowax 20 M* on *Chromosorb W 95;* 2.5 m × 4 mm glass columns) or a *Hupe-Busch-APG-402* instrument (25% *Carbowax* on *Chromosorb W 40-80;* 2 m × 40 mm metal columns). Working temperature: 150–210°. Recording of spectra was carried out on the following apparatus: IR.: *Perkin-Elmer-125* spectrometer; characteristic band positions are given in cm^{-1}. ^{1}H-NMR.: *Varian A 60* instrument (60 MHz). MS.: The molecular ions (M^+) and fragment ions are given as *m/z* with relative peak intensities in % of the most abundant peak. All other analytical methods and instrumentation are as detailed in [5].

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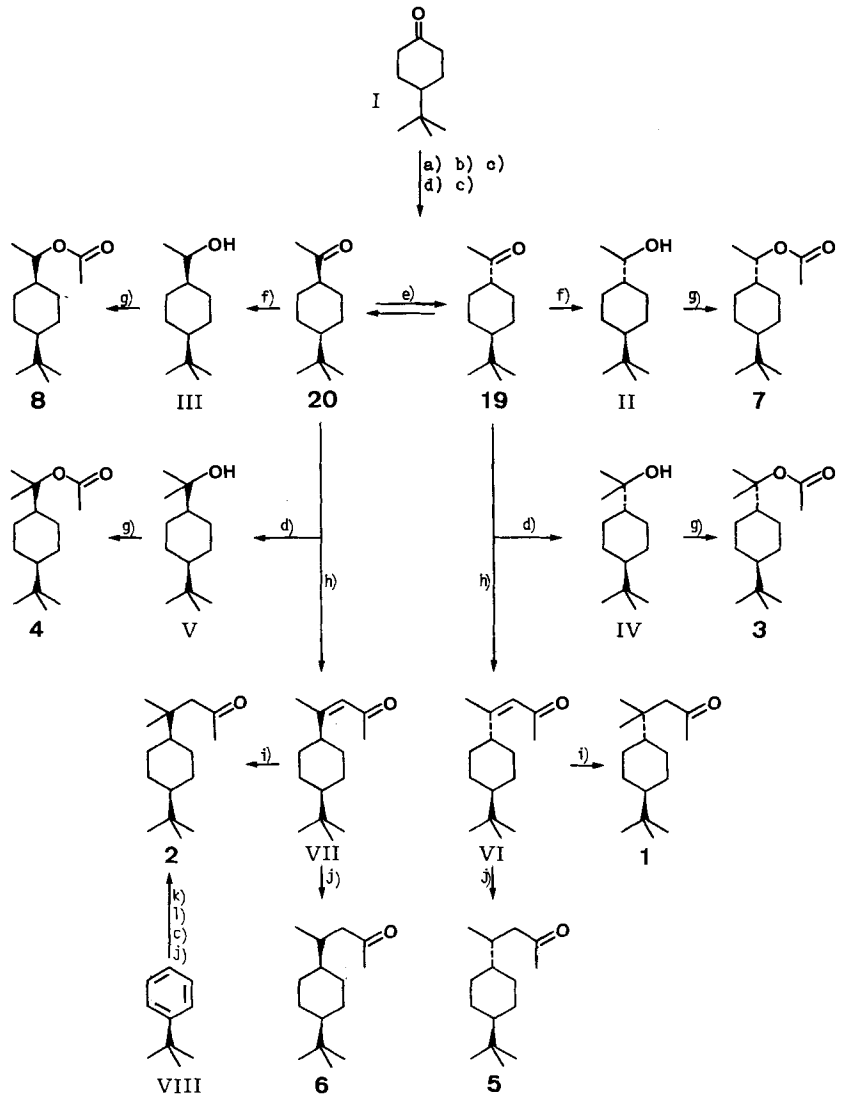
[4]) We are grateful to Dr. *W. Sieber* of *Sandoz*, Basle, for these results (CASP = Computer Assisted Synthesis Planning).

