116. Substituted 2-Phenyl- and 2-Cyclohexyl-*trans*-decalins, New Classes of Nematic Liquid Crystals

by **Martin Petrzilka**[1]) and **Kuno Schleich**

Central Research Units, *F. Hoffmann-La Roche & Co., Ltd.*

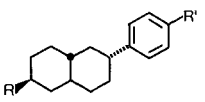
Dedicated to Professor Dr. *Walter Boguth* on the occasion of his 65th birthday

(31.III.82)

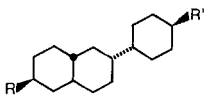
Summary

Versatile procedures for the preparation of the title compounds are described. Representatives of ketones (**12** and **27**), hydrocarbons (**19** and **28**), acids (**13**), esters (**15** and **20**), ethers (**22**) and nitriles (**18**) possess wide-range nematic phases, provided their terminal chains R^2 and R^3 contain at least three methylene units.

Introduction. – Increasing interest in electrooptical displays based on the twisted nematic effect [1] has led in past years to a continuous search for new classes of nematic liquid crystals. A recent communication by *Zollinger et al.* [2] on substituted 2-phenylnaphthalenes has induced us to present our own work on related systems. We report here[2]) on the chemical and some physical[3]) aspects of 2-phenyl-*trans*-decalins **A** and 2-cyclohexyl-*trans*-decalins **B**.



A



B

By choosing these systems as promising candidates of new classes with liquid crystalline properties it appeared to us, that several regio- and stereochemical requirements have to be fulfilled to achieve the elongated molecular shape inherent to mesogenic compounds: *(i)* suitable substituents should be introduced most favourably at C(2) and C(6) of the decalin system; *(ii)* the phenyl ring in **A** and the cyclohexyl ring in **B** should preferentially be substituted at C(4′); *(iii)* all substituents, which are connected to a cyclohexane ring, have to be disposed equatorially, and *(iv)* the decalin system must be *trans*-fused. By analogy to previous results obtained by us[4]) and others [3] [4] the presence of hydrogenated

[1]) Author to whom correspondence should be addressed.
[2]) A presentation of the results concerning 2,6-disubstituted tetralins is in preparation.
[3]) A more detailed discussion of the physical aspects of these systems will be published in due time.
[4]) Unpublished work.

0018-019X/82/4/1242-16$01.00/0

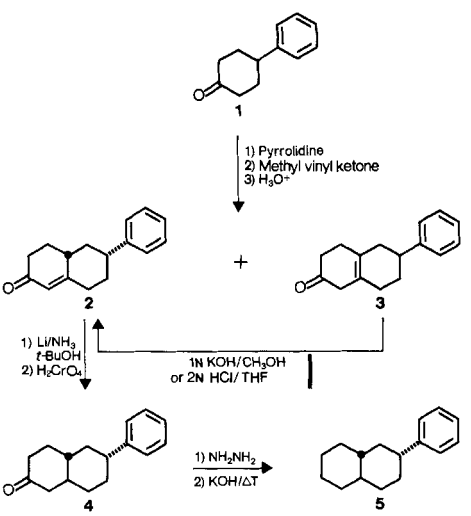
rings in these novel systems **A** and **B** could lead to mesogens, which are of lower viscosity than their aromatic counterparts.

Results and discussion. – Inspection of the target structures **A** and **B** reveals that their synthesis needs a control over the relative configuration of four and six asymmetric centres, respectively. Furthermore, it seems reasonable to assume that **B** might result from **A** *via* hydrogenation under suitable conditions.

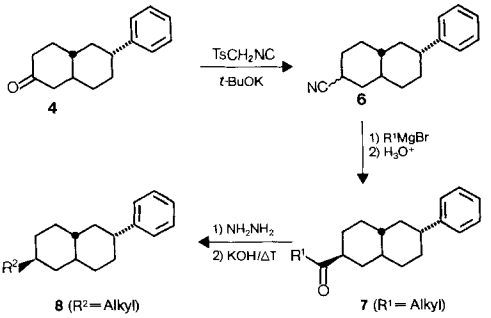
Thus for a convergent assembling of **A** we chose the tricyclic ketone **4** – the synthesis of which is delineated in *Scheme 1* – as an appropriate precursor allowing for the successive attachment of the missing substituents at a later stage. Owing to the concomitant formation of the β,γ-unsaturated ketone **3** in the initial *Robinson* annulation, the desired α,β-unsaturated ketone **2** was obtained in moderate yield (45–50%) which could be considerably improved by repeated acidic or basic equilibration and fractional crystallization of the mother liquors. The following Li/NH_3-reduction to **4** proceeded in high yield and with remarkably high stereoselectivity; the corresponding *cis*-decalin system could in fact not be detected. Additional *Huang-Minlon* reduction then led to the hydrocarbon **5**, serving later as a starting material for the preparation of 4′-monosubstituted 2-phenyldecalins, *e.g.* **12a**, **18a** and **19a** *(cf. Table 1)*.

For the stereoselective introduction of the 6β-substituent in **A** two different approaches were elaborated (*Schemes 2* and *3*). Although both of them led to **8** in good overall yield, the one depicted in *Scheme 2* appears to be less attractive for several reasons: not only must expensive tosylmethylisocyanide be used, but almost the complete reaction sequence must be repeated for every new chain-length R^2 in **8**. Moreover, the nitriles **6** usually resulted as an approx. (1:1)-mixture of epimers. These, however, could be converted mainly into the thermodynamically more stable 6β-substituted ketones **7** by treatment with a *Grignard* reagent, followed

Scheme 1



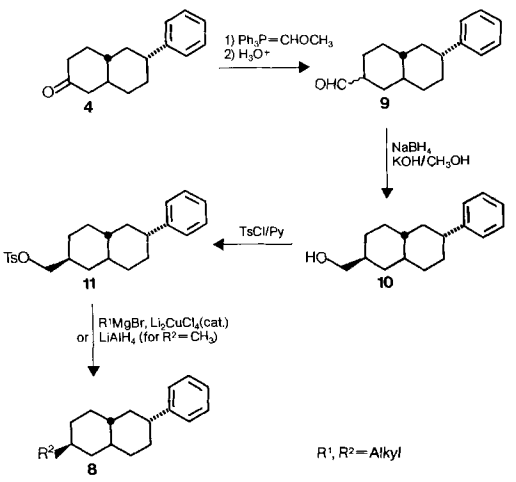
Scheme 2



by acidic or basic equilibration. Depending on the chain length of R^1 in **7**, the amount of undesired 6α-epimer varied between 1.4% ($R^1 = C_4H_9$) and 18% ($R^1 = H$)[5]).

The alternative approach was much more convergent *(Scheme 3)*. Accordingly, all of the target intermediates **8** could be obtained in a single step from a common precursor, the *p*-toluenesulfonate **11**, using the *Fouquet-Schlosser* [5] C,C-coupling procedure. Furthermore, the otherwise hardly accessible 6β-methyl derivative of **8** ($R^2 = CH_3$) resulted almost quantitatively from $LiAlH_4$-reduction of **11** in a stereochemically pure form. The $NaBH_4$-reduction, used in the preparation of **11**, deserves special mention. If this reaction, starting with an epimeric mixture of aldehydes **9** (α-CHO/β-CHO $\approx$ 1 : 4), is carried out under equilibrating conditions, the 6β-hydroxymethyl derivative **10** is formed as the sole product. Apparently, equilibration proceeds at a much faster rate than reduction, and on the other hand an equatorial aldehyde group in **9** seems to be attacked significantly more easily than an axial one.

Scheme 3



[5]) For the preparation of this aldehyde see *Exper. Part* (**4** → **9**).

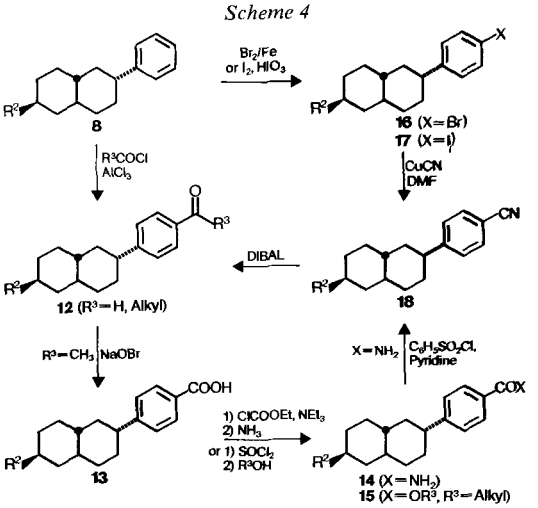
At this stage we were not disappointed by the lack of liquid crystalline properties of the monosubstituted phenyldecalins **8a–f** *(cf. Table 1)*, since for the occurrence of this behaviour both terminal chains are generally required. Conversely, this also holds true when the 6β-substituent in **A** is missing and the phenyl ring, the functionalization of which is illustrated in *Scheme 4*, is *para*-substituted as in **12a**, **18a** and **19a** *(cf. Table 1)*.

Thus, *Friedel-Crafts* acylation of **8** afforded mainly the ketones **12**; small amounts (3–5%) of the corresponding *ortho*-isomers could be removed by one or two fractional crystallizations. Although the methyl ketones **12** ($R^2 = CH_3$) obtained in this way could be converted in three steps into the nitriles **18** by standard techniques, we found it more convenient to prepare **18** *via* halogenation of **8** followed by cyanation (CuCN/DMF) of the resulting halides **16** or **17**. Especially iodination [6] was of considerable value, since the *ortho*-isomers (*ca.* 10–20%) could be removed completely by a single crystallization of **17**; the corresponding brominated *ortho*- and *para*-isomers could not be separated by any of the current methods. Moreover, **17** showed markedly higher reactivity towards the cyanation conditions than **16**.

