125. Synthesis and Mesomorphic Properties of 2,6-Disubstituted Tetralins

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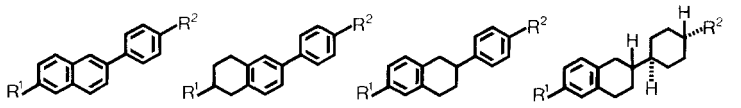
Dedicated to Professor Dr. *Walter Boguth* on the occasion of his 65th birthday

(31.III.82)

Summary

Synthesis and mesomorphic behavior of nine members of each of the two classes of 6-phenyl- and 2-phenyltetralins and five members of the 2-*trans*-cyclohexyltetralins are reported. The synthesis of one member of each class is described in detail. Besides the target compounds, more than twenty intermediates showed liquid crystalline properties; their transition temperatures are recorded (see *Tables 1–6*).

Introduction. – Until recently [1], only a few liquid crystalline 2,6-disubstituted naphthalenes were known [2], distinguished by their high UV. stability, low volatility and little tendency to form smectic mesophases. In order to study the effect of non-aromatic rings in a tricyclic system such as the 2-phenylnaphthalenes (**A**), several members of three new classes: the 6-phenyl (**B**), the 2-phenyl (**C**) and the 2-*trans*-cyclohexyltetralins (**D**) have been prepared and their phase transitions measured *(Tables 1–6)*.



A B C D

Results and discussion. – a) *Mesomorphic properties.* In contrast to the naphthalenes and decalins, two classes of phenyltetralins **B** and **C**, are possible with a distinctly different geometry. The molecular structure of the 6-phenyltetralins **B** may be compared with the known liquid crystalline biphenyls **E**. Also a structural resemblance of the mesomorphic *(cf. Table 3)* 2-phenyltetralins **C** with the non-mesomorphic biphenyl ethanes **F** is recognizable. In class **C** the two aromatic rings connected through a cyclohexene ring seem to occupy a conformation that contributes to the thermal stability of the mesophase more favourable than the free rotating nuclei of the biphenylethane **F**.

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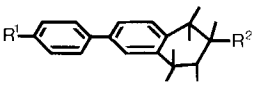
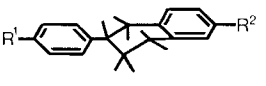
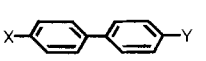
A comparison of *Tables 1* and *2* reveals that the different molecular geometry of classes **B** and **C** is also reflected in their mesomorphic behavior. The low melting point is a common feature of both classes but enantiotropic mesophases with strong smectic tendencies prevail in **B**, and smectic mesophases are completely absent in **C**. Contrary to the biphenylethanes **F** most of the members of the class **C** exhibit monotropic mesophases. Thus, five members of a new class **D**, the 2-*trans*-cyclohexyltetralins, were synthesized *(cf. Table 3)*. In other cases a beneficial effect on the liquid crystal properties by replacing a benzene by a cyclohexane ring was observed [4]. The compounds of class **D** exhibit the same low melting points as the members of classes **B** and **C** and relatively large nematic temperature ranges. Their applicability as components in liquid crystal mixtures for electro-optical display devices is currently under investigation.



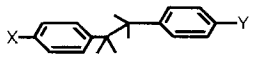
B
6-Phenyltetralins



C
2-Phenyltetralins



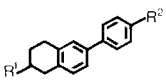
E
Biphenyls



F
Biphenylethanes

b) *Synthesis.* The 6-phenyltetralins **B** were prepared according to *Schemes 1–2.* The common starting material for all members of this class, the 6-phenyl-2-tetralone **54**, was obtained in a four-step synthesis from 4-acetylbiphenyl **49** *(Scheme 1).* In a modified *Willgerodt-Kindler* reaction [5] the carbonyl compound **49** is converted, by heating with sulfur and morpholine at normal pressure, to the thiomorpholide **50**. The hydrolysis of **50** with potassium hydroxide gave the acid **51** which, treated with thionyl chloride at room temperature gave the corresponding acid chloride **52**. In analogy to the one-step procedure of *Burckhalter & Campbell* [6], a modified

Table 1. *Data of 6-phenyltetralins* **B**



	R^1	R^2	M.p. °C	Add. transition	Clp.[e]) °C	ΔH (kcal/mol)	Mesophase
1	C_4H_9	C_6H_{13}	30.9	56.7 (28.5)	60.5	a) b)	smect./nem.
2	C_4H_9	C_2H_5	r.t.[a])	33.7	49.0	b)	smect./nem.
3	C_5H_{11}	C_2H_5	38.6	33.7	61.3	4.9	smect./nem.
4	C_6H_{13}	C_2H_5	30.9	41.0	57.5	4.1	smect./nem.
5	OC_2H_5	C_6H_{13}	35	–	~8	b)	(smect.)
6	OC_4H_9	C_5H_{11}	44.5	–	[c])	2.4	smect.
7	OC_5H_{11}	C_5H_{11}	42.1	36.0	[c])	2.1	smect.
8	C_5H_{11}	CN	79.5	–	108.6	7.1	nem.
9	OC_4H_9	CN	86.4	–	[d])	9.1	–

[a]) Several smectic transitions. [b]) Several endothermic transitions; measurement of ΔH is not feasible. [c]) One transition only (m.p.); smectic texture observed by polarizing microscopic examination below m.p. [d]) No mesophase observed by supercooling. [e]) Clearing point.

Table 2. *Data of 2-phenyltetralins* **C**

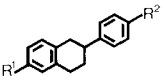
		R^1	R^2	$T_{C\to N}$	$T_{I\to N}$	ΔH (kcal/mol)
	**10**	OC_3H_7	OC_4H_9	59.3	71.2	7.5
	11	C_5H_{11}	OC_4H_9	54.8	48.2	5.6
	12	OC_4H_9	C_6H_{13}	43.5	36.5	5.7
	13	C_5H_{11}	C_3H_7	18.6	−18.7	–
	14	C_6H_{13}	C_6H_{13}	7.8	− 8.0	4.6
	15	OC_4H_9	H	42.5	–	–
	16	H	C_4H_9	liquid	–	–
	17	CN	C_4H_9	82.8	41.4	–
	18	OC_4H_9	CN	91.9	90.5	5.0

Table 3. *Data of 2-*trans*-cyclohexyltetralins* **D**

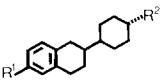
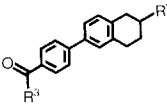
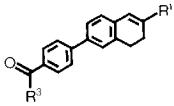
		R^1	R^2	$T_{C\to N}$	$T_{N\to I}$	ΔH (kcal/mol)
	**19**	C_4H_9	C_5H_{11}	31.0	44.8	6.9
	20	C_3H_7	C_5H_{11}	39.4	55.0	6.7
	21	C_4H_9	C_3H_7	2.1	25.1	2.8
	22	C_5H_{11}	C_3H_7	26.2	44.2	5.9
	23	OC_3H_7	C_5H_{11}	45.9	90.3	5.5

Table 4. *Data of 6-phenyltetralins* **B**

Intermediates I		R^1	R^3	M.p. °C	Add. transitions	Clp. °C	ΔH (kcal/mol)	Mesophase
	**24**	C_4H_9	C_5H_{11}	90.9	119(?)	122.0	2.1	nem.
	25	C_4H_9	CH_3	74.3	–	95.9	5.2	nem.
	26	C_5H_{11}	CH_3	76.9	–	105.1	6.1	nem.
	27	C_6H_{13}	CH_3	82.6	–	101.5	6.7	nem.
	28	C_5H_{11}	OH	186.7	–	284.0	3.0	nem.
	29	OC_2H_5	C_5H_{11}	59.8	72.5	79.0	4.6	smect./nem.
	30	OC_4H_9	OC_4H_9	28	–	43.4	~3.7[a])	smect.
	31	OC_4H_9	OH	165.4	180.7	240	5.7	smect./nem.
Intermediates II								
	**32**	OC_4H_9	C_4H_9	123.4	–	151.7	[a])	smect.
	33	OC_5H_{11}	C_4H_9	91.7	115.7	152.7	[a])	smect.
	34	OC_4H_9	OC_4H_9	76.8	–	88.7	3.3	smect.
	35	OAc	C_4H_9	106.8	120.6	144.1	~5.6[a])	nem.