1. Preparation of *1–8*[5]. – *The mixture of* **19** *and* **20** [21] was separated into pure compounds by prep. GC. *(Hupe-Busch).* cis-*1-(4'*-t-*Butylcyclohexyl)-1-ethanone* (**20**) (peak 1): IR. (neat): 1700. – ^{1}H-NMR. (90 MHz): 0.80 (*s*, 9 H); 2.16 (*s*, 3 H). – ^{13}C-NMR. (22.63 MHz): 23.9 (C(3'), C(5')); 27.6 (C(2'), C(6'),



a) $(Ph)_3PCH_3I/BuLi/Et_2O$ [10]; b) B_2H_6/THF, $NaOH/H_2O_2$ [11]; c) CrO_3/pyridine/CH_2Cl_2 [12]; d) $MeMgI/Et_2O$ [13]; e) NaOH/EtOH; f) $LiAlH_4/Et_2O$ [14]; g) AcCl/Ac_2O/dimethylaniline [15]; h) diisopropylamine/BuLi, *N*-(isopropyliden)isopropylamine [16] [17]; i) CH_3MgI–CuI/Et_2O [18]; j) H_2, 5% Pd/C, AcOEt; k) 4-methyl-3-penten-2-one/$AlCl_3$/HCl [19]; l) Li/NH_3/*t*-BuOH [20].

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[5]) Roman numerals are used throughout this work for starting materials and intermediates not submitted to sensory evaluation.

(CH_3)$_3$C); 28.1 (C(2)); 32.5 ((CH_3)$_3$*C*); 47.1 (C(4')); 48.1 (C(1')); 211.9 (C(1)). – MS.: 182 (18, M^+), 167 (6), 164 (8), 149 (7), 126 (37), 111 (18), 97 (12), 83 (33), 71 (58), 57 (84), 43 (100), 41 (38).

trans-*1-(4'-t-Butylcyclohexyl)-1-ethanone* (**19**) (peak 2): IR. (neat): 1695. – ^{1}H-NMR. (90 MHz): 0.86 (*s*, 9 H); 2.14 (*s*, 3 H). – ^{13}C-NMR. (22.63 MHz): 26.5 (C(3'), C(5')); 27.3 ((CH_3)$_3$C); 28.1 (C(2)); 28.5 (C(2'), C(6')); 32.2 ((CH_3)$_3$*C*); 47.1 (C(4')); 51.5 (C(1')); 212.5 (C(1)). – MS.: 182 (20, M^+), 167 (5), 164 (9), 149 (9), 125 (38), 111 (11), 97 (7), 83 (31), 71 (35), 57 (90), 43 (100), 41 (36).

Equilibration. Each isomer (100 mg of **19** or **20**) was stirred with KOH (50 mg) in EtOH (10 ml) at r.t. for 24 h. After 3 h, the equilibrium was reached in each case (GC.): 92% of **19** and 8% of **20**.

trans-*1-(4'-t-Butylcyclohexyl)ethyl acetate* (**7**)[6]: IR. (neat): 1730. – ^{1}H-NMR.: 0.83 (*s*, 9 H); 1.15 (*d*, *J* = 6, 3 H); 2.01 (*s*, 3 H); 4.7 (*m*, 1 H). – MS.: 226 (0, M^+), 166 (7), 121 (77), 120 (100), 105 (21), 77 (23), 57 (51), 43 (51).

cis-*1-(4'-t-Butylcyclohexyl)ethyl acetate* (**8**)[6]: IR. (neat): 1725. – ^{1}H-NMR.: 0.83 (*s*, 9 H); 1.71 (*d*, *J* = 6, 3 H); 2.05 (*s*, 3 H); 5.13 (*m*, 1 H). – MS.: 226 (0, M^+), 166 (12), 151 (11), 110 (94), 95 (45), 81 (72), 67 (45), 57 (100), 43 (92).

trans-*1-(4'-t-Butylcyclohexyl)-1-methylethyl acetate* (**3**): M.p. 43–45°. – IR. (neat): 1710. – ^{1}H-NMR.: 0.83 (*s*, 9 H); 1.4 (*s*, 6 H); 1.96 (*s*, 3 H). – ^{13}C-NMR.: s. *Scheme 2*. – MS.: 240 (0, M^+), 180 (20), 165 (10), 137 (10), 123 (23), 109 (27), 101 (55), 81 (40), 67 (30), 57 (84), 43 (100).