As can be seen from the melting and clearing points listed in *Table 1*, all the aldehydes[6]) and ketones **12** (R = H, alkyl), acids **13**, esters **15** and nitriles **18** exhibit nematogenic mesophases provided that the 6β-substituent R^2 is an alkyl group.

The rather high transition temperatures of acids **13** must certainly be attributed to their existence as dimers. To study the influence of the chain length of the end groups R^2 and R^3 on the transition temperatures, a large number of homologues of ketones **12** and nitriles **18** have been prepared; within these series the usual odd-even effect [7] was observed, the degree of alternation diminishing as the number of methylene units is increased *(cf. Fig. 1)*.

Scheme 4



[6]) Conveniently prepared by diisobutylaluminium hydride reduction of **18**, see *Exper. Part.*

Table 1. *Transition temperatures and enthalpies of 2-phenyl- and 2-cyclohexyl-*trans*-decalin derivatives*

Compound	R^2	R^3	$T_{C\text{-}N}$[a]) (°C)	$T_{N\text{-}I}$[b]) (°C)	ΔH (kcal mol^{-1})
5	–	–	16	–	
8a	CH_3	–	43.7	–	4.34
8b	C_2H_5	–	29.9	–	5.12
8c	C_3H_7	–	61.2	–	5.34
8d	C_4H_9	–	45.6	–	4.53
8e	C_5H_{11}	–	56.0	–	5.60
8f	C_7H_{15}	–	54.4	–	9.57
12a	H	C_4H_9	42.5	–	
12b	CH_3	C_2H_5	83.8	(79.0)[c])	6.06
12c	CH_3	C_4H_9	58.8	62.0	4.43
12d	C_2H_5	C_4H_9	44.8/49.2/61.6[d])	76.0	
12e	C_3H_7	H	61.3	94.0	4.77
12f	C_3H_7	CH_3	70.5	92.5	5.64
12g	C_3H_7	C_2H_5	69.7	122.5	6.77
12h	C_3H_7	C_3H_7	58.9/64.3[d])	88.9	
12i	C_3H_7	C_4H_9	52.8/56.0/58.0[d])	98.7	
12j	C_3H_7	C_5H_{11}	55.4/62.9[d])	95.2	
12k	C_3H_7	C_6H_{13}	62.4	99.2	7.41
12l	C_4H_9	C_4H_9	70.2	97.5	8.17
12m	C_5H_{11}	H	55.0	98.8	
12n	C_5H_{11}	CH_3	68.3	97.1	7.56
12o	C_5H_{11}	C_2H_5	75.2	125.7	7.59
12p	C_5H_{11}	C_3H_7	59.8	95.7	7.02
12q	C_5H_{11}	C_4H_9	63.4	104.0	8.42
12r	C_7H_{15}	C_2H_5	60.1	122.0	6.77
13a	C_3H_7	–	143.7	312.5	3.42
13b	C_5H_{11}	–	137.6	302.5	3.33
15a	C_5H_{11}	CH_3	60.4	111.5	7.34
15b	C_5H_{11}	C_3H_7	52.0	73.9	
18a	H	–	58.1	–	
18b	CH_3	–	88.5	(73.9)[c])	5.21
18c	C_2H_5	–	74.5	95.5	5.83
18d	C_3H_7	–	77.3	126.5	5.54
18e	C_4H_9	–	61.3	116.0	5.74
18f	C_5H_{11}	–	72.8	125.1	7.10
18g	C_7H_{15}	–	78.6	117.5	8.63
19a	H	C_5H_{11}	– 2.5/9.2[d])	–	
19b	C_3H_7	CH_3	67.0	(55.3)[c])	5.83
19c	C_3H_7	C_2H_5	37.2	–	3.94
19d	C_3H_7	C_3H_7	31.8	44.0	5.54
19e	C_3H_7	C_4H_9	26.3	30.8	3.88
19f	C_3H_7	C_5H_{11}	33.2/35.0[d])	45.2	
19g	C_3H_7	C_6H_{13}	22.6	38.7	5.22
19h	C_3H_7	C_7H_{15}	49.9	(47.4)[c])	8.49
19i	C_5H_{11}	CH_3	49.5	61.0	6.75
19j	C_5H_{11}	C_2H_5	27.9	46.0	5.10
19k	C_5H_{11}	C_3H_7	39.6	56.9	6.82
19l	C_5H_{11}	C_4H_9	34.4	48.4	5.69
19m	C_5H_{11}	C_5H_{11}	39.9	59.7	5.31
19n	C_7H_{15}	C_3H_7	44.6	65.3	7.96
20a	C_5H_{11}	CH_3	56.1	102.1	7.35
20b	C_5H_{11}	C_2H_5	53.5/57.7[d])	110.0	

Table 1 (continued)

Compound	R^2	R^3	$T_{C\text{-}N}$[a]) (°C)	$T_{N\text{-}I}$[b]) (°C)	ΔH (kcal mol^{-1})
22a	C_5H_{11}	C_3H_7	62.9	89.9	7.95
22b	C_5H_{11}	C_4H_9	70.2	96.0	9.44
25	–	–	37.5	–	
27a	C_3H_7	C_4H_9	100.4	136.2	8.59
27b	C_3H_7	C_6H_{13}	94.3	128.5	9.09
27c	C_5H_{11}	C_2H_5	98.3	147.0	10.27
27d	C_5H_{11}	C_3H_7	92.5	138.2	6.53
27e	C_5H_{11}	C_4H_9	89.3	138.6	8.82
27f	C_7H_{15}	C_2H_5	107.5	141.0	10.12
28a	C_3H_7	C_5H_{11}	77.8	138.0	9.64
28b	C_3H_7	C_7H_{15}	65.4[c])	131.7	8.25
28c	C_5H_{11}	C_3H_7	76.8	136.5	8.84
28d	C_5H_{11}	C_5H_{11}	70.0[f])	140.5	4.50
28e	C_7H_{15}	C_3H_7	88.2	125.2	8.73

[a]) Crystal-nematic transition (m.p.). [b]) Nematic-isotropic transition (clearing point). [c]) Values in parentheses indicate monotropy. [d]) Different crystalline modifications were observed. [e]) At 79.8° smectic A-nematic transition. [f]) At 90.5° smectic A-nematic transition.

According to the molecular statistical theory of *Maier & Saupe* [8] the nematic-isotropic transition temperatures ($T_{N\text{-}I}$) should be proportional to the second power of the anisotropy of molecular polarizability. Thus replacement of a cyano group in **18** by an alkoxy or alkyl group should lead to nematogens with lower clearing points. Starting from ketones **12** either the hydrocarbons **19** or the ethers **22** were prepared conveniently by the reactions outlined in *Scheme 5*. As anticipated, these compounds exhibited narrower mesophases and in some cases, *e.g.* **19b** and **19h**, showed a monotropic behaviour or even lost their mesogenic properties completely, *e.g.* **19c** (*cf. Table 1* and *Fig. 1*).

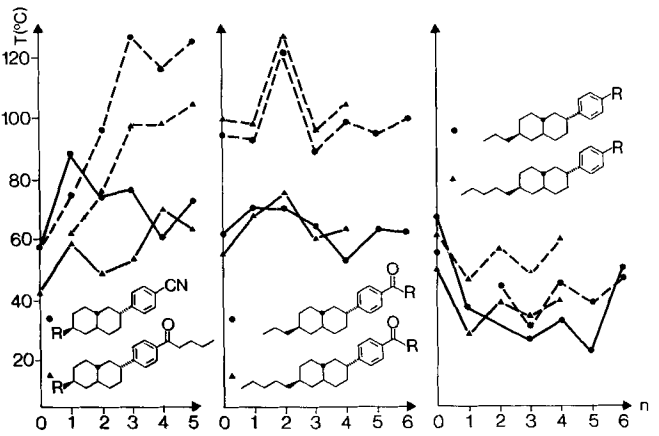
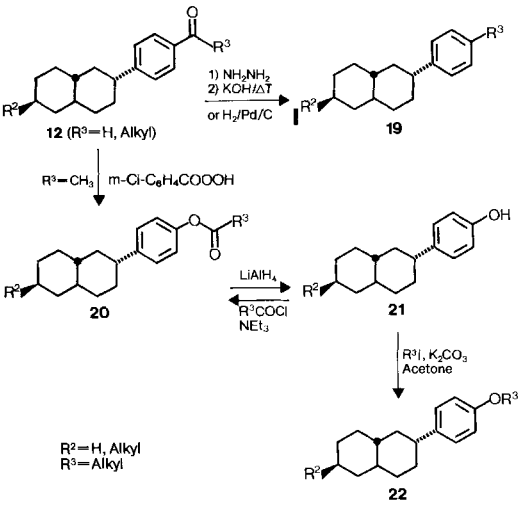


Fig. 1. *Transition temperatures* ($T_{C\text{-}N}$: ——; $T_{N\text{-}I}$: – – –) *plotted against the number of C-atoms* (n) *in the alkyl chains* (R) *of the compounds depicted*