[a]) Several endothermic transitions, determination of ΔH not feasible.

Darzens reaction, the acid chloride **52** was converted under the influence of aluminium chloride in a smooth and rapid reaction below 0° to the 6-phenyltetralone **54**. A slight modification of the conditions was necessary, since the original procedure[2]) failed to give the desired tetralones.

[2]) According to [6], this reaction is not applicable to biphenyl- and *p*-nitrophenylacetyl chlorides.

Table 5. *Data of 2-phenyltetralins* **C**

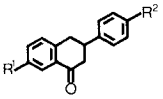
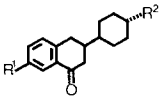
Intermediates		R^1	R^2	$T_{C\to N}$	$T_{N\to I}$	ΔH (kcal/mol)
	**36**	OC_3H_7	OC_4H_9	93.1	–	–
	37	C_5H_{11}	OC_4H_9	61.0	37.0	–
	38	C_5H_{11}	C_3H_7	35.5	–	–
	39	OC_4H_9	C_6H_{13}	78.7	–	–
	40	C_6H_{13}	C_6H_{13}	liquid	–	–
	41	OC_4H_9	H	85.1	–	–
	42	H	C_4H_9	liquid	–	–
	43	H	OC_4H_9	55.5	–	–

Table 6. *Data of 2-*trans*-cyclohexyltetralins* **D**

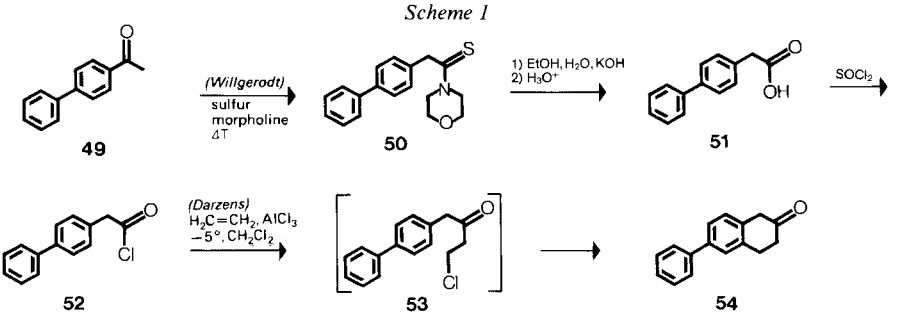
Intermediates		R^1	R^2	$T_{C\to N}$	$T_{N\to I}$	ΔH (kcal/mol)
	**44**	C_5H_{11}	C_3H_7	52.1	36.8	6.0
	45	C_3H_7	C_5H_{11}	48.5	64.5	8.1
	46	C_4H_9	C_3H_7	43.0	30.7	5.5
	47	C_4H_9	C_5H_{11}	49.9	42.3	5.9
	48	OC_3H_7	C_5H_{11}	76.7	80.9	6.7

In spite of a ketone IR.-absorption at 1724 cm^{-1}, the 6-phenyltetralone **54** reacts more likely in its enol form. Thus a *Grignard* conversion was not feasible. After consumption of one mole of alkyl magnesium bromide in a *Zerewittinoff* reaction with the enol of **54**, the unchanged ketone **54** was recovered. At room temperature with acetic anhydride in pyridine, the enol acetate **55** (R^1=OAc) was obtained quantitatively. The ketone **54** had to be acylated to **57** before preparation of the enol ethers **32–35**, because the latter are insufficiently stable under *Friedel-Crafts* acylation conditions. The ketone **57** was then heated in alcohol/toluene with catalytic amounts of concentrated sulfuric acid, to obtain the enol ethers **32–35**. The Pd-catalyzed hydrogenation of these compounds in an aprotic solvent does not stop after absorption of one equivalent of hydrogen. Thus the hydrogenation of **32–35** to the target compounds **5–7** were usually not run to completion, and the ethers **29–31** were isolated as by-products.

The *Wittig* reaction of the tetralone **54** with an alkylidene phosphorane requires high temperatures, resulting in isolation mainly of the isomerized endocyclic olefin **55**, which is hydrogenated to the 2-alkyltetralin **56**. Acylation of **56** yields the mesomorphic ketones **24–27** and, after hydrogenation, the liquid crystalline target compounds **1–4**. In contrast to the regioselective *Friedel-Crafts* acylation of the tetralone **54** to **57** in CH_2Cl_2, **56** is converted mainly to the unwanted isomer under identical conditions. In this case the desired regioselectivity is obtained by using nitrobenzene as solvent.

The nitriles **8** and **9** were prepared by conversion of the carboxyl group of the acids **28** and **31**. Both acids were obtained either by degradation of the acetophenone derivative **26** with bromine in NaOH-solution, or by direct substitution of

Scheme 1



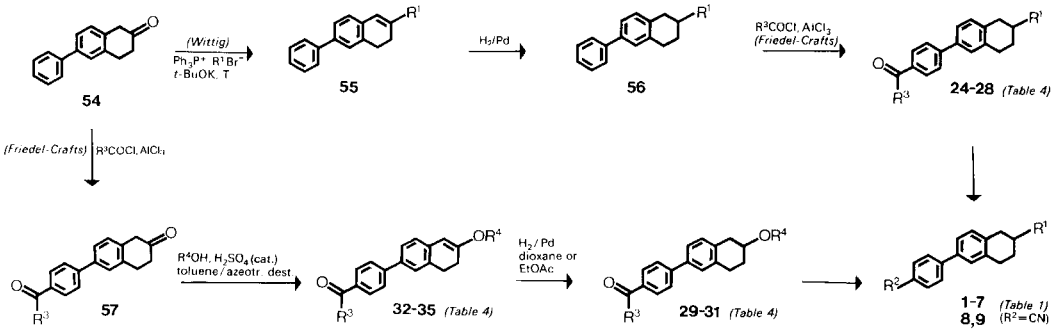
the tetralone **54** with oxalyl chloride [7] to the acid chloride **57** ($R^3 = Cl$) and further transformation of this compound **57** → **34** → **30** → **31**.

The preparation of the 2-phenyltetralins **10–18** (Ring A aromatic) and of the 2-*trans*-cyclohexyltetralins **19–23** (Ring A saturated) is outlined in *Schemes 3* and *4*.

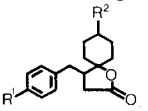
A good approach to the deoxybenzoins **63** is the *Friedel-Crafts* acylation of alkylbenzenes **60** with phenylacetyl chlorides **59**. The class-**D**-equivalent *trans*-alkylcyclohexylbenzylketones **63** were obtained by *Grignard* reaction of benzylmagnesium chlorides **58** with either *trans*-4-alkylcyclohexanecarbonitriles **61**, or in analogy to *Sato* [8], at low temperature with the corresponding carboxylic acid chlorides **62**.

The *Reformatsky* reaction of **63** with bromoacetates gave the hydroxy esters **64**. These compounds were dehydrated and hydrogenated in a one-step procedure to the esters **65** and hydrolyzed to the acids **66**. Under mild *Friedel-Crafts* conditions the acid chlorides of **66** reacted readily and exclusively to the six-membered ring ketones **36–48** [9]. These ketones were reduced to the target compounds **10–23**. In the case of class **D** derivatives (Ring A saturated), the conversion of **64** to **65** required vigorous conditions and gave an almost (1:1)-mixture of the desired product **65** and a spirolactone[3]).