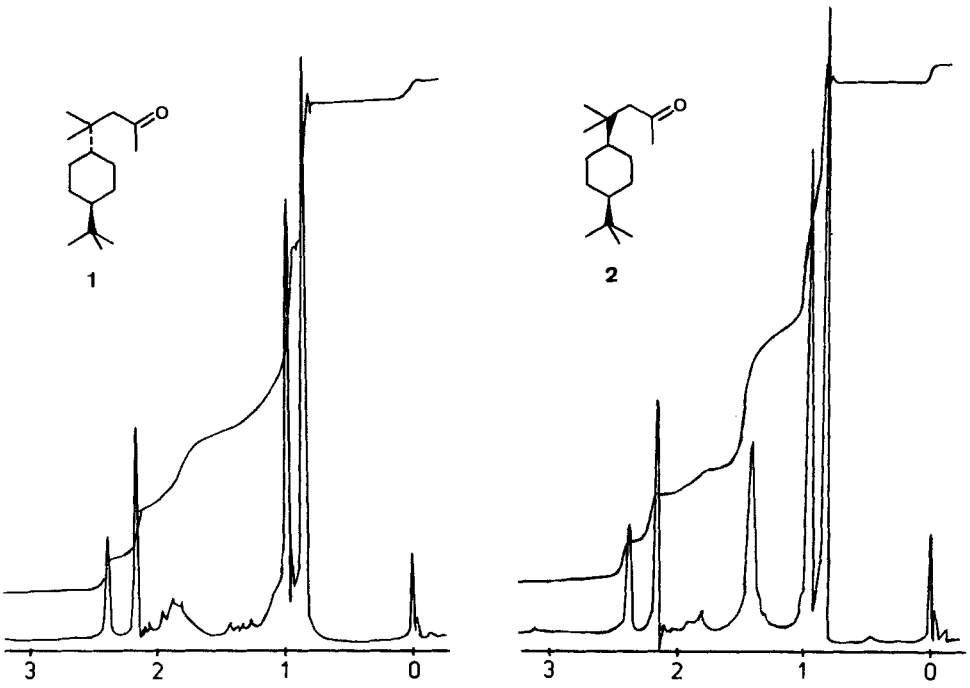


Fig. 1. *^{1}H-NMR. spectra* (60 MHz) *of* **1** *and* **2**

[6]) Mixture of stereoisomers in the side-chain.

cis-*1-(4'-t-Butylcyclohexyl)-1-methylethyl acetate* (**4**): IR. (neat): 1718. – ^{1}H-NMR.: 0.85 (*s*, 9 H); 1.45 (*s*, 6 H); 1.96 (*s*, 3 H). – ^{13}C-NMR.: s. *Scheme 2.* – MS.: 240 (0, M^+), 180 (5), 166 (6), 152 (12), 137 (11), 123 (10), 109 (17), 95 (52), 81 (55), 67 (42), 57 (100), 43 (55).

trans-*4-(4'-t-Butylcyclohexyl)-4-methyl-2-pentanone* (**1**): The product was recrystallized several times from petroleum ether until m.p. was constant: 45.5–46.5°. – IR. ($CDCl_3$): 1700. – ^{1}H-NMR. ($CDCl_3$): s. *Figure 1.* – ^{13}C-NMR.: s. *Scheme 2.* – MS.: 238 (0, M^+), 223 (1), 200 (9), 180 (62), 163 (7), 137 (9), 123 (32), 109 (19), 99 (24), 83 (43), 69 (18), 57 (71), 43 (100).