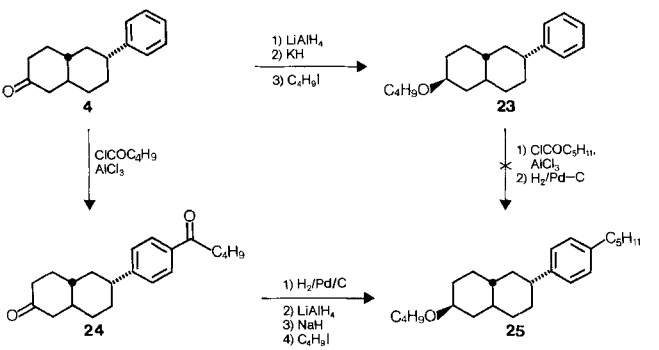
Scheme 5



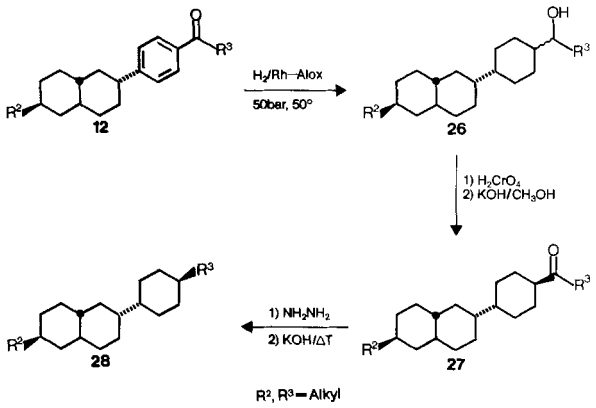
For comparison we have also synthesized the ether **25** carrying an alkoxy substituent in the 6β-position. Since attempted preparation of this compound by initial introduction of the 6β-substituent, followed by *para*-functionalization of the phenyl moiety, failed owing to interference of the alkoxy group during *Friedel-Crafts* acylation of **23**, the more lengthy route *via* **24** was chosen, which led to a low yield of the desired ether **25** *(Scheme 6)*. In contrast to **19m** and **22b**, this compound exhibits no liquid crystalline properties, thereby demonstrating how subtle changes may strongly influence the mesogenic behavior *(cf. Table 1)*.

Finally, in view of the earlier results of *Deutscher* [3] and *Eidenschink* [4], who found that replacement of a phenyl unit by a cyclohexane ring leads in certain classes of liquid crystals to new mesogens with enhanced (N-I)-transition temperatures, we wondered what effect this operation would have in our system. The synthesis of the compounds in question, **27** and **28**, was accomplished by hydrogenation

Scheme 6



Scheme 7



of the ketones **12** over a rhodium catalyst (50 bar, 50°), followed by *Jones* oxidation of the resulting diastereoisomeric alcohols **26** and basic equilibration to afford the all-*trans* ketones **27** in excellent overall yields. Additional *Huang-Minlon* reduction gave the hydrocarbons **28**, which, like their precursors **27**, exhibited remarkably large mesophases, high (N-I)-transition temperatures and in some cases smectic tendencies, *e.g.* in **28b** and **28d** *(cf. Table 1)*. Apparently the anisotropy of molecular shape is here of greater importance for the mesomorphic range than the anisotropy of molecular polarizability.

In summary, we have introduced two new core elements to the chemistry of liquid crystals, namely the 2-phenyl-*trans*-decalin system **A** and the 2-cyclohexyl-*trans*-decalin system **B**, a number of representatives of which (*e.g.* **12**, **15**, **18**, **19**, **20**, **22**, **27** and **28**) possess interesting chemical and physical[3]) properties.

We thank the following colleagues for the measurements and interpretations of spectra and transition temperatures: Dr. *G. Englert* and Dr. *W. Arnold* (NMR.), Dr. *W. Vetter* and Mr. *W. Meister* (MS.), Dr. *L. Chopard* (IR.), Mr. *F. Wild* and Mr. *B. Halm* (Thermoanalysis).

Experimental Part

(With the competent collaboration of Mr. *P. Lorenz* and Mr. *J. Reichardt*)

General. All reactions were carried out under argon. Solvents were passed through alumina (activity I) or distilled before use. Usual workup refers to successive washing of the organic phases with sat. aq. $NaHCO_3$-solution and/or H_2O and sat. aq. NaCl-solution followed by drying ($MgSO_4$ or K_2CO_3) and removal of the solvents at reduced pressure. Thin layer chromatography (TLC.) was performed using *Merck* 0.25 mm *(60F 254)* silica gel plates. Preparative flash chromatography was carried out according to [9] at a pressure of 0.5 bar using silica gel (*Merck*, 230–400 mesh). The transition temperatures listed in *Table 1* were determined on a *Mettler DTA TA 2000* and are corrected. Gas chromatography (GC.) was carried out on a *Perkin-Elmer Sigma 3B+10B*, glass columns (2.2 mm ID, 2.5 m, stationary phase on *Chromosorb W* 80/100 mesh), 6.5 bar N_2, retention time (t_R) in min, area percentages. Capitals in parentheses refer to columns and temperatures used: A = 5% *SE-30*, temperature programme: 150° (4 min) 150–280° (8°/min); B = 5% *Carbowax*, temperature programme: 150° (4 min),

150–220° (8°/min). – IR. spectra: in KBr, $\tilde{\nu}_{max}$ in cm^{-1}. – ^{1}H-NMR. spectra: in $CDCl_3$ at 270 MHz unless otherwise specified, internal standard tetramethylsilane ($\delta = 0$ ppm), abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quartet, *m* = multiplet, br. = broad, *J* = spin-spin coupling constant (Hz). – Mass spectra (MS.): signals are given in *m/z* (rel.-%).

*Preparation of 6α-phenyl-3*H*-(4,4aβ)-5,6,7,8-hexahydronaphthalen-2-one* (**2**). A mixture of 4-phenylcyclohexanone (**1**) (174 g, 1.0 mol) and pyrrolidine (149 ml, 1.8 mol) in 700 ml of benzene was heated to reflux for 17 h with separation of water. The solvent and excess pyrrolidine was distilled off at reduced pressure and the resulting yellow crystalline enamine redissolved in 700 ml of benzene. This solution was maintained at 25° with external cooling while methyl vinyl ketone was added dropwise over 70 min. After complete addition the mixture was refluxed for 18 h before adding an aqueous buffer (pH 5) (68 g of NaOAc, 83 ml of HOAc, 83 ml of H_2O) and refluxing for 4 h longer. The organic layer was separated, combined with the ether extracts of the aqueous phase, washed with 2N HCl (2×) and worked up as usual. Distillation (134–180°/0.04–0.02 Torr) of the resulting brown oil[7]) gave 167 g of a slightly yellow crystalline mass[8]), which upon fractional crystallization from 2.4 l of hexane (55° → RT. → 0°) furnished 99.1 g (40.2%) of **2** as colorless crystals contaminated by 6.4% of **3**. The concentrated mother liquor was redissolved in 500 ml of THF/2N HCl 3:2 and heated to reflux for 6 h. During this operation the ratio of **2**/**3** changed from 44:56 to 82:18 (GC.). Extraction with ether (2×), usual workup and crystallization from 1 l of hexane gave another 33.6 g (14%) of **2** contaminated by 5.4% of **3**. By an additional crystallization from hexane **2** could be obtained in a purity of 97%, m.p. 78–79°. – TLC. (toluene/ethyl acetate 9:1): Rf (**1**) 0.37; Rf (**2**) 0.25; Rf (**3**) 0.42. – GC. (A): t_R (**1**) 5.22; t_R (**2**) 14.37; t_R (**3**) 13.38. – IR.: 1663, 1619, 1598, 1491, 756, 700. – ^{1}H-NMR. (80 MHz): 1.19–2.70 (11H); 2.82 (*t*×*t*, *J* = 12 and 3.5, 1H); 5.86 (br. *s*, 1H); 7.01–7.44 (*m*, 5H). – MS.: 226 (100, $C_{16}H_{18}O^+$), 198 (13), 170 (30), 104 (84), 94 (88).

*Preparation of 6α-phenyl-1*H*-(4aβ,8aα)-octahydronaphthalen-2-one* (**4**). A solution of 1.6 g (0.23 g atom) of lithium wire in 280 ml of liquid ammonia was treated at −33° with a solution of 15.0 g (66.3 mmol) of **2**[9]) and 6.7 ml (70 mmol) of *t*-BuOH in 50 ml of ether. After the resulting blue solution had been stirred for 2 min, solid NH_4Cl was added to destroy the excess lithium and the ammonia was allowed to evaporate. The residue was partitioned between water and ether and worked up as usual. A solution of the resulting crude product (14.0 g) in cold (0°) acetone was oxidized with excess 8N H_2CrO_4 [10] at 0° for 15 min and the excess oxidant was destroyed with 2-propanol. The resulting mixture was concentrated, the residue partitioned between water and ether and worked up as usual. Distillation (130–139°/0.04 Torr) of the resulting yellow, viscous oil gave 11.05 g (76.3%) of **4** as a colorless slowly crystallizing oil. By additional crystallization from hexane at −20° analytically pure **4** was obtained, m.p. 58–59°. – TLC. (ethyl acetate/petroleum ether 1:9): Rf 0.19. – GC. (A): t_R 12.91. – IR.: 1710, 1600, 1582, 1495, 760, 700. – ^{1}H-NMR.: 1.17–1.64 (6H); 1.79–1.88 (*m*, 1H); 1.88–2.04 (3H); 2.12 (*d*×*d*, *J* = 13 and 12, 1H); 2.31–2.47 (3H); 2.68 (*t*×*t*, *J* = 12 and 3.5, 1H); 7.15–7.35 (5H). – MS.: 228 (100, $C_{16}H_{20}O^+$), 184 (58), 104 (62), 91 (57).