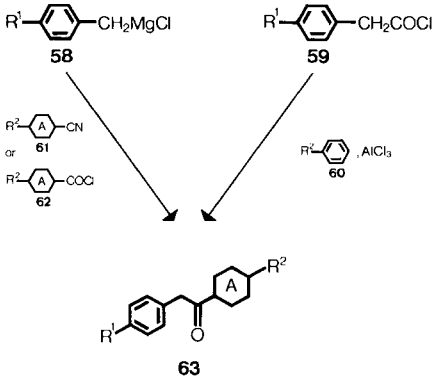
Scheme 2 (cf. Tables 1 *and* 4)



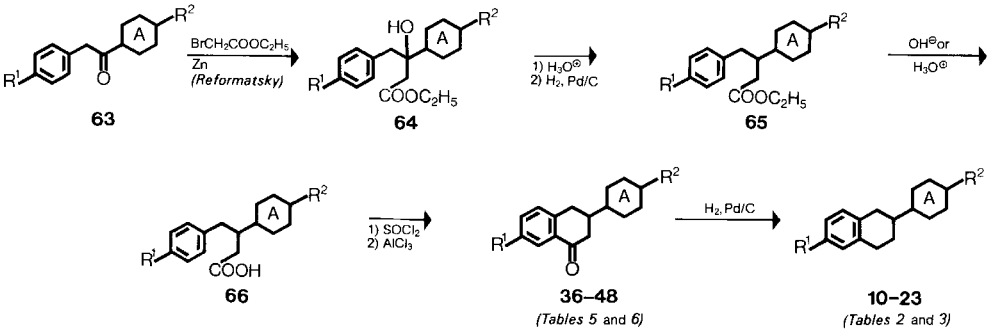
[3]) The following structure is in full agreement with all spectral and analytical data.



Scheme 3



Scheme 4 (see Tables 2, 3, 5 *and* 6)



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.), Dr. *A. Dirscherl* (microanalysis), Mr. *F. Wild* and Mr. *B. Halm* (DTA.), and Mr. *P. Marugg* (GC.).

Experimental Part

With the competent collaboration of Mr. *A. Rageot* and Mr. *D. Häni.*

General remarks. Transition temperatures and heats of melting were measured with a *Mettler TA 200* thermoanalyzer system which was also used for the determination of the purity. All compounds listed in *Tables 1–6* were more than 99% (mol-%) pure. For the microscopic determination of the transition temperatures, a *Mettler* hot stage *FP 52* and a *Mettler PF 5* electronic recording apparatus was used. Mass spectra were recorded on a *MS 9* (*AEI* Manchester) spectrometer, signals are given in *m/z* (rel.%). The ^{1}H-NMR. spectra were recorded at 60 MHz *(Varian T-60)*, 80 MHz *(Bruker WP-80)* or 270 MHz *(Bruker HX-270)*. All compounds gave spectra in accordance with the expected structure. Some 270-MHz-spectra are reported ($CDCl_3$, TMS) abbreviations: *s* singlet, *d* doublet, *t* triplet, *qa* quadruplet, *m* multiplet, *br* broad, *J* spin-spin coupling constant (Hz). IR. spectra in KBr, $\tilde{\nu}_{max}$ in cm^{-1}. Thin-layer chromatography (TLC.) was conducted on *Merck F-254* silica gel coated glass plates. These plates were visualized either with UV. light or spraying with a solution of 4-hydroxybenzaldehyde/H_2SO_4 in methanol and developed in one of the following solvents: (a) = CH_2Cl_2; (b) = CH_2Cl_2/MeOH 95:5; (c) = hexane/CH_2Cl_2 1:1. – GC. analysis were performed on a *Perkin Elmer* Mod. *3920* instrument

equipped with a FID detector and a *Varian Vista CDS 401* data system. All values indicated were measured in peak area percentages and were not calibrated. The carrier gas was N_2 (30 ml/min) and the following temperature programs and glass columns were used: (A) = 2 m 5% *SE-30* on *Gaschrom Q*, temp. 160–300°, 4°/min; (B) = 2 m 10% *QF-1* on *Gaschrom Q*, temp. 150–250°, 4°/min; (C) = 1 m 5% *OV-17* on *Gaschrom Q*, temp. 150–330°, 4°/min; (D) = 2 m 5% *Poly S-178* on *Gaschrom Q*, temp. 160–300°, 8°/min.

Preparation of biphenylthioacetylmorpholide (**50**) [5]. A mixture of 117 g (0.6 mol) of 4-acetylbiphenyl (**49**), 33.6 g (1.04 mol) of sulfur and 91.4 g (1.05 mol) of morpholine was heated in an oil bath (135–145°) to reflux (115–125°) for 3 h. The reaction was monitored by TLC.(a). After completion of the reaction, the mixture was diluted with 500 ml of toluene and left at r.t. overnight. The crystallized product was collected, washed with methanol/ether and dried: 124 g **50** (70%) of white TLC.-pure crystals, m.p. 144.2–144.4°. A second crop (31.9 g, 18%) of the same quality was isolated and the remaining mother liquors (31 g) discarded. – IR.: 1610*w*, 1563*w*, 1497*s*, 1486*s*, 1109*s*, 846*m*, 834*m*, 817*m*, 764*m*, 754*m*, 736*m*, 695*m*.

$C_{18}H_{19}NOS$ (297.42) Calc. C 72.69 H 6.44 N 4.71% Found C 72.45 H 6.49 N 4.65%

Preparation of biphenylacetic acid (**51**). To 166.3 g (0.56 mol) of **50** dissolved under vigorous stirring at 75° in 1000 ml of ethanol and heated to reflux, 10% aqueous KOH was slowly added, to avoid precipitation of the thiomorpholide. At the same rate as the KOH-solution was added, ethanol was evaporated until the ethanol was replaced by the aqueous KOH-solution and a reflux temperature of 100° was reached. The reaction was followed by TLC.(b). After stirring for 2 h at 100°, the cooled solution was extracted with 1 l of ethyl acetate and the extract (1.75 g) discarded. The aqueous phase was acidified with conc. HCl-solution and extracted with 2 l of ethyl acetate. The organic phase was washed with water, dried (Na_2SO_4), evaporated to a volume of 200 ml and cooled in a refrigerator for crystallization. A first crop 60.1 g **51** (69.1%) and a second crop 9.2 g (10.6%) were collected and the mother liquor (29 g) discarded. An analytical sample was prepared by recrystallization from ethyl acetate, m.p. 160.8–163.3°. – IR.: 2754*m*, 2662*m*, 2580*m*, 1695*s*, 1490*s*, 937*m*. – MS.: 212 (48, M^+), 167 (100), 165 (25).

$C_{14}H_{12}O_2$ (212.25) Calc. C 79.23 H 5.70% Found C 79.12 H 5.60%

Preparation of 6-phenyl-2-tetralone (**54**) [6]. A solution of 100 g (0.47 mol) of **51**, 148 ml of thionyl chloride and 1.6 ml of DMF in 250 ml of benzene was stirred for 5 h at r.t. The crude acid chloride **52** was obtained by evaporating the excess reagent and solvent under vacuum at 40° in a rotary evaporator. The crystalline residue was redissolved in 500 ml CH_2Cl_2 and this solution added dropwise at −5° within 2 h to a well stirred suspension of 129 g (0.97 mol) of aluminium chloride in 1500 ml of CH_2Cl_2. At the same time a strong stream of dry ethylene was passed into the cooled mixture. In order to prevent self-condensation of the acid chloride, good agitation, a high excess of ethylene and a sufficiently diluted reaction mixture were necessary. At the end of the acid chloride **52** addition, the dark red mixture was kept at 0–10° by external cooling and 1000 ml of water were added slowly. The two clear phases were separated, the aqueous phase extracted with 500 ml of CH_2Cl_2 and the combined organic phases washed with water, dried and evaporated. After column chromatography of the crude product (128.9 g) on 2000 g of silica gel with hexane/toluene 4:1 and 1:1 and toluene, 3 fractions with the desired product **54** were eluted. Fraction 1: 2.6 g (GC. (A): 39% **54**); fraction 2: 37.9 g (86% **54**); fraction 3: 28.1 g (99.5% **54**), m.p. 81.0–81.7°. The chemical yield of the combined fractions 2 and 3 is 57.6%. – IR.: 1718*s*, 1600*m*, 1571*w*, 1487*s*, 831*w*. – MS.: 222 (92, M^+), 194 (25), 193 (26), 180 (100), 178 (34).