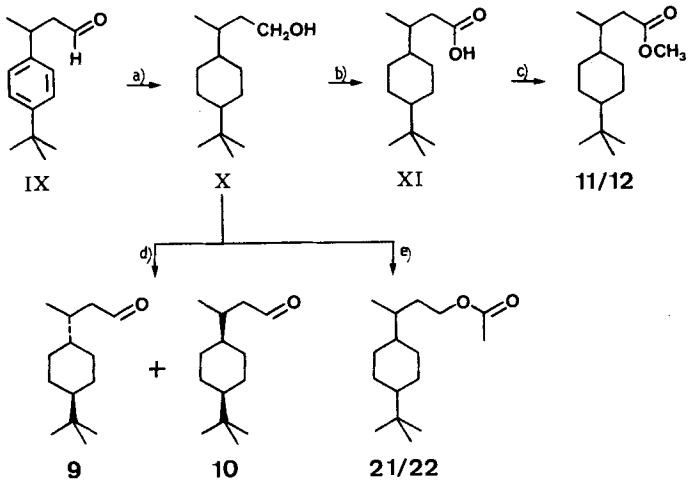
cis-*4-(4'-t-Butylcyclohexyl)-4-methyl-2-pentanone* (**2**): IR. (neat): 1700. – ^{1}H-NMR. ($CDCl_3$): s. *Figure 1.* – ^{13}C-NMR.: s. *Scheme 2.* – MS.: 238 (0, M^+), 205 (4), 180 (71), 123 (45), 109 (21), 99 (48), 83 (36), 81 (36), 67 (29), 57 (93), 43 (100).

trans-*4-(4'-t-Butylcyclohexyl)-2-pentanone* (**5**)[6]): IR. (neat): 1720. – ^{1}H-NMR.: 0.82 (*s*, 9 H); 0.95 (*d*, J = 7, 3 H); 2.04 (*s*, 3 H). – ^{13}C-NMR.: s. *Scheme 2.* – MS.: 224 (0, M^+), 166 (77), 149 (23), 109 (73), 85 (100), 67 (29), 57 (85), 43 (78).

cis-*4-(4'-t-Butylcyclohexyl)-2-pentanone* (**6**)[6]): IR. (neat): 1720. – ^{1}H-NMR.: 0.835 (*s*, 9 H); 0.95 (*d*, J = 7, 3 H); 2.04 (*s*, 3 H). – ^{13}C-NMR.: s. *Scheme 2.* – MS.: 224 (0, M^+), 166 (34), 109 (45), 85 (100), 67 (18), 57 (54), 43 (48).

2. Preparation of *9–12* and *21/22*. – *The starting material IX* was a product from *BASF* (Germany).

Methyl trans- *and* cis-*3-(4'-t-butylcyclohexyl)butanoate* (**11/12**)[6]): IR. (neat): 1742. – ^{1}H-NMR.: 0.83 (*s*, 9 H); 0.92 (*d*, J = 6, 3 H); 3.7 (*s*, 3 H).



a) H_2, 130 atm/160°, monoglyme, Ru/Cu 5% *(Deduco 4215-04114);* b) $(C_5H_5NH)_2Cr_2O_7$/DMF [22]; c) MeOH/H_2SO_4, 2 h reflux; d) $(C_5H_5NH)_2Cr_2O_7/CH_2Cl_2$ [22]; e) Ac_2O/pyridine [23].

The mixture of **9** *and* **10** was separated by chromatography on silica gel with AcOEt/cyclohexane 1:4. trans-*3-(4'-t-Butylcyclohexyl)butanal* (**9**)[6])[7]): ^{1}H-NMR. (90 MHz): 0.84 (*s*, 9 H); 0.975 (*d*, J = 6, 3 H); 9.8 (*m*, 1 H).

cis-*3-(4'-t-Butylcyclohexyl)butanal* (**10**)[6])[7]): ^{1}H-NMR. (90 MHz): 0.84 (*s*, 9 H); 0.925 (*d*, J = 6, 3 H); 9.75 (*m*, 1 H).