Preparation of 6α-phenyl-(4aβ,8aα)-decahydronaphthalene-2-carbonitrile (**6**). A solution of 6.33 g (25.5 mmol) of **4** and 5.47 g (28.0 mmol) of tosylmethyl isocyanide in 100 ml of 1,2-dimethoxyethane and 20 ml of *t*-BuOH was treated with 5.66 g (50.4 mmol of solid *t*-BuOK at such a rate that the reaction temperature did not exceed 0°. After complete addition the mixture was allowed to warm to r.t., stirred for 75 min, concentrated *in vacuo* and partitioned between water and ether. Usual workup afforded 6.14 g of a yellow oil, consisting (NMR., GC.) of 46% of **6** (2α-cyano) and 51% of **6** (2β-cyano). This material was used for the following transformation (**6** → **7**) without further purification. For the analytical data given below a sample was additionally chromatographed on silica gel (3% ethyl acetate/petroleum ether). – TLC. (ethyl acetate/petroleum ether 1:9): Rf 0.33 and 0.35. – GC. (A): t_R (**6**, 2α-cyano) 14.12. t_R (**6**, 2β-cyano) 14.50. – IR.: 2236, 1600, 1585, 1491, 761, 751, 701. – ^{1}H-NMR.: 0.94–2.18 (14H); 2.48 (*t*×*t*, *J* = 12.5 and 3.5, *ca.* 0.55H, H_{ax} at C(2)); 2.51–2.65 (1H); 2.99–3.06 (*m*, *ca.* 0.45H. H_{eq} at C(2)); 7.12–7.35 (5H). – MS.: 239 (60, $C_{17}H_{21}N^+$), 117 (47), 104 (100), 91 (46).

Preparation of butyl 2β-[6α-phenyl-(4aβ,8aα)-decahydronaphthyl] ketone (**7**, $R^1 = C_4H_9$). A solution of butylmagnesium bromide (50 mmol) in 50 ml of ether was treated at r.t. with a solution of 6.14 g

[7]) GC. (A): 11.4% **1**, 61.3% **2**, 17.8% **3**.
[8]) GC. (A): 1.2% **1**, 26.9% **2**, 69.1% **3**.
[9]) GC. (A): 92.5% **2**, 3.9% **3**.

of crude **6** (α-cyano/β-cyano 46:51), in 40 ml of ether and heated to reflux for 18 h. After cooling to 0° 50 ml of a 2N HCl were carefully added and in the following the mixture was heated to reflux for 1 h. The organic layer was separated, combined with the ether extracts of the aqueous phase and worked up as usual to yield 7.54 g of a crystallizing oil, consisting (GC.) of 93.8% of **7** (2β-COC_4H_9), 1.3% (2α-COC_4H_9) and 0.9% of **6**. This material was used for the following transformation (**7**→**8**) without further purification. For the analytical data given below a sample was crystallized once from methanol at 0°, m.p. 58–59°. – GC. (A): t_R 18.62. – TLC. (3% ethyl acetate/petroleum ether): Rf 0.40. – IR.: 1698, 1602, 1493, 762, 754, 701. – ^{1}H-NMR.: 0.91 (*t*, *J* = 7.5, 3 H); 0.98–1.61 (12 H); 1.67–1.97 (6 H); 2.37–2.50 (*m* with *t* at 2.44, *J* = 7.5, 3 H); 2.58 (*t* × *t*, *J* = 12 and 3.5, 1 H); 7.12–7.35 (5 H). – MS.: 298 (33, $C_{21}H_{30}O^+$), 280 (27), 238 (27), 213 (68), 198 (13), 135 (35), 117 (48), 109 (43), 91 (100), 85 (59), 57 (63), 41 (37).

The homologous ketones **7** ($R^1 = C_2H_5$, C_3H_7) were prepared similarly in comparable yields[10]. After equilibration the ratio of $2\beta/2\alpha$-epimers of **7** ($R^1 = C_2H_5$ and C_3H_7) were 85:9.4 and 90:6.4, respectively.

Data of **7** ($R^1 = C_2H_5$): m.p. 60–61°; GC. (A): t_R 15.65.

Data of **7** ($R^1 = C_3H_7$): m.p. 53–54°; GC. (A): t_R 17.22.

Preparation of 2β-pentyl-6α-phenyl-(4aβ,8aα)-decahydronaphthalene (**8e**) *from* **7** ($R^1 = C_4H_9$). A mixture of 7.54 g of crude **7** ($R^1 = C_4H_9$) and 2.72 ml (56 mmol) of hydrazine hydrate in 30 ml of diethyleneglycol and 30 ml of ethanol was heated to reflux for 105 min. Then 3.37 g (60 mmol) of solid KOH was added, and after distilling off ethanol the mixture was gradually heated to 225° and kept at this temperature for 2.5 h. The recooled mixture was poured into 200 ml of water and extracted with petroleum ether (3 × 200 ml) affording after the usual workup 6.64 g of a crystallizing oil. Filtration of this material through a short column of silica gel (hexane) gave 5.65 g (78.5% based on **4**) of pure **8e** as colorless crystals, m.p. 55–56°. – GC. (A): t_R 16.05. – TLC. (hexane). Rf 0.44. – IR.: 1602, 1491, 1463, 1450, 759, 750, 695. – ^{1}H-NMR.: 0.58–0.74 (*m*, 1 H); 0.83–1.95 (*m* with *t* at 0.89, *J* = 7.5, 25 H); 2.57 (*t* × *t*, *J* = 12 and 3.5, 1 H); 7.11–7.35 (5 H). – MS.: 284 (57, $C_{21}H_{32}^+$), 204 (11), 135 (20), 117 (22), 104 (100), 91 (31), 69 (59).

Following the above procedure the homologous hydrocarbons **8c** and **8d** were prepared in comparable yields, and **4** was converted to **5** in 82% yield[10][11]. – GC. (A): t_R (**8c**) 12.88; t_R (**8d**) 15.00; t_R (**5**) 9.00.

Analogous reduction of an epimeric (2β-CHO/2α-CHO ≈ 4:1) mixture of aldehydes **9** (for their preparation *cf.* following experiment) led to a mixture of the corresponding epimeric 2-methyl-derivatives, from which neither by chromatography nor by crystallization the desired 2β-epimer **8a** ($R^1 = CH_3$) could be isolated pure.

Preparation of 6α-phenyl-(4aβ,8aα)-decahydronaphthalene-2-carbaldehyde (**9**). To a suspension of 22.6 g (65.8 mmol) of (methoxymethyl)triphenylphosphonium chloride in 75 ml of dry *t*-butyl methyl ether at −10° was added 7.9 g (70 mmol) of solid *t*-BuOK over 10 min. After stirring an additional 30 min at 0° a solution of 10.0 g (43.9 mmol) of **4** in 40 ml of dry *t*-butyl methyl ether was added over 10 min to the deep-orange mixture. Stirring was continued for 1 h at r.t. before the mixture was poured into 150 ml of a 2% aq. $NaHCO_3$-solution. Extraction with ether (3 × 100 ml) followed by the usual workup furnished a semi-crystalline residue, which was triturated with 500 ml of warm hexane and cooled to −20°. Precipitated triphenylphosphine oxide was filtered off, and the filtrate was concentrated *in vacuo* to afford 12.0 g of a colorless liquid. This crude product was redissolved in 100 ml of 2N HCl/THF 1:4 and refluxed for 1 h. Dilution with water (100 ml) and extraction with ether (3 × 100 ml) followed by the usual workup gave 12.0 g of a slightly yellow viscous oil, consisting (NMR., GC.) of an epimeric (2β-CHO/2α-CHO ≈ 4:1) mixture of aldehyde **9**. This material was used for the following transformation (**9**→**10**) without further purification. – GC. (B): t_R (**9**, 2α-CHO) 19.64, t_R (**9**, 2β-CHO) 20.45. – TLC. (hexane/ether 9:1): Rf (**9**, 2α-CHO) 0.12, Rf (**9**, 2β-CHO) 0.17. – ^{1}H-NMR.: 0.92–2.67 (16 H); 7.12–7.34 (5 H); 9.63 (*d*, *J* = 2, *ca.* 0.8 H); 9.77 (*s*, *ca.* 0.2 H).

An identical mixture of the epimeric aldehydes **9** (2β-CHO/2α-CHO ≈ 4:1) resulted from the reduction of nitriles **6** with DIBAL, followed by acidic equilibration.

---

[10]) The IR., ^{1}H-NMR. and mass spectra of these compounds are in agreement with their assigned structures.