$C_{14}H_{16}O$ (222.29) Calc. C 86.45 H 6.35% Found C 86.16 H 6.53%

Preparation of 3-butyl-7-phenyl-1,2-dihydronaphthalene (**55**, $R^1 = C_4H_9$). A solution of 56.8 g (0.356 mol) of **54** in 150 ml of toluene was added at 70° in one portion to a stirred, preheated, viscous, deep red suspension of 131 g (0.33 mol) of butyltriphenylphosphonium bromide and 42 g (0.38 mol) of *t*BuOK in 900 ml of toluene. The resulting mixture was allowed to reflux (105°) for 1 h, then an additional portion of 30 g (0.075 mol) of butyltriphenylphosphonium bromide was added and heating continued for 1 h. The reaction was monitored by TLC.(a), following the disappearance of **54**. The mixture was then poured on ice, acidified with conc. HCl-solution (250 ml), extracted with 3 l of ether, the ether layer washed with water, dried and evaporated. The oily residue was suspended in 500 ml of boiling hexane, the precipitated triphenylphosphine oxide was collected and recrystallized from 100 ml of CH_2Cl_2 and

500 ml of hexane and the product-free triphenylphosphine oxide discarded. The combined hexane filtrates were evaporated to dryness under reduced pressure. Chromatography of the residue (99.3 g) on silica gel (1000 g) with hexane gave the desired product, 51 g (GC.(B): 87% **55**) (yield: 67%). An analytical sample was prepared by recrystallization from ethanol at 0°, m.p. 43–45.5°. – IR.: 1648*m*, 1664*w*, 1562*w*, 1486*m*, 833*w*, 770*m*, 705*m*. – MS.: 262 (60, M^+), 219 (100), 205 (25).

$C_{20}H_{22}$ (262.40) Calc. C 91.55 H 8.45% Found C 91.40 H 8.67%

Preparation of 2-butyl-6-phenyl-1,2,3,4-tetrahydronaphthalene (**56**, $R^1 = C_4H_9$). A solution of 42 g (0.16 mol) of **55** in 500 ml of ethanol was treated with 5 g of 10% Pd/C and H_2 overnight. The solution was filtered, the filtrate evaporated, and the residue chromatographed with hexane on 1000 g of silica gel to give 35.9 g (GC.(B): 92.5% **56**), (yield: 78.5%). An analytical sample was prepared by recrystallization from ethanol, m.p. 28.6–29.2°. – IR.: 1603*w*, 1570*w*, 1486*s*, 833*w*, 821*w*, 766*s*, 702*m*. – MS.: 264 (100, M^+), 207 (15), 180 (70), 165 (20).

$C_{20}H_{24}$ (264.41) Calc. C 90.85 H 9.15% Found C 91.01 H 9.08%

Further elution with hexane gave small amounts of 2-butyl-6-phenylnaphthalene (m.p. 77.9–80.8°), a by-product formed by dehydrogenation.

Preparation of 4-(6-butyl-5,6,7,8-tetrahydro-2-naphthyl)phenyl pentyl ketone (**24**). To a solution of 15.9 g (0.06 mol) **56** ($R^1 = C_4H_9$) and 9.6 g (0.07 mol) of hexanoyl chloride in 400 ml of nitrobenzene, 18.7 g (0.14 mol) aluminium chloride was added at 25° in small portions. After addition the external cooling was removed. The mixture was allowed to warm to r.t. and was stirred an additional 2 h. The progress of the reaction was followed by TLC.(c). The solution was poured into water, diluted with CH_2Cl_2 (200 ml), the organic layer separated, washed with water, dried and the solvents removed under reduced pressure (90°/0.1 Torr). The resulting solid was recrystallized from ethyl acetate to give 16.8 g (GC.(C): 99.0% **24**) and 7.2 g of mother liquor (GC.: 32% **24**, 30% **56** ($R^1 = C_4H_9$) and 5% (isomer of **24**)). An analytical sample was prepared by recrystallization from ethyl acetate/ethanol, m.p. 90.5–90.9°, clp. 122.0°. – IR.: 1683*s*, 1605*m*, 1576*w*, 1558*w*, 1520*w*, 1492*w*, 814*m*. – MS.: 362 (25, M^+), 306 (75), 291 (100).

$C_{26}H_{34}O$ (362.56) Calc. C 86.13 H 9.45% Found C 85.90 H 9.42%

Preparation of 2-butyl-6-(p-hexylphenyl)-1,2,3,4-tetrahydronaphthalene (**1**). A solution of 9 g (0.025 mol) of **24** in 150 ml of ethanol was treated with 1 g 10% Pd/C and H_2 for 5 h. The solution was filtered, the filtrate evaporated and the residue chromatographed with hexane on 400 g of silica gel to give 7.1 g **1** and after recrystallization from hexane 5.4 g (GC.(C): 99.3% **1**), m.p. 30.9°; clp. 60.5°. – IR.: 2955*m*, 2924*s*, 2854*m*, 1560*w*, 804*m*. – ^{1}H-NMR.: 1.01 (*t*, $J = 7$, CH_2CH_3); 1.04 (*t*, $J = 7$, CH_2CH_3); 1.26–1.43 (*m*, 13 H); 1.57–1.76 (*m*, 3 H); 1.94 (*m*, $\Sigma J = 29$, 1 H); 2.41 ($d \times d$, $J = 11$ and 16, H_{ax}–C(1)); 2.62 (*t*, $J = 8$, C_6H_5–CH_2); 2.84 (*m*, 2 H–C(4)); 2.88 ($d \times d \times d$, $J = 16$, 6 and 2, H_{eq}–C(1)); 7.11 (*d*, $J = 8$, H–C(8)); 7.30 (*d*, $J = 2$, H–C(5)); 7.33 ($d \times d$, $J = 8$ and 2, H–C(7)); 7.21 and 7.48 (centres of *AA'BB'*-spectrum, 4 H). – MS.: 348 (100 M^+), 277 (90), 264 (25), 193 (27).

$C_{26}H_{36}$ (348.57) Calc. C 89.59 H 10.41% Found C 89.63 H 10.56%

Preparation of 4-(6-butyl-5,6,7,8-tetrahydro-2-naphthyl)phenyl methyl ketone (**25**). To a solution of 4.9 g (0.015 mol) of **56** ($R^1 = C_4H_9$) and 1.4 g (0.017 mol) of acetyl chloride in 110 ml of nitrobenzene, 4.0 g (0.03 mol) aluminium chloride was added with stirring at 15–20° in small portions. After addition the mixture was stirred an additional hour at r.t. After the usual workup the crude product was chromatographed with hexane/CH_2Cl_2 3:1 and 1:1 on 350 g of silica gel. The resulting main fraction, 2.3 g (GC.(C): 97.8% **25**) was recrystallized from hexane, m.p. 74.3°; clp. 95.9°. – IR.: 1682*s*, 1673*s*, 1603*m*, 1576*w*, 1556*w*, 1518*w*, 1361*m*, 845*w*, 808*m*. – MS.: 306 (100, M^+), 291 (70), 249 (10), 222 (35), 178 (15), 165 (10).