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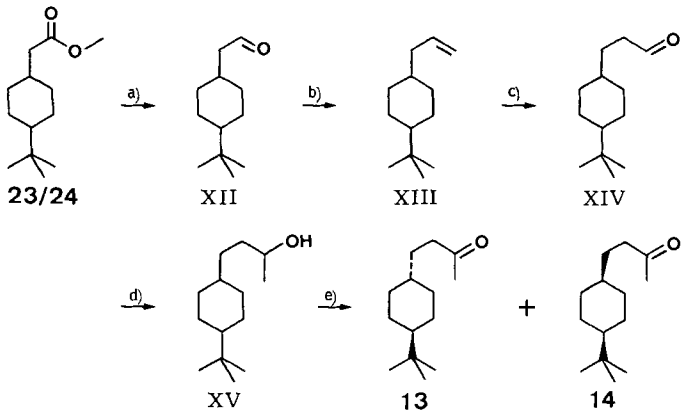
[7]) Prepared by Mr. *R. Chappaz* and Mr. *W. Schenck, Firmenich SA.*

trans- *and* cis-*3-(4'-t-Butylcyclohexyl)butyl acetate* (**21/22**): IR. (neat): 1745. – ^{1}H-NMR.: 0.85 (*s*, 9 H); 0.90 (*d*, J = 6, 3 H); 1.95 (*s*, 3 H); 4.02 (*t*, J = 7, 2 H). – MS.: 254 (0, M^+), 166 (7), 125 (18), 109 (26), 95 (22), 83 (43), 81 (47), 69 (60), 67 (26), 57 (100), 56 (63), 55 (43), 43 (59), 41 (50).

3. Preparation of *13* and *14*. – *Preparation of* **23/24** see below.

The mixture of **13** *and* **14** was separated into the pure compounds by prep. GC. trans-*4-(4'-t-Butylcyclohexyl)-2-butanone* (**13**): ^{1}H-NMR. (90 MHz): 0.82 (*s*, 9 H); 2.13 (*s*, 3 H). – MS.: 210 (21, M^+), 192 (2), 177 (5), 152 (7), 135 (32), 121 (7), 109 (13), 95 (48), 81 (29), 71 (50), 57 (100), 43 (87).

cis-*4-(4'-t-Butylcyclohexyl)-2-butanone* (**14**): ^{1}H-NMR. (90 MHz): 0.83 (*s*, 9 H); 2.15 (*s*, 3 H). – MS.: 210 (< 1, M^+), 192 (2), 177 (5), 152 (9), 135 (22), 121 (8), 109 (9), 95 (47), 81 (30), 71 (62), 57 (100), 43 (88).

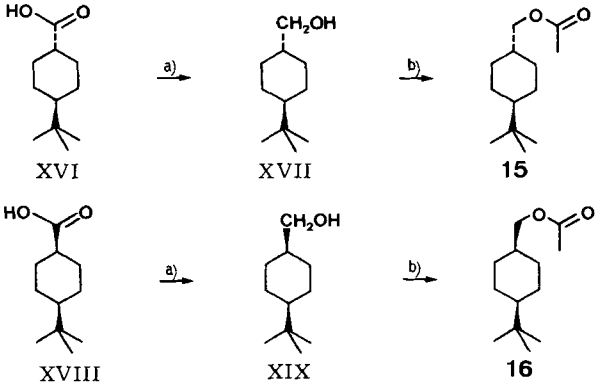


a) $NaAlH_2(OCH_2CH_2OCH_3)_2$ (*Vitride*)/toluene/ – 70° [24]; b) $(Ph)_3PCH_3I/BuLi/Et_2O$ [10]; c) B_2H_6/THF, $NaOH/H_2O_2$ [11] and CrO_3/pyridine/CH_2Cl_2 [12]; d) $MeMgI/Et_2O$ [13]; e) CrO_3/pyridine/CH_2Cl_2 [12]

4. Preparation of *15* and *16*. – *Preparation of the two pure acids*, see [25].

trans-*(4-t-Butylcyclohexyl)methyl acetate* (**15**): IR. (neat): 1745. – ^{1}H-NMR.: 0.85 (*s*, 9 H); 2.05 (*s*, 3 H); 3.88 (*d*, J = 5, 2 H). – MS.: 212 (0, M^+), 152 (20), 137 (10), 97 (51), 81 (42), 67 (21), 57 (100), 43 (59).