[11]) For the transition temperatures of these compounds *cf. Table 1.*

Preparation of 6α-phenyl-(4aβ,8aα)-decahydronaphthalene-2β-methanol (**10**). To a cooled (0°) solution of 12.0 g of crude **9** (2β-CHO/2α-CHO ≈ 4:1) in 150 ml of 0.1N methanolic KOH was added portionwise 0.95 g (25 mmol) of solid $NaBH_4$ over 20 min. After complete addition the mixture was stirred for an additional 20 min at 0° then poured into 200 ml of water. Extraction with CH_2Cl_2 (3×200 ml) followed by the usual workup gave 11.25 g of crystalline alcohol **10**, which did not contain (NMR., GC.) any of the corresponding C(2)-epimer. This material was used for the following transformation (**10**→**11**) without further purification. For the analytical data given below a sample was crystallized from hexane at 0°, m.p. 96–98°. – GC. (A): t_R 14.42. – TLC. (toluene/ethyl acetate 9:1): Rf 0.21. – IR.: 3417, 1603, 1582, 1495, 1073, 1047, 1030, 1012, 760, 699. – ^{1}H-NMR.: 0.67–0.82 (*qa*, *J* = 11.5, 1H); 0.91–1.96 (15H); 2.58 (*t*×*t*, *J* = 12.5 and 3.5, 1H); 3.49 (*t*, *J* = 5.5, 2H); 7.13–7.32 (5H). – MS.: 244 (96, $C_{17}H_{24}O^+$), 143 (17), 117 (43), 109 (54), 104 (100), 91 (80).

Preparation of the tosylate **11** *of* **10**. To a solution of 11.25 g of crude **10** in 10 ml of dry pyridine was added at 0° a solution of 14.5 g (76 mmol) of *p*-toluenesulfonyl chloride over 5 min. The ice-bath was removed and the mixture was stirred overnight at r.t. Ice was added and after careful acidification with 25 ml of conc. HCl-solution the product was extracted with CH_2Cl_2 (3×100 ml). Usual workup afforded 18.4 g of a yellow crystalline mass, which after crystallization from 350 ml of methanol at 0° furnished 11.70 g of **11** as colorless needles. Double recrystallization of the concentrated mother liquors gave another 1.55 g of pure **11**; total yield, 80% (based on **4**), m.p. 88.0–88.8°. – TLC. (toluene/ethyl acetate 9:1): Rf 0.58. – IR.: 1598, 1495, 1359, 1189, 1177, 942, 833, 814, 754, 699. – ^{1}H-NMR.: 0.71 (*qa*, *J* = 11.5, 1H); 0.91–1.30 (6H); 1.46 (*qa*×*d*, *J* = 12.5 and 3.5, 1H); 1.59–1.94 (7H); 2.45 (*s*, 3H); 2.55 (*t*×*t*, *J* = 12 and 3.5, 1H); 3.85 (*d*, *J* = 6, 2H); 7.14–7.34 (5H); *AA'BB'*-system centered at 7.37 and 7.82 (4H). – MS.: 398 (3, $C_{24}H_{30}O_3S^+$), 226 (100), 143 (38), 122 (66), 104 (56), 91 (84).

Preparation of **8e** *from* **11**. A cooled (−60°) solution of butylmagnesium bromide (*ca.* 480 ml), prepared from 53 ml (487 mmol) of butyl bromide and 12.2 g (0.5 g-atoms) of magnesium turnings, in 300 ml of ether was treated successively with 32 ml of a 0.1N Li_2CuCl_4 in dry THF [5] and a solution of 80 g (200 mmol) of **11** in 250 ml of dry THF over a period of 20 min. After complete addition the heterogeneous greyish mixture was stirred at −10° for 40 h, then carefully quenched with 220 ml of 25% aq. HCl-solution. Extraction with hexane followed by the usual workup yielded 60.0 g of a crystalline mass. Filtration through a short column of silica gel (20-fold) with hexane afforded 56.5 g (99%) of pure **8e**, identical with the product prepared from **7**).

Similarly the hydrocarbons **8b**, **8c**, **8d** and **8f** were prepared in comparable yields[10][11]). – GC. (A): t_R (**8b**) 12.50, t_R (**8f**) 18.10. For the GC. (A) of **8c** and **8d** *cf.* under preparation of **8e** from **7**.

Preparation of 2β-methyl-6α-phenyl-(4aβ,8aα)-decahydronaphthalene (**8a**) *from* **11**. To a slurry of 95 mg (2.5 mmol) of $LiAlH_4$ in 10 ml of dry THF was added at r.t. a solution of 1.0 g (2.5 mmol) of **11** in 10 ml of dry THF. After complete addition the mixture was heated to reflux for 18 h, then carefully quenched with 10 ml of 2N HCl. Extraction with ether (3×30 ml) followed by the usual workup gave 560 mg of crude product, which after filtration through a short column of silica gel (hexane) afforded 528 mg (92%) of analytically pure **8a** as colorless crystals, m.p. 43.7°. – GC. (A): t_R 9.85. – TLC. (hexane): Rf 0.74. – IR.: 1608, 1584, 1494, 762, 753, 699. – ^{1}H-NMR. (90 MHz): 0.55–2.06 (*m* with *t* at 0.89, *J* = 6, 18H); 2.57 (*t*×*t*, *J* = 12 and 3.5, 1H); 7.11–7.26 (5H). – MS.: 228 (93, $C_{17}H_{24}^+$), 148 (9), 124 (24), 104 (100).

Preparation of methyl 4-[6β-pentyl-2α-(4aα,8aβ)-decahydronaphthyl]phenyl ketone (**12n**) *from* **8e**. To a cooled (−5°) solution of 7.0 g (24.6 mmol) of **8e** and 2.2 ml (31.2 mmol) of acetyl chloride in 100 ml of CH_2Cl_2 was added over 30 min 3.7 g (28.0 mmol) of aluminum chloride. After complete addition the mixture was stirred for 2.5 h at r.t. then carefully (ice-bath) quenched with 50 ml of 2N HCl. Extraction with CH_2Cl_2 and successive washing of the organic layers with 2N HCl and 2N NaOH followed by the usual workup gave 7.56 g (94%) of colorless crystals, consisting (GC.) of 98% of **12n** and 1.1% of the corresponding *ortho*-isomer. For the following transformation (**12n**→**13b**) this material was used without further purification. For the analytical data given below a sample was additionally crystallized from acetone at 0°[11]). – GC. (A): t_R 20.98. – TLC. (toluene/ethyl acetate 9:1): Rf 0.32. – IR.: 1680, 1607, 1574, 1272, 828. – ^{1}H-NMR. (400 MHz): 0.67 (*qa*, *J* = 12, 1H); 0.81–1.93 (*m* with *t* at 0.90, *J* = 7, 25H); 2.57 (*s*, 3H); 2.64 (*t*×*t*, *J* = 11.5 and 3.5, 1H); *AA'BB'*-system centred at 7.30 and 7.88 (4H). – MS.: 326 (14, $C_{23}H_{34}O^+$), 311 (100), 43 (18).

The ketones **12a–d**, **12f–l** and **12o–r** were prepared similarly in comparable yields[10][11]). – GC. (A) (t_R): **12a** = 19.02, **12b** = 17.30, **12c** = 19.47, **12d** = 20.15, **12f** = 18.82, **12g** = 19.30, **12h** = 20.04, **12i** = 21.99, **12j** = 22.74, **12k** = 24.27, **12l** = 23.15, **12o** = 22.37, **12p** = 23.51, **12q** = 24.86, **12r** = 24.80.

Preparation of 4-[6β-pentyl-2α-(4aα,8aβ)-decahydronaphthyl]benzonitrile (**18f**) *from* **12n** *(via* **13** and **14**). To a solution of 2.70 g (8.3 mmol) of **12n** in 33 ml of dioxane was added within 5 min 23.1 ml of cold (0°) aq. HOBr-solution (from 21 ml of 6N NaOH and 2.1 ml of bromine). After a few minutes a voluminous precipitate appeared, which upon warming to 50° increased considerably. After stirring for 1 h the mixture was brought to pH 1 with 4N HCl (*ca.* 40 ml) and extracted with CH_2Cl_2 (3 × 100 ml). Usual workup gave 3.1 g of a crystalline crude product, which upon crystallization from $CHCl_3$ at −20° afforded 1.88 g (65%) of **13b** as colorless plates[10][11]). – GC. (A): t_R (**13b**)[12]) 22.58. – TLC. ($CHCl_3$/ethyl acetate 1:1): Rf 0.23–0.38. Following the above procedure **12f** was converted to **13a** in 80% yield[10][11]).

To a cold (0°) solution of 1.88 g (5.7 mmol) of **13b** and 1.03 ml (7.4 mmol) of triethylamine in 27 ml of $CHCl_3$ was added 0.75 ml (7.5 mmol) of ethyl chloroformate. After stirring an additional 15 min, ammonia bubbled through the mixture for 10 min caused a voluminous precipitate. The mixture was stirred for another 50 min and concentrated *in vacuo*. The solid residue was triturated with 25 ml of water, filtered off and dried over solid KOH at 50° at reduced pressure (12 Torr) overnight. The resulting 1.08 g (58%) of amide **14** ($R^2 = C_5H_{11}$) were used for the following transformation (**14** → **18f**) without further purification. An analytically pure sample was obtained by additional crystallization from $CHCl_3$ at −20°[10]), m.p. 232–235°. – TLC. ($CHCl_3$/etbyl acetate 1:1): Rf 0.28. By acidification of the filtrate and extraction with $CHCl_3$ followed by the usual workup 730 mg (39%) of starting material **13b** could be recovered.

Following the above procedure **13a** was converted to **14** ($R^2 = C_3H_7$) in 80% yield, m.p. 233–235°[10]).