$C_{22}H_{26}O$ (306.45) Calc. C 86.23 H 8.55% Found C 86.03 H 8.65%

Preparation of 4-(6-pentyl-5,6,7,8-tetrahydro-2-naphthyl)benzoic acid (**28**). To a stirred and cooled solution of 30.7 g (0.767 mol) of NaOH in 160 ml of water 44 g (14.2 ml, 0.275 mol) of Br_2 was slowly added at 0–5° over about 15–20 min. To this mixture a solution of 19 g (0.0593 mol) of 4-(6-pentyl-5,6,7,8-tetrahydro-2-naphthyl)phenyl methyl ketone (**26**) in 460 ml of dioxane was added at the same

temperature rather quickly but dropwise in order to avoid precipitation of **26**. After the addition, the mixture was allowed to warm to r.t. and was then stirred at 35–45° until TLC.(a) showed that no ketone **26** remained. At the end of the reaction some sodium salt of **28** separates as a white solid. The mixture was diluted with 400 ml of water, acidified with about 55–60 ml of conc. HCl-solution and extracted with 2 l of ethyl acetate. The organic phase was washed with water, dried (Na_2SO_4) and the solvent removed. The resulting product 17.0 g **28** (88%) was sufficiently pure for further use. An analytical sample was prepared by recrystallization from ethyl acetate/ethanol, m.p. 186.7°; clp. 284.0° (nem.). – IR.: 2680*m*, 2560*m*, 1684*s*, 1604*m*, 1577*w*, 1560*w*, 1522*w*, 1492*w*, 1294*s*, 858*w*, 808*m*. – MS.: 322 (100, M^+), 224 (60).

$C_{22}H_{26}O_2$ (322.45) Calc. C 81.95 H 8.13% Found C 81.64 H 8.10%

Preparation of 4-(6-pentyl-5,6,7,8-tetrahydro-2-naphthyl)benzonitrile (**8**). 4-(6-Pentyl-5,6,7,8-tetrahydro-2-naphthyl)benzoic acid (**28**) (14.5 g, 0.045 mol) was suspended in a solution of 400 ml of toluene, 20 ml of thionyl chloride and 0.5 ml of DMF and the mixture heated at 90° for 1.5 h. The solvent and excess reagent of the resulting solution were removed under vacuum with a rotary evaporator, and the crystalline crude acide chloride **28** ($R^3 = Cl$), m.p. 36–43°; clp. 56.0° (nem.) redissolved at 40° in 400 ml of dioxane. At this temperature a dry stream of ammonia was passed into the stirred solution for 1 h. When the amide **28** ($R^3 = NH_2$)-formation was completed, the solvent was evaporated, the crude amide suspended in 300 ml of 1,2-dichloroethane, 10 ml of phosphoric chloride and 200 ml of toluene and the mixture heated for 2.5 h at reflux. The mixture was then diluted with 2 l of ethyl acetate and the organic phase washed with water, dried (Na_2SO_4) and evaporated. Chromatography of the resulting crystalline benzonitrile 13.3 g (GC.(C): 97% **8**) on 1000 g of silica gel with toluene gave the following fractions. Fraction 1: 5.9 g (GC.: 99.2% **8**); fraction 2: 5.2 g (GC.: 98.4% **8**) and fraction 3: 1.3 g (GC.: 91% **8**). Fraction 1 was recrystallized from ethanol to give 3.8 g pure **8**, m.p. 79.5°; clp. 108.6°. – IR.: 2224*m*, 1604*m*, 1490*m*, 835*w*, 808*m*. – ^{1}H-NMR.: 0.91 (*t*, $J = 7$, CH_2CH_3); 1.24–1.48 (*m*, H_{ax}–C(7) and 8 H); 1.73 (*m*, $\Sigma J = 40$, H–C(6)); 1.97 (*m*, $\Sigma J = 32$, H_{eq}–C(7)); 2.43 (*d*×*d*, $J = 11$ and 17.5, H_{ax}–C(5)); 2.83 (*d*×*t*, $J = 18$ and 6, 2 H–C(8)); 2.92 (*d*×*d*, $J = 17$ and 5, H_{eq}–C(5)); 7.18 (*d*, $J = 8$, H–C(4)); 7.30 (*d*, $J = 2$, H–C(1)); 7.33 (*d*×*d*, $J = 8$ and 2, H–C(3)); 7.67 and 7.69 (centres of *AA'BB'*-spectrum, 4 H). – MS.: 303 (100, M^+), 232 (25), 205 (90).

$C_{22}H_{25}N$ (303.45) Calc. C 87.08 H 8.30 N 4.62% Found C 86.96 H 8.47 N 4.66%

Preparation of 6-(4-valerylphenyl)-2-tetralone (**57**, $R^3 = C_4H_9$). To a solution of 31.9 g (0.144 mol) of 6-phenyl-2-tetralone (**54**) and 17.3 g (17.28 ml, 0.144 mol) of valeryl chloride in 300 ml of CH_2Cl_2, 38.27 g (0.287 mol) of aluminium chloride was added with stirring at −10° in small portions. After addition, the dark green solution was stirred for 1.25 h at 15°, then poured on ice. After the usual workup a crystalline product 43.3 g (GC.: 82% **57**, $R^3 = C_4H_9$) (yield: 82%), m.p. 104–108° was obtained, which was sufficiently pure for further use, but in our hands resisted all further purification attempts.

A sample (1.2 g) was treated with 2 ml of pyridine/acetic anhydride 1:1 overnight at r.t. After the usual workup and recrystallization from toluene/hexane 0.65 g of the pure *6-(4-valerylphenyl)-3,4-dihydro-2-naphthyl acetate* (**35**) was obtained, m.p. 106.8°; clp. 144.1° (nem.). – IR.: 1755*s*, 1680*s*, 1662*m*, 1601*m*, 1552*w*, 1519*w*, 1489*w*, 1369*m*, 1215*s*, 850*w*, 815*w*, 796*w*. – MS.: 348 (10, M^+), 306 (100), 264 (45), 249 (75).

$C_{23}H_{24}O_3$ (348.44) Calc. C 79.28 H 6.94% Found C 79.17 H 6.85%

Preparation of 4-(6-butoxy-7,8-dihydro-2-naphthyl)phenyl butyl ketone (**32**). A mixture of 20 g (0.065 mol) of 6-(4-valerylphenyl)-2-tetralone (**57**, $R^3 = C_4H_9$), 10 ml of butanol, 0.25 ml of aqueous H_2SO_4-solution (10% *v/v*) and 100 ml of toluene was heated under N_2 at reflux for 3 h. During that time 100 ml of toluene were removed and continuously replaced by the same amount of toluene/butanol 10:1. The cooled mixture was diluted with 1.5 l of ether, the ether solution washed several times with water, dried (Na_2SO_4) and the solvent evaporated. The resulting crude product (31 g) was chromatographed on 800 g of silica gel with hexane/toluene 1:1 and 1:4. Pure **32**, 11.8 g, (49%) was eluted and recrystallized from ethanol, m.p. 123.4°; clp. 151.7° (nem.). – IR.: 1678*s*, 1635*s*, 1598*s*, 1568*w*, 1550*w*, 1519*w*, 1490*w*, 1273*m*, 1263*m*, 1206*m*, 1179*s*, 834*m*. – MS.: 362 (100, M^+), 306 (65), 264 (45), 249 (90).

$C_{25}H_{30}O_2$ (362.51) Calc. C 82.83 H 8.34% Found C 82.90 H 8.60%

Further elution with CH_2Cl_2/ether gave 8.2 g (41%) of unchanged starting material **57** ($R^3 = C_4H_9$).