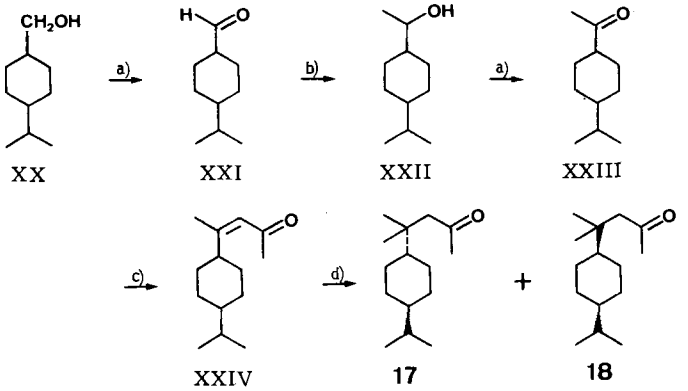
cis-*(4-t-Butylcyclohexyl)methyl acetate* (**16**): IR. (neat): 1745. – ^{1}H-NMR.: 0.83 (*s*, 9 H); 2.08 (*s*, 3 H); 4.03 (*d*, J = 8, 2 H). – MS.: 212 (0, M^+), 152 (12), 137 (10), 96 (78), 81 (64), 67 (32), 57 (100), 43 (67).



a) $LiAlH_4/Et_2O$ [14]; b) Ac_2O/pyridine [23]

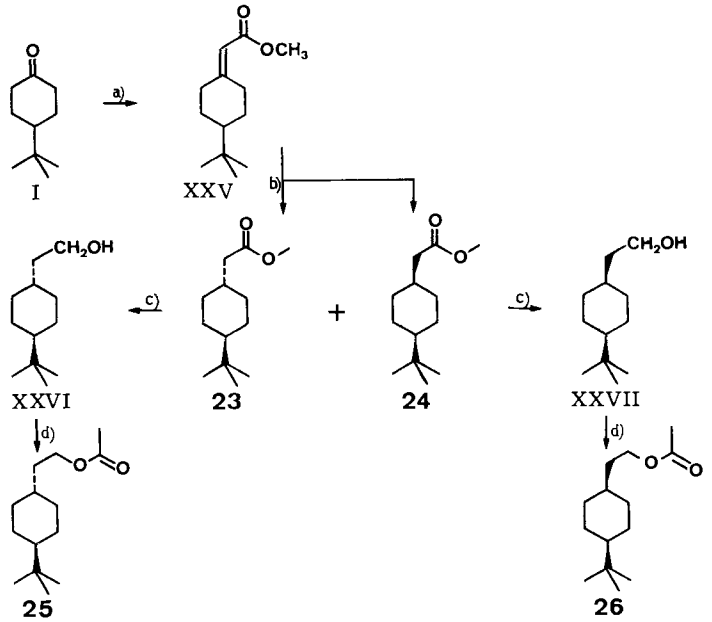
5. Preparation of *17* and *18*. – *The isomers* **17** *and* **18** were separated by prep. GC. trans-*4-(4'-Isopropylcyclohexyl)-4-methyl-2-pentanone* (**17**): ^{1}H-NMR. (90 MHz): 0.84 (*d*, $J = 6$, 9 H); 0.95 (*s*, 6 H); 2.13 (*s*, 3 H); 2.25 (*s*, 2 H). – MS.: 224 (1, M^+), 166 (69), 151 (2), 123 (33), 109 (12), 99 (19), 83 (20), 69 (40), 55 (24), 43 (100).