A suspension of 1.05 g (3.2 mmol) of **14** ($R^2 = C_5H_{11}$) in 9.2 ml of dry pyridine was treated with 1.3 ml (10.1 mmol) of benzenesulfonyl chloride and stirred overnight at r.t. Then the mixture was poured into a mixture of 30 g of ice and 30 ml of 2N HCl and extracted with ether (3 × 100 ml). Usual workup followed by flash chromatography on silica gel (ethyl acetate/petroleum ether 3:97) afforded 931 mg (94%) of **18f** as colorless crystals. An analytically pure sample was obtained by additional crystallization from methanol at 0°[11]). – GC. (A): t_R 19.80. – TLC. (ethyl acetate/petroleum ether 3:97). Rf 0.33. – IR.: 2222, 1606, 1502, 840, 830. – ^{1}H-NMR. (400 MHz): 0.65 (*qa*, J = 12, 1H); 0.81–0.90 (*m* with *t* at 0.88, J = 7, 25H); 2.60 (*t* × *t*, J = 11.5 and 3.5, 1H); *AA'BB'*-system centred at 7.29 and 7.56 (4H). – MS.: 309 (90, $C_{22}H_{31}N^+$), 238 (80), 204 (44), 142 (56), 135 (100), 116 (74), 109 (67), 95 (67), 81 (54), 67 (69), 55 (64), 41 (72).

Following the above procedure **14** ($R^2 = C_3H_7$) was converted to **18d**[10][11]), GC. (A): 17.71.

Conversion of **8e** *to* **18f** *(*via **16**). To a refluxing solution of 284 mg (1 mmol) of **8e** and 60 mg (1.08 mmol) of iron powder in 5 ml of CCl_4 was added over 15 min 1.15 ml of a 1M solution of Br_2 in CCl_4. After complete addition the mixture was heated to reflux for an additional 80 min, before being partitioned between 10% aq. $Na_2S_2O_3$-solution and $CHCl_3$. Washing of the organic layers with 1N NaOH followed by the usual workup gave 354 mg of an oil, consisting (GC.) of 12% of **8e**, 68% of **16** ($R^2 = C_5H_{11}$) and 15% of the corresponding *ortho*-bromo derivative. This mixture was used for the following transformation (**16** → **18**) without further purification. – GC. (A): t_R (**16**, $R^2 = C_5H_{11}$) 19.97, t_R of the corresponding *ortho*-bromo derivative: 19.11.

A mixture of these bromo derivatives (354 mg) and 107 mg (1.2 mmol) of CuCN in 4 ml of dry DMF was heated to reflux for 24 h. The cooled mixture was poured into 10 ml of 30% aq. NaCN-solution and extracted with ether (3 × 30 ml). The usual workup gave 281 mg of an oil, which after flash chromatography on 20 g of silica gel (hexane/toluene 2:1) afforded together with some *ortho*-nitrile 140 mg (45% based on **8e**) of **18f**, as colorless crystals. For the analytical data of **18f** *cf.* conversion of **12n** to **18f** (*via* **13** and **14**). – GC. (A): t_R of *ortho*-nitrile: 19.30. – TLC. (hexane/toluene 2:1): Rf (**18f**) 0.19, Rf (*ortho*-nitrile) 0.27.

Following the above procedure **5** was converted to **18a**[10][11]), GC. (A): t_R 14.36.

Conversion of **8e** *to* **18f** *(*via **17**) [6]. A mixture of 10.0 g (35.2 mmol) of **8e**, 1.4 g (7.7 mmol) of HIO_3, 3.6 g (28.6 mmol) of I_2, 47 ml of acetic acid, 13 ml of water, 13 ml of CCl_4 and 2 ml of conc. sulfuric acid was heated to reflux for 18 h. The cooled mixture was poured into 50 ml of a 10% aq. $Na_2S_2O_3$-solution and extracted with hexane (3 × 100 ml). Usual workup gave 15.2 g of

[12]) Silylated with *N,O*-bis(trimethylsilyl)acetamide in ether.

crude product, consisting (GC.) of 3.2% of **8e**, 79.9% of **17** ($R^2 = C_5H_{11}$) and 15.9% of the corresponding *ortho*-iodo derivative. A single crystallization from acetone at 0° afforded 10.5 g (73%) of pure **17** ($R^2 = C_5H_{11}$), m.p. 89.3. – GC. (A): t_R 20.65. – TLC. (hexane): Rf 0.45. – IR.: 1632, 1562, 1485, 836, 807. – ^{1}H-NMR.: 0.65 (*qa*, J = 11.5, 1 H); 0.79–1.90 (*m* with *t* at 0.88, J = 7, 25 H); 2.51 ($t \times t$, J = 11.5 and 3.5, 1 H); *AA'BB'*-system centred at 6.95 and 7.58 (4 H). – MS.: 410 (100, $C_{21}H_{31}I^+$), 230 (37), 217 (21), 109 (16), 95 (16).

Following the above procedure the hydrocarbons **8a**, **8b**, **8c**, **8d** and **8f** were converted to the corresponding iodo derivatives **17** ($R^2 = CH_3$, C_2H_5, C_3H_7, C_4H_9 and C_7H_{15}) in comparable yields[10]. M.p. of **17** ($R^2 = CH_3$): 88.1, ($R^2 = C_2H_5$): 77.5, ($R^2 = C_3H_7$): 93.1, ($R^2 = C_4H_9$): 55.0, ($R^2 = C_7H_{15}$): 87.4. – GC. (A): t_R (**17**, $R^2 = CH_3$): 15.90, ($R^2 = C_2H_5$): 17.50, ($R^2 = C_3H_7$): 18.50, ($R^2 = C_4H_9$): 19.87, ($R^2 = C_7H_{15}$): 23.15.

A mixture of 10.5 g (25.6 mmol) of **17** ($R^2 = C_5H_{11}$) and 3.6 g (39.7 mmol) of CuCN in 100 ml of anhydrous DMF was heated to reflux for 18 h. The cooled mixture was carefully poured into 70 ml of 25% NH_4OH-solution and extracted with hexane (3 × 150 ml). Usual workup followed by flash chromatography of the residue on silica gel (ethyl acetate/petroleum ether 3:97) afforded 7.20 g (91%) of **18f** as colorless crystals. One crystallization from 40 ml of acetone at −20° furnished 6.13 g of analytically pure **18f**; for the analytical data *cf.* conversion of **12n** to **18f** (*via* **13** and **14**).

Following the above procedure the iodo derivatives **17** ($R^2 = CH_3$, C_2H_5, C_3H_7, C_4H_9 and C_7H_{15}) were converted to the nitriles **18b**, **18c**, **18d**, **18e** and **18g**, respectively, in comparable yields[10][11]. – GC. (A): t_R (**18b**) 15.14, t_R (**18c**) 16.55, t_R (**18d**) 17.71, t_R (**18e**) 18.81, t_R (**18g**) 21.90.

Preparation of propyl 4-[6β-pentyl-2α-(4aα,8aβ)-decahydronaphthyl]benzoate (**15b**) *from* **13b**. To a cold (0°) solution of 0.35 ml (4.7 mmol) of propanol in 7.5 ml of dry pyridine was added dropwise a solution of 1.28 g (3.9 mmol) of the acid chloride derived from acid **13b** ($SOCl_2$, 2 h, reflux) in 10 ml of dry benzene. After stirring at r.t. for 18 h the mixture was poured into 15 g of ice and 15 ml of conc. hydrochloric acid and extracted with ether (3 × 50 ml). The organic layers were washed with ice-cold 1N NaOH and then worked up as usual. Crystallization of the residue from methanol at 0° afforded 1.16 g (80%) of **15b** as colorless crystals[11]. – GC. (A): t_R 23.05. – TLC. (ethyl acetate/petroleum ether 1:9): Rf 0.58. – IR.: 1715, 1609, 1575, 1507, 1276, 1270, 857, 842. – ^{1}H-NMR.: 0.66 (*qa*, J = 11, 1 H); 0.84–1.97 (*m* with 2 *t* at 0.89 and 1.02, J = 7, 30 H); 2.63 ($t \times t$, J = 12 and 3.5, 1 H); 4.26 (*t*, J = 7, 2 H); *AA'BB'*-system centred at 7.26 and 7.96 (4 H). – MS.: 370 (19, $C_{25}H_{38}O_2^+$), 328 (85), 311 (100), 204 (26), 148 (38), 135 (40).

Following the above procedure **13b** was converted to **15a** in 94% yield[10][11]. – GC. (A): t_R 22.10.

Preparation of 4-[6β-pentyl-2α-(4aα,8aβ)-decahydronaphthyl]benzaldehyde (**12m**) *from* **18f**. A cold (0°) solution of 518 mg (1.67 mmol) of **18f** in 20 ml of toluene was treated with 1.6 ml (1.92 mmol) of a 20% DIBAL-solution in toluene over 10 min. After complete addition the mixture was stirred for 30 min at 0° and for 100 min at r.t., before it was carefully quenched with 25 ml of 2N H_2SO_4 and extracted with $CHCl_3$ (3 × 100 ml). The usual workup gave 520 mg (100%) of aldehyde **12m** (GC.: 95%), which after repeated crystallization from hexane furnished analytically pure material[11]. – GC. (A): t_R 19.97. – TLC. (ethyl acetate/petroleum ether 3:97): Rf 0.18. – IR.: 2754, 1706, 1609, 1579, 830. – ^{1}H-NMR. (80 MHz): 0.62–2.06 (26 H); 2.39–2.89 (1 H); *AA'BB'*-system centred at 7.33 and 7.78 (4 H); 9.94 (*s*, 1 H). – MS.: 312 (100, $C_{22}H_{32}O^+$), 204 (23), 135 (43), 109 (42), 91 (54).

Following the above procedure **18d** was converted to **12e**[10][11]. – GC. (A): t_R 17.77.