Preparation of 2-butoxy-6-(4-pentylphenyl)-1,2,3,4-tetrahydronaphthalene (**6**). A solution of 7.7 g (0.021 mol) of 4-(6-butoxy-7,8-dihydro-2-naphthyl)phenyl butyl ketone (**32**) in 100 ml of ethyl acetate was treated with 0.3 g of 10% Pd/C and H_2 at r.t. overnight. The solution was filtered, the filtrate chromatographed with hexane/toluene 9:1 and 1:1 on 450 g of silica gel. The following two products were isolated: 6.4 g **6** (an analytical sample was prepared by recrystallization from ethanol, m.p. 44.5° *(cf. Table 1)*) and 1.1 g of 4-(6-butoxynaphthyl)phenyl butyl ketone, a by-product formed by dehydrogenation.

Data of **6**. – IR.: 1613*w*, 1494*m*, 1104*s*, 848*w*, 803*m*. – ^{1}H-NMR.: 0.90 (*t*, $J = 7$, CH_2CH_3); 0.93 (*t*, $J = 7$, CH_2CH_3); 1.29–1.47 (*m*, 6 H); 1.53–1.71 (*m*, 4 H); 1.82 (*m*, $\Sigma J = 46$, H_{ax}–C(3)); 2.12 (*m*, $\Sigma J = 34$, H_{eq}–C(3)); 2.51 (*t*, $J = 8$, $C_6H_5CH_2$); 2.73–2.90 (*m*, H_{ax}–C(1) and H_{ax}–C(4)); 2.99 (*d*×*t*, $J = 16$ and 11, H_{eq}–C(4)); 3.12 (*d*×*d*, $J = 16$ and 5, H_{eq}–C(1)); 3.54 (*d*×*t*, $J = 11$ and 7, OCH_2); 3.73 (*m*, $\Sigma J = 28$, H–C(2)); 7.13 (*d*, $J = 8$, H–C(8)); 7.30 (*d*, $J = 2$, H–C(5)); 7.32 (*d*×*d*, $J = 8$ and 2, H–C(7)); 7.22 and 7.47 (centres *AA'BB'* spectrum, 4 H). – MS.: 350 (45, M^+), 293 (8), 276 (100), 250 (30), 219 (42), 193 (28).

$C_{25}H_{34}O$ (350.55) Calc. C 85.66 H 9.78% Found C 85.72 H 10.03%

Preparation of 2-pentoxy-6-(4-pentylphenyl)-1,2,3,4-tetrahydronaphthalene (**7**). A solution of 4 g (0.0106 mol) of 4-(6-pentoxy-7,8-dihydro-2-naphthyl)phenyl butyl ketone (**33**) in 100 ml of ethyl acetate was treated with 0.5 g of 10% Pd/C and H_2 for 2 h at r.t. The catalyst was filtered off, the solvent evaporated and the residue chromatographed on 240 g of silica gel with hexane/toluene 9:1 and 1:1. After recrystallization of the main fraction from ethanol/hexane 1.9 g of pure **7** was obtained, m.p. 42.1°. – IR.: 1578*w*, 1560*w*, 1494*m*, 1104*s*, 803*m*. – MS.: 364 (41, M^+), 276 (100), 250 (28), 219 (36), 193 (24).

$C_{26}H_{36}O$ (364.57) Calc. C 85.66 H 9.95% Found C 85.31 H 9.99%

Preparation of butyl 4-(6-butoxy-7,8-dihydro-2-naphthyl)benzoate (**34**). To an ice-cooled mixture of 11 g (0.05 mol) of 6-phenyl-2-tetralone (**54**) and 8.4 ml (0.1 mol) of oxalyl chloride in 100 ml of CH_2Cl_2, 20 g (0.15 mol) of aluminium chloride was added in small portions. The mixture was stirred at 5–10° (monitored by TLC.(a)) for 10 min, then poured on ice and extracted with ethyl acetate. After the usual workup, the resulting red-brown oil, the acid chloride **57** ($R^3 = Cl$), was used for the next step without further purification. The compound was dissolved in a mixture of 190 ml of toluene, 10 ml of butanol and 0.3 ml of aqueous H_2SO_4-solution (10% *v/v*) and refluxed for 4 h. During that time 200 ml of toluene were removed and continuously replaced by the same amount of toluene/butanol 10:1. The cooled solution was diluted with 1.5 l of ethyl acetate, washed with water, dried (Na_2SO_4) and the solvent evaporated. After chromatography of the crude product (18.1 g) on 1400 g of silica gel with toluene, two fractions were isolated: 3.2 g (GC.(C): 50% **34**) and 5.1 g (GC.: 68% **34**), combined and used for the next step (for an analytical sample see next step).

Preparation of butyl 4-(6-butoxy-5,6,7,8-tetrahydro-2-naphthyl)benzoate (**30**). The crude enol ether **34** (8.3 g) was hydrogenated in 350 ml of ethyl acetate with 0.9 g of 10% Pd/C for 6 h at r.t. The solution was filtered, the filtrate evaporated, and the residue chromatographed with toluene and toluene/CH_2Cl_2 1:1 on 1000 g of silica gel to give 0.85 g of starting material **34** (GC.: 86% **34**) and 4.8 g **30** (GC.(C): 97% **30**). Analytical samples of both compounds were prepared by recrystallization from ethanol/hexane and hexane respectively.

Data of butyl 4-(6-butoxy-7,8-dihydro-2-naphthyl)benzoate (**34**). M.p. 76.8°; clp. 88.7°. – IR.: 1714*s*, 1634*s*, 1602*s*, 1552*m*, 1520*w*, 1491*m*, 1281*s*, 1260*s*, 1181*s*, 838*m*. – MS.: 378 (92, M^+), 376 (17), 322 (100), 305 (12), 266 (19).

$C_{25}H_{30}O_3$ (378.51) Calc. C 79.33 H 7.99% Found C 79.30 H 8.11%

Data of butyl 4-(6-butoxy-5,6,7,8-tetrahydro-2-naphthyl)benzoate (**30**). M.p. 28°; clp. 43.4°. – IR.: 1715*s*, 1607*w*, 1577*w*, 1561*w*, 1519*w*, 1277*s*, 1101*s*, 858*m*, 815*m*. – MS.: 380 (24, M^+), 306 (100), 280 (20) 250 (23).

$C_{25}H_{32}O_3$ (380.53) Calc. C 78.91 H 8.48% Found C 78.82 H 8.58%

Preparation of 4-(6-butoxy-5,6,7,8-tetrahydro-2-naphthyl)benzoic acid (**31**). A solution of 0.6 g of KOH in 100 ml of water was added to a preheated solution of 3 g of **30** in 100 ml of dioxane and the resulting mixture refluxed for 3 h. The mixture was then diluted with 300 ml of 1N NaOH, extracted

with 1 l of ethyl acetate. The extract was washed with water, dried (Na_2SO_4) and evaporated to produce 1.0 g of starting material (GC.(C): 87% **30** and 15% **31**). The aqueous layer was acidified with conc. HCl-solution and then extracted with 1 l of ethyl acetate. The organic phase was dried (Na_2SO_4) and evaporated to yield 1.7 g of the pure acid **31**. An analytical sample was prepared by recrystallization from ethyl acetate, m.p. 165.4°; clp. 240.0°. – IR.: 2668*m*, 2546*m*, 1687*s*, 1607*s*, 1578*w*, 1561*w*, 1522*w*, 1493*w*, 1290*s*, 1232*m*, 1181*m*, 1103*s*, 860*w*. – MS.: 324 (18, M^+), 250 (100), 224 (38).