cis-*4-(4'-Isopropylcyclohexyl)-4-methyl-2-pentanone* (**18**): ^{1}H-NMR.: 0.88 (*d*, $J = 6$, 6 H); 0.97 (*s*, 6 H); 2.14 (*s*, 3 H); 2.25 (*s*, 2 H). – MS.: 224 (0, M^+), 166 (60), 151 (2), 123 (32), 109 (11), 99 (25), 83 (21), 69 (41), 55 (22), 43 (100).



a) CrO_3/pyridine/CH_2Cl_2 [12]; b) MeMgI/Et_2O [13]; c) diisopropylamine/BuLi, *N*-(isopropyliden)-isopropylamine [16] [17]; d) MeMgI–CuI/Et_2O [18]

6. Preparation of *23–26*. – *The mixture of* **23** *and* **24** was separated by spinning band column distillation. *Methyl* trans-*(4-t-butylcyclohexyl)acetate* (**23**): IR. (neat): 1740. – ^{1}H-NMR.: 0.835 (*s*, 9 H);



a) $(CH_3O)_2P(O)CH_2COOCH_3$/MeONa/petroleum ether 30–50° [26]; b) H_2, 5% Pd/C, AcOEt; c) $LiAlH_4/Et_2O$ [14]; d) Ac_2O/pyridine [23]

2.1 (*d*, $J=6$, 2 H); 3.59 (*s*, 3 H). – MS.: 212 (< 1, M^+), 197 (2), 181 (10), 157 (92), 156 (66), 155 (54), 123 (47), 113 (25), 95 (39), 81 (63), 74 (58), 57 (100), 56 (53), 41 (46).

Methyl cis-*(4-t-butylcyclohexyl)acetate* (**24**): IR. (neat): 1740. – ^{1}H-NMR.: 0.84 (*s*, 9 H); 2.26 (*s*, 2 H); 3.6 (*s*, 3 H). – MS.: 212 (< 1, M^+), 197 (1), 181 (13), 157 (95), 156 (86), 155 (9), 123 (34), 113 (28), 95 (32), 81 (56), 74 (59), 57 (100), 56 (40), 41 (44).

trans-*2-(4'-t-Butylcyclohexyl)ethyl acetate* (**25**): ^{1}H-NMR. (90 MHz): 0.85 (*s*, 9 H); 2.08 (*s*, 3 H); 4.12 (*t*, $J=6$, 2 H). – ^{13}C-NMR. (22.63 MHz): 20.7 (CH_3CO); 27.0 (C(3'), C(5')); 27.4 (($CH_3)_3C$); 32.2 (C(1'), ($CH_3)_3C$); 33.5 (C(2'), C(6')); 35.9 (C(2)); 47.9 (C(4')); 62.5 (C(1)); 170.5 (CH_3CO). – MS.: 226 (0, M^+), 171 (8), 166 (5), 111 (60), 110 (51), 109 (44), 95 (26), 81 (44), 69 (23), 67 (49), 57 (100), 56 (59), 43 (60), 41 (38), 29 (16), 28 (17).

cis-*2-(4'-t-Butylcyclohexyl)ethyl acetate* (**26**): ^{1}H-NMR. (90 MHz): 0.84 (*s*, 9 H); 2.08 (*s*, 3 H); 4.11 (*t*, $J=6$, 2 H). – ^{13}C-NMR. (22.63 MHz): 21.0 (CH_3CO); 21.6 (C(3'), C(5')); 27.5 (($CH_3)_3C$); 29.2 (C(2)); 29.8 (C(1')); 30.5 (C(2'), C(6')); 32.6 (($CH_3)_3C$); 48.5 (C(4')); 63.6 (C(1)); 171.0 (CH_3CO). – MS.: 226 (0, M^+), 171 (4), 166 (7), 111 (48), 110 (69), 109 (41), 95 (29), 81 (59), 69 (25), 67 (55), 57 (100), 56 (46), 43 (69), 41 (46), 29 (20), 28 (28).

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