Preparation of 6α-(4-heptylphenyl)-2β-propyl-(4aβ,8aα)-decahydronaphthalene (**19h**) *from* **12k**. The solution of 350 mg (0.95 mmol) of **12k** in 10 ml of abs. EtOH was treated with H_2 at normal pressure and r.t. in the presence of 50 mg of 10% Pd/C until the uptake of H_2 ceased. The mixture was filtered through *Celite* and concentrated *in vacuo*. The residue was redissolved in 50 ml of ether, again filtered through *Celite* and concentrated to dryness affording 316 mg (94%) of **19h** as colorless crystals. An analytically pure sample was obtained by additional crystallization from methanol at 0°[11]. – GC. (A): t_R 21.24. – TLC. (hexane): Rf 0.51. – IR.: 1513, 825. – ^{1}H-NMR.: 0.65 (*qa*, J = 11.5, 1 H); 0.79–1.93 (*m* with *t* at 0.88, 34 H); 2.45–0.66 (3 H); 7.12 (*s*, 4 H). – MS.: 354 (100, $C_{26}H_{42}^+$), 269 (54), 202 (82), 117 (68), 91 (74).

The same transformation (**12** → **19**) may be accomplished by *Huang-Minlon* reduction (*cf.* **7** → **8e**). Using either this or the above procedure the ketones **12a**, **12f**, **12g**, **12h**, **12i**, **12j**, **12n**, **12o**, **12p**, **12q** and **12r** and aldehydes **12e** and **12m** were converted to the hydrocarbons **19a**, **19c**, **19d**, **19e**, **19f**,

19g, **19j**, **19k**, **19l**, **19m**, **19n**, **19b**, and **19i**, respectively, in high yields[10][11]). – GC. (A) (t_R): **19a** = 16.22, **19b** = 14.96, **19c** = 16.10, **19d** = 16.50, **19e** = 17.85, **19f** = 19.07, **19g** = 20.10, **19i** = 16.96, **19j** = 18.59, **19k** = 19.68, **19l** = 20.64, **19m** = 21.61, **19n** = 21.14.

Preparation of 2β-pentyl-6α-(4-propoxyphenyl)-(4aβ,8aα)-decahydronaphthalene (**22a**) *from* **12n**. A mixture of 7.0 g (21.4 mmol) of **12n** and 8.2 g (47.5 mmol) of *m*-chloroperbenzoic acid (approx. 90%) in 200 ml of CH_2Cl_2 was stirred in the dark at r.t. for 80 h. Partitioning between 10% aq. $Na_2S_2O_3$-solution and CH_2Cl_2 followed by the usual workup gave a solid, which after flash chromatography on silica gel (ethyl acetate/petroleum ether 3:97) afforded 6.35 g (87%) of pure acetate **20a**, as colorless crystals[11]). This material may additionally be recrystallized from methanol at −20°. – GC. (A): t_R 20.88. – TLC. (ethyl acetate/petroleum ether 3:97): Rf 0.24. – IR.: 1764, 1610, 1509, 1368, 1216, 1204, 850. – ^{1}H-NMR. (80 MHz): 0.74–2.06 (26 H); 2.30 (*s*, 3 H); 2.59 (1 H); *AA'BB'*-system centred at 6.98 and 7.21 (4 H). – MS.: 342 (approx. 1, $C_{23}H_{34}O_2^+$), 300 (100), 133 (14), 120 (55), 107 (20).

To a suspension of 1.63 g (42.8 mmol) of $LiAlH_4$ in 100 ml of dry ether was added at r.t. a solution of 6.35 g (18.5 mmol) of **20a** in 200 ml of dry ether over a period of 15 min. After stirring for an additional hour at r.t. the mixture was carefully quenched with 150 ml of 1N H_2SO_4 and extracted with ether. Usual workup afforded 5.31 g (95%) of **21** ($R^2 = C_5H_{11}$) as colorless plates, m.p. 148–149°. – GC. (A): t_R 19.25. – TLC. (ethyl acetate/petroleum ether 1:9): Rf 0.22. – IR.: 3407, 1609, 1597, 1511, 1375, 1234, 825, 724. – ^{1}H-NMR. (400 MHz): 0.62 (*qa*, *J* = 12, 1 H); 0.84–1.90 (*m* with *t* at 0.87, *J* = 7, 25 H); 2.50 (*t* × *t*, *J* = 11.5 and 3.5, 1 H); 4.50 (*s*, 1 H); *AA'BB'*-system centred at 6.73 and 7.07 (4 H). – MS.: 300 (59, $C_{21}H_{32}O^+$), 159 (9), 133 (27), 120 (100), 107 (36).

A mixture of 1.20 g (4.0 mmol) of **21** ($R^2 = C_5H_{11}$), 1.47 ml (15.1 mmol) of propyl iodide and 2.1 g (15.1 mmol) of K_2CO_3 (powder) in 40 ml of acetone was heated to reflux for 40 h. The cooled mixture was partitioned between 1N NaOH and ether and worked up as usual affording 1.37 g (100%) of ether **22a** (CG.: 98.4%). Additional crystallization from acetone at −20° furnished an analytically pure sample[11]). – GC. (A): t_R 20.52. – TLC. (hexane): Rf 0.16. – IR.: 1613, 1581, 1515, 1249, 1179, 837, 813. – ^{1}H-NMR.: 0.64 (*qa*, *J* = 11.5, 1 H); 0.82–1.93 (*m* with 2 *t* at 0.90 and 1.03, *J* = 7, 30 H); 2.58 (*t* × *t*, *J* = 12 and 3.5, 1 H); 3.90 (*t*, *J* = 7, 2 H); *AA'BB'*-system centred at 6.83 and 7.11 (4 H). – MS.: 342 (100, $C_{24}H_{38}O^+$), 162 (30), 120 (52), 107 (26).

Following the above procedure **21** ($R^2 = C_5H_{11}$) was converted to **22b**[10][11]). – GC. (A): t_R 21.83.

Preparation of 4-[6β-pentyl-2α-(4aα,8aβ)-decahydronaphthyl]phenyl propionate (**20b**) *from* **21** ($R^2 = C_5H_{11}$). To a solution of 1.2 g (4.0 mmol) of **21** ($R^2 = C_5H_{11}$), 59 mg (0.4 mmol) of 4-pyrrolidinopyridine and 0.7 ml (8.0 mmol) of propionyl chloride in 30 ml of dry ether was added at r.t. a solution of 1.12 ml (8.0 mmol) of triethylamine in 10 ml of ether. After stirring for 3 h at r.t. the mixture was poured on water and extracted with ether. Washing of the organic layers with sat. $CuSO_4$-solution followed by the usual workup and crystallization of the crude product from 30 ml of methanol at 0° afforded 1.18 g (83%) of **20b** as colorless crystals[11]). – GC. (A): t_R 21.48. – TLC. (ethyl acetate/petroleum ether 1:9): Rf 0.54. – IR.: 1763, 1605, 1592, 1507, 1207, 1171, 1148, 829, 806. – ^{1}H-NMR.: 0.65 (*qa*, *J* = 11.5, 1 H); 0.82–1.93 (*m* with 2 *t* at 0.90 and 1.27, *J* = 7, 28 H); 2.55–2.71 (*m* with *qa* at 2.57, *J* = 7, 3 H); *AA'BB'*-system centred at 7.00 and 7.20 (4 H). – MS.: 356 (< 1, $C_{24}H_{36}O_2^+$), 300 (100), 120 (41).

Preparation of 2β-butoxy-6α-phenyl-(4aβ,8aα)-decahydronaphthalene (**23**) *from* **4**. To a suspension of 190 mg (5.0 mmol) of $LiAlH_4$ in 5 ml of dry ether was added dropwise at r.t. a solution of 500 mg (2.19 mmol) of **4** in 10 ml of ether. After stirring for 30 min at r.t. the mixture was carefully quenched with 20 ml of 1N H_2SO_4 and extracted with ether. The usual workup then gave 495 mg (98%) of colorless crystals, consisting (GC.) of a (5:95)-mixture of epimeric alcohols (HO_α- and HO_β–C(2)). The pure β-epimer could be obtained by an additional crystallization from hexane at 0°, m.p. 132°. – GC. (A): t_R 12.63. – TLC. (toluene/ethyl acetate 3:1): Rf 0.19. – IR.: 3452, 1606, 1494, 1063, 1037, 762, 755, 700. – ^{1}H-NMR. (400 MHz): 0.99–2.05 (*m*, 15 H); 2.53 (*t* × *t*, *J* = 11.5 and 3.5, 1 H); 3.64 (*t* × *t*, *J* = 10.5 and 4.5, 1 H); 7.16–7.33 (*m*, 5 H). – MS.: 230 (45, $C_{16}H_{22}O^+$), 212 (55), 169 (22), 156 (28), 143 (33), 117 (37), 108 (78), 104 (100), 91 (85).

To a suspension of 72 mg (0.56 mmol) of KH in 10 ml of 1,2-dimethoxyethane was added at r.t. a solution of 66 mg (0.29 mmol) of the above obtained 6α-phenyl-4aβ,8aα-decahydro-2β-naphthalenol. After stirring for 30 min at 40° 0.4 ml (2.89 mmol) of butyl iodide were added and the mixture was heated to reflux for 18 h. Partitioning between water and ether followed by the usual workup gave 120 mg of an oil, which after flash chromatography on silica gel (toluene) afforded 16 mg

(20%) of **23** as colorless crystals. This material may additionally be recrystallized from methanol at −50°, m.p. 59.5°. – GC. (A): t_R 15.76. – TLC. (toluene): Rf 0.42. – IR.: 1600, 1494, 1479, 1133, 1110, 763, 755, 738, 700. – ^{1}H-NMR. (90 MHz): 0.79–2.21 (21 H); 2.56 (*m*, 1 H); 3.25 (*m*, 1 H); 3.47 (*t*, J = 6.5, 2 H); 7.10–7.33 (5 H). – MS.: 286 (5, $C_{20}H_{30}O^+$), 212 (100), 197 (7), 184 (33), 169 (11), 156 (17), 143 (18), 117 (24), 108 (43), 91 (53).