$C_{21}H_{24}O_3$ (324.42) Calc. C 77.75 H 7.46% Found C 77.60 H 7.46%

Preparation of 4-(6-butoxy-5,6,7,8-tetrahydro-2-naphthyl)benzonitrile (**9**). A suspension of 3.9 g of the acid **31**, 10 ml of thionyl chloride and 0.3 ml of DMF in 150 ml of toluene were stirred overnight at r.t. The solvent and excess reagent of the resulting solution were removed under vacuum in a rotary evaporator and the oily crude acid chloride **31** ($R^3 = Cl$) redissolved at 40° in 200 ml of dioxane. At this temperature a dry stream of ammonia was passed into the stirred solution for 1 h. After removal of the solvent, the crude amide **31** ($R^3 = NH_2$) was suspended in a mixture of 20 ml of dichloroethane, 5 ml of phosphoric chloride and 100 ml of toluene and refluxed for 2.5 h. The resulting solution was cooled, diluted with 1 l of ethyl acetate, the organic phase washed with water, dried (Na_2SO_4) and evaporated to afford 2.4 g of the TLC.(c) pure nitrile **9**. For analysis a sample was recrystallized from ethanol/hexane, m.p. 86.4°. – IR.: 2222*s*, 1604*s*, 1576*w*, 1553*w*, 1490*m*, 1098*s*, 853*m*, 811*m*. – ^{1}H-NMR.: 0.93 (*t*, $J = 7$, CH_2CH_3); 1.32–1.47 (*m*, 2 H); 1.53–1.67 (*m*, 2 H); 2.86 (*m*, $\Sigma J = 40$, H_{ax}–C(7)); 2.09 (*m*, $\Sigma J = 30$, H_{eq}–C(7)); 2.76–2.90 (*m*, H_{ax}–C(5) and H_{ax}–C(8)); 2.95–3.07 (*m*, H_{eq}–C(8)); 3.12 (*d*×*d*, $J = 12$ and 5, H_{eq}–C(5)); 3.54 and 3.57 (*d*×*t*, $J = 9$ and 7, OCH_2); 3.77 (*d*×*d*×*d*×*d*, $J = 3$, 5, 8.5 and 11.5, H–C(6)); 7.17 (*d*, $J = 8$, H–C(4)); 7.30 (*d*, $J = 2$, H–C(1)); 7.33 (*d*×*d*, $J = 8$ and 2, H–C(3)); 7.63 and 7.67 (centres of *AA'BB'* spectrum, 4 H). – MS.: 305 (7, M^+), 231 (100), 205 (36).

$C_{21}H_{23}NO$ (305.42) Calc. C 82.58 H 7.59 N 4.59% Found C 82.35 H 7.66 N 4.53%

Preparation of 4-pentylbenzyl 4-propylphenyl ketone (**63**, $R^1 = C_5H_{11}$, $R^2 = C_3H_7$. *Ring A aromatic*). A solution of 72.35 g (0.3 mol) of 4-pentylbenzyl bromide in 250 ml of ether was added dropwise at 10–25° to an ice-cooled suspension of 14.6 g (0.6 g-atoms) of magnesium turnings in 250 ml of ether. The mixture was stirred for a further 15 min at r.t., then cooled to 5° and at that temperature a solution of 43.56 g (0.3 mol) of 4-propylbenzonitrile in 50 ml of ether was added in one portion. After stirring for a total of 5 h at r.t., the mixture was poured into ice water, acidified with diluted H_2SO_4-solution, the ether layer separated and the aqueous layer extracted with 1 l of ethyl acetate. The combined organic phase were washed with water, dried (Na_2SO_4) and evaporated. The resulting solid, a (2:5)-mixture (GC.(C)) of starting material (4-propylbenzonitrile) and the desired **63** was chromatographed on 1500 g of silica gel with hexane/toluene mixtures to give 56.2 g of crystals sufficiently pure[4]) for further use (yield 59%). For analysis a sample was recrystallized twice from ethyl acetate/hexane; m.p. 51.5–52.5°. – IR.: 1685*s*, 1606*m*, 1571*w*, 1517*m*, 839*w*, 810*m*. – MS.: 308 (2, M^+), 161 (5), 147 (100), 91 (11).

$C_{22}H_{28}O$ (308.47) Calc. C 85.66 H 9.15% Found C 85.64 H 9.17%

From the topmost fractions some 4-pentyltoluene and 1,2-di-(4-pentylphenyl)ethane were isolated. These products were formed from the *Grignard* reagent.

Preparation of 4-butoxybenzyl phenyl ketone (**63**, $R^1 = OC_4H_9$, $R^2 = H$. *Ring A aromatic*). A solution of 59.6 g (0.286 mol) of 4-butoxyphenylacetic acid, 119 g (1 mol) of thionyl chloride, 2 ml of DMF in 350 ml of benzene was stirred overnight at r.t. The crude acid chloride **59** ($R^3 = OC_4H_9$) was then obtained by evaporating the excess reagents and solvent under vacuum at 40° in a rotary evaporator. The crude product was redissolved in 500 ml of CH_2Cl_2 and 78.1 g (1 mol) of benzene, aluminium chloride (133.3 g, 1 mol) was added in small portions at −30° and the resulting mixture was stirred for an additional 5 h at −15° to −5°. The mixture was poured into ice/water, diluted with 2 l of ether, the organic layer washed with water, dried (Na_2SO_4) and evaporated. After chromatography of the resulting solid (113 g) on 1500 g of silica gel with hexane/toluene mixtures, 68.5 g 4-butoxybenzyl phenyl ketone (**63**) was obtained (62.6%). An analytical sample was prepared by recrystallization from ethyl acetate,

[4]) GC.(C): 4-pentylbenzyl 4-propylphenyl ketone (**63**, 58%) and 4-propylbenzonitrile (21%).

m.p. 93.0–93.3°. – IR.: 1691*s*, 1610*m*, 1583*w*, 1513*w*, 1242*s*, 1178*m*, 999*m*, 822*m*, 794*m*, 753*m*, 689*m*. – MS.: 268 (19, M^+), 163 (71), 107 (100), 105 (97).

$C_{18}H_{20}O_2$ (268.36) Calc. C 80.56 H 7.51% Found C 80.38 H 7.74%

Preparation of benzyl 4-propylcyclohexyl ketone (**63**, $R^1 = H$, $R^2 = C_3H_7$. *Ring A saturated).* Some benzyl chloride was added at r.t. to 72 g (3 g-atom) magnesium turnings in 1000 ml of tetrahydrofuran. After initiation of the exothermic reaction, the mixture was cooled to 0–5°, stirred and further benzyl chloride (total 253 g; 2 mol) was added dropwise for 1.5 h. The *Grignard*-solution was filtered into a dropping funnel and added dropwise for 2 h to a stirred and cooled (−55°) solution of 339.6 g (1.8 mol) of *trans*-4-propylcyclohexanecarbonyl chloride (**62**, $R^2 = C_3H_7$) in 1000 ml of tetrahydrofuran. The mixture was stirred for an additional hour and allowed to reach r.t., then poured onto ice. The aqueous layer was acidified with 20% H_2SO_4-solution, the solvent evaporated and the residue (503.5 g) subjected to column chromatography on 2000 g of silica gel with hexane/toluene to give 330 g of pure **63** ($R^1 = H$, $R^2 = C_3H_7$) (74%) and 26.8 g of 1,2-diphenylethane (6%). – IR.: 1706*s*, 1603*w*, 1496*m*, 756*m*, 711*s*. – MS.: 244 (0.6, M^+), 153 (41), 125 (61), 91 (34), 83 (59), 69 (100), 55 (32), 41 (22).