Attempts to converted **23** to **25** *via Friedel-Crafts* acylation followed by hydrogenation over Pd/C failed.

Preparation of 2β-butoxy-6α(4-pentylphenyl)-(4aβ,8aα)-decahydronaphthalene (**25**) *from* **4** (via **24**). A cold (0°) solution of 10.0 g (43.8 mmol) of **4** and 6.3 ml (51.7 mmol) of valeryl chloride in 1 l of CH_2Cl_2 was treated with 14.6 g (109 mmol) of $AlCl_3$ over a period of 10 min. After stirring for 18 h at r.t. the mixture was poured into 1 l of ice/water and extracted with CH_2Cl_2. The organic layers were washed with 2N HCl affording after the usual workup a brown oil. Flash chromatography on silica gel (ethyl acetate/petroleum ether 1:9) gave 11.3 g (83%) of oily **24** (GC.: 94%), which was used in the following step without further purification. – GC. (A): t_R 21.51. – TLC. (toluene/ethyl acetate 3:1): Rf 0.37.

Diketone **24** (2.70 g, 8.6 mmol) in 80 ml of abs. EtOH was hydrogenated at normal pressure and r.t. in the presence of 300 mg of 10% Pd/C (H_2 uptake: 380 ml). The mixture was filtered through *Celite* and concentrated *in vacuo*. The remaining 2.30 g of yellow oil in 40 ml of dry ether were added over 10 min to a suspension of 640 mg (16.8 mmol) of $LiAlH_4$ in 10 ml of ether. After stirring for 30 min at r.t. the mixture was carefully quenched with 50 ml of 2N H_2SO_4 and extracted with ether (3 × 50 ml). The usual workup gave 1.9 g of a semi-crystalline residue, which after crystallization from hexane at −20° afforded 480 mg (20%) of 6α-(*p*-pentylphenyl)-4aβ,8aα-decahydro-2β-naphthalenol as colorless crystals 96.5% pure (GC.), m.p. 96–98°. – GC. (A): t_R 18.52. – TLC. (toluene/ethyl acetate 3:1): Rf 0.40. – IR.: 3422, 1514, 1061, 1034, 818. – ^{1}H-NMR. (60 MHz): 0.67–2.17 (*m* with *s* at 1.58, 24 H); 2.26–2.81 (3 H); 3.64 (*m*, 1 H); 7.10 (*s*, 4 H). – MS.: 300 (100, $C_{21}H_{32}O^+$), 243 (66), 211 (46), 174 (63), 117 (72), 91 (66).

To a suspension of 460 mg (19.2 mmol) of NaH in 10 ml of dry DMF was added successively a solution of 392 mg (1.3 mmol) of the above obtained alcohol in 10 ml of DMF and 1.52 ml (11.0 mmol) of butyl iodide. After stirring for 3 days at 50° the mixture was carefully quenched with 100 ml of water, extracted with hexane (3 × 50 ml) and worked up as usual. Flash chromatography of the residue on silica gel (hexane and 2% ether/hexane) followed by crystallization from methanol at −20° afforded pure **25** as colorless crystals[11]). – GC. (A): t_R 20.76. – TLC. (hexane/ether 19:1): Rf 0.23. – IR.: 1606, 1514, 1109, 842, 823, 805. – ^{1}H-NMR. (400 MHz): 0.84–2.11 (*m* with 2 *t* at 0.88 and 0.92, J = 7, 30 H); 2.49–2.59 (*m*, 3 H); 3.24 (*m*, 1 H); 3.46 (*t*, J = 7, 2 H); 7.10 (*s*, 4 H). – MS.: 356 (34, $C_{25}H_{40}O^+$), 282 (49), 254 (24), 211 (34), 174 (100), 161 (48), 134 (63), 117 (55).

Preparation of ethyl 4-[6β-heptyl-2α-(4aα,8aβ)-decahydronaphthyl]cyclohexyl ketone (**27f**) *from* **12r**. A solution of 9.0 g (24.4 mmol) of **12r** in 120 ml of abs. EtOH was treated with H_2 (50 atm/50°) in the presence of 5 g of 5% Rh on *Alox* for 22 h. The mixture was concentrated *in vacuo*, partitioned between water and ether and worked up as usual. To a solution of the resulting crude product in 150 ml of acetone was then added dropwise at r.t. 8N H_2CrO_4 [10] until the orange color of the reagent persisted. After stirring an additional hour at r.t. excess oxidant was destroyed by the addition of 2-propanol and the green reaction mixture was partitioned between water and CH_2Cl_2. Usual workup gave 8.5 g of a crystalline mass, consisting (GC.) of 23.2% of **27f** and 64.6% of the corresponding C(4′)-epimer. A solution of this material in 200 ml of 1N methanolic KOH was heated to reflux for 2 h. The cooled mixture was partitioned between water and CH_2Cl_2 and worked up as usual. Recrystallization of the remaining solid, consisting (GC.) of 88.9% of **27f** and 0.7% of the corresponding C(4′)-epimer, from 400 ml of acetone at 0° afforded 7.1 g (78%) of analytically pure **27f** as colorless crystals[11]). – GC. (A): t_R (**27f**) 24.01; t_R of C(4′)-epimer: 23.48. – TLC. (ethyl acetate/petroleum ether 3:97): Rf of **27f** = 0.29; Rf of C(4′)-epimer: 0.36. – IR.: 1705, 1373, 723. – ^{1}H-NMR.: 0.47–1.95 (*m* with 2 *t* at 0.88 and 1.03, J = 7, 43 H); 2.27 (*t* × *t*, J = 12 and 3.5, 1 H); 2.65 (*qa*, J = 7, 2 H). – MS.: 374 (49, $C_{26}H_{46}O^+$), 356 (52), 345 (14), 327 (10), 317 (23), 233 (45), 137 (30), 123 (45), 109 (44), 95 (62), 81 (62), 67 (53), 57 (100).

Following the above procedure the aromatic ketones **12i**, **12k**, **12o**, **12p** and **12q** were converted to the saturated ketones **27a**, **27b**, **27c**, **27d** and **27e** in comparable yields[10])[11]). – GC. (A) t_R: **27a** = 21.14; **27b** = 23.54; **27c** = 21.10; **27d** = 22.20; **27e** = 23.20.

Preparation of **28** *from* **27**. Following the procedure outlined for the transformation **7**→**8e** the ketones **27a**, **27b**, **27c**, **27e** and **27f** were converted to the hydrocarbons **28a**, **28b**, **28c**, **28d** and **28e**, respectively, in yields of 80–90%[10][11]). Analytical data of **28e**: GC. (A): t_R 21.49. – TLC. (hexane): Rf 0.66. – IR.: 1375. – ^{1}H-NMR.: 0.48–1.41 (*m* with 2 *t* at 0.86 and 0.88, J = 7, 39 H); 1.52–1.79 (9 H). – MS.: 360 (62, $C_{26}H_{48}^+$), 261 (10), 234 (100), 135 (82), 124 (72), 109 (49), 95 (79), 81 (95), 69 (97).

GC. (A) t_R: **28a** = 18.81; **28b** = 21.17; **28c** = 19.03; **28d** = 21.14.

REFERENCES

[1] *M. Schadt & W. Helfrich*, Appl. Phys. Lett. *18*, 127 (1971).

[2] *U. Lauk, P. Skrabal & H. Zollinger*, Helv. Chim. Acta *64*, 1847 (1981).

[3] *H.-J. Deutscher, F. Kuschel, S. Konig, H. Kresse, D. Pfeiffer, A. Wiegeleben, J. Wulf & D. Demus*, Z. Chem. *17*, 65 (1977); *H.-J. Deutscher, B. Laaser, W. Dolling & H. Schubert*, J. Prakt. Chem. *320*, 194 (1978).

[4] *R. Eidenschink, D. Erdmann, J. Krause & L. Pohl*, Angew. Chem. Intern. Ed. *16*, 100 (1977); *L. Pohl, R. Eidenschink, J. Krause & D. Erdmann*, Phys. Lett. *60A*, 421 (1977).

[5] *G. Fouquet & M. Schlosser*, Angew. Chem. *86*, 50 (1974).

[6] *R. Dabrowski, Z. Witkiewicz & K. Kenig*, Mol. Cryst. Liq. Cryst. *58*, 251 (1980).

[7] *G. W. Gray*, in 'Molecular Structure and the Properties of Liquid Crystals', Academic Press Inc., N.Y., Chapter IX, 1962.

[8] *W. Maier & A. Saupe*, Z. Naturforsch. *14A*, 882 (1959); *W. Maier & A. Saupe*, Z. Naturforsch. *15A*, 287 (1960).

[9] *W. C. Still, M. Kahn & A. Mitra*, J. Org. Chem. *43*, 2923 (1978).

[10] *D. C. Kleinfelter & P. von R. Schleyer*, Org. Syn. *42*, 79 (1962).