$C_{17}H_{24}O$ (244.38) Calc. C 83.55 H 9.90% Found C 83.66 H 10,21%

Preparation of ethyl 3-hydroxy-4-(4-pentylphenyl)-3-(4-propylphenyl)butyrate (**64**, $R^1 = C_5H_{11}$, $R^2 = C_3H_7$. *Ring A aromatic).* To a mixture of 19.6 g (0.3 mol) of zinc dust (which has been activated with 25% HCl-solution, washed with water, alcohol, ether and dried at 70°) and 46.6 g (0.151 mol) 4-pentylbenzyl 4-propylphenyl ketone (**63**) in 300 ml of benzene and 50 ml of ether, 3.54 g (0.213 mol) ethyl bromoacetate was added in portions. After the first addition, the stirred mixture was heated to 70° by evaporating the lower boiling solvent fraction until the reaction started. After the complete addition (0.5 h), the mixture was stirred for 2 h at 70–75° until TLC.(a) showed that no starting material **63** remained. The mixture was diluted with 200 ml of water, acidified with 10 ml of conc. sulfuric acid and extracted with 2 l of ethyl acetate. The organic phase was washed with water, dried (Na_2SO_4), the solvent removed and the liquid residue (64.7 g) subjected to column chromatography on 1000 g of silica gel with hexane/toluene mixtures to give 57.1 g (95%) of the analytically pure liquid **64** ($R^1 = C_5H_{11}$, $R^2 = C_3H_7$). – IR.: 3494*m*, 1714*s*, 1613*w*, 1512*m*, 1187*s*, 1155*s*, 843*m*, 805*m*. – MS.: 378 (21, $M-H_2O$), 332 (7), 305 (6), 275 (3), 235 (64), 161 (8), 147 (100), 119 (5).

$C_{26}H_{36}O_3$ (396.57) Calc. C 78.75 H 9.15% Found C 78.66 H 9.34%

Preparation of ethyl 4-(4-pentylphenyl)-3-(4-propylphenyl)butyrate (**65**, $R^1 = C_5H_{11}$, $R^2 = C_3H_7$. *Ring A aromatic).* A solution of 52 g (0.131 mol) of **64**, (above), 2 ml of aqueous 70% $HClO_4$-solution in 150 ml of acetic acid was concentrated to ¼ of its volume by evaporating the solvent under vacuum at 50° in a rotary evaporator. Owing to this treatment **64** was dehydrated (in 10 min) to the corresponding (*Z*/*E*)-stilbene. The reaction was monitored by TLC.(a). The cooled mixture was diluted with 170 ml of ethanol and treated with 3 g of 10% Pd/C and H_2 at r.t. for 2 h. The solution was filtered, the filtrate diluted with 1.5 l of ether, the organic phases washed with water, dried (Na_2SO_4) and evaporated to dryness. The resulting pure oily product (47.9 g, GC.(C): 99.4%) (yield: 95%) was chromatographed on 900 g of silica gel with hexane/toluene mixtures to give 36.6 g of the analytically pure **65** ($R^1 = C_5H_{11}$, $R^2 = C_3H_7$). – IR.: 1736*s*, 1613*w*, 1514*m*, 1258*m*, 1215*m*, 1176*m*, 1145*m*, 841*m*, 807*m*, 727*w*. – MS.: 380 (4, M^+), 292 (26), 219 (42), 167 (100).

$C_{26}H_{36}O_2$ (380.57) Calc. C 82.06 H 9.54% Found C 82.05 H 9.56%

*Preparation of ethyl 3-(*trans*-4-pentylcyclohexyl)-4-phenylbutyrate* (**65**, $R^1 = H$, $R^2 = C_5H_{11}$. *Ring A saturated).* Analogously to the above synthesis, 138 g (0.38 mol) of **64** ($R^1 = H$, $R^2 = C_5H_{11}$) was treated in 150 ml of acetic acid with 10 ml of aqueous 70% $HClO_4$-solution at 50°, diluted with 500 ml of ethanol and hydrogenated with 12 g of 10% Pd/C. After the usual workup the liquid residue (118.1 g) was subjected to column chromatography on 2000 g of silica gel with hexane/toluene mixtures to give 54.5 g (41%) of liquid **65** ($R^1 = H$, $R^2 = C_5H_{11}$). – IR.: 1735*s*, 1603*w*, 1584*w*, 1495*w*, 1151*m*, 744*m*, 699*m*. – MS.: 344 (0.3, M^+), 299 (8), 256 (100), 104 (78), 91 (53).

$C_{23}H_{36}O_2$ (344.54) Calc. C 80.18 H 10.53% Found C 80.31 H 10.54%

Further elution gave 34.8 g (29%) of liquid *trans*-4-benzyl-8-pentyl-1-oxaspiro[4,5]decan-2-one (*cf.* footnote [3]). – IR.: 1780*s*, 1603*w*, 1505*w*, 1235*m*, 1200*m*, 1140*m*, 745*w*, 701*w*. – MS.: 314 (19, M^+), 254 (4), 223 (20), 201 (72), 146 (66), 145 (46), 118 (69), 91 (100).

$C_{21}H_{30}O_2$ (314.47) Calc. C 80.21 H 9.62% Found C 80.17 H 9.61%

Preparation of 4-(4-Pentylphenyl)-3-(4-propylphenyl)butyric acid (**66**, $R^1 = C_5H_{11}$, $R^2 = C_3H_7$. *Ring A aromatic*). To avoid precipitation of the starting material, an aqueous solution of 16.8 g (0.42 mol) of NaOH in 60 ml of water was added for 1 h dropwise at 50° to a stirred solution of 36.3 g (0.095 mol) of **65** in 90 ml of CH_2Cl_2 and 810 ml of methanol. The resulting mixture was refluxed (57°) for 2 h until TLC. (a) showed that no starting material remained. After the usual workup the crystalline acid **66** (33 g) (GC.(C): 99% **66**) (yield: 97%) was obtained. An analytical sample was prepared by recrystallization from hexane, m.p. 61.7–62.3°. – IR.: 2650*m*, 2671*m*, 1708*s*, 1514*m*, 806*m*. – MS.: 352 (14, M^+), 292 (15), 191 (100), 161 (58), 149 (73).

$C_{24}H_{32}O_2$ (352.51) Calc. C 81.77 H 9.95% Found C 81.65 H 9.41%

Preparation of 7-pentyl-3-(4-propylphenyl)-3,4-dihydro-1(2H)-naphthalenone (**38**). A solution of 29.2 g (0.08 mol) of **66**, 30 ml (0.413 mol) of thionyl chloride, 1 ml of DMF in 100 ml of toluene was stirred overnight at r.t. The crude acid chloride was obtained by evaporating the excess reagents and solvent under vacuum at 50° in a rotary evaporator. The crude product was redissolved in 300 ml of CH_2Cl_2, cooled to −50° and to this solution 28 g (0.209 mol) of aluminium chloride was added in one portion. The resulting mixture was stirred for 2 h at −50°, then poured into ice water. The aqueous phase was extracted with 1.5 l of ether, the ether phase washed with water, dried (Na_2SO_4), evaporated and recrystallized from hexane to give 13.9 g pure **38** (GC.(C): 99.8% **38**) and 6.4 g (GC.: 95.5% **38**) mother liquors, m.p. 35.5°. – IR.: 1685*s*, 1611*m*, 1570*w*, 1513*m*, 1496*m*, 819*m*, 802*m*. – MS.: 334 (12, M^+), 188 (100), 160 (7), 131 (15).

$C_{24}H_{30}O$ (334.50) Calc. C 86.18 H 9.04% Found C 85.98 H 9.17%

Preparation of 6-pentyl-2-(4-propylphenyl)-1,2,3,4-tetrahydronaphthalene (**13**). A solution of 9.9 g (0.0296 mol) **38** in 100 ml of ethanol/dioxane 1:1 was treated with 1.5 g of 10% Pd/C and H_2 for 3.5 h at r.t. The catalyst was filtered off, the solvent evaporated and the residue (9.6 g) crystallized twice from hexane to give 7.0 g of pure **13**, m.p. 18.6°; clp. −18.7° (nem.). – IR.: 1614*w*, 1513*m*, 1503*m*, 838*m*, 814*m*. – ^{1}H-NMR.: 0.90 (*t*, $J = 7$, CH_3 of the pentyl group); 0.95 (*t*, $J = 7$, CH_3 of the propyl group); 1.29–1.39 (*m*, 4 H); 1.56–1.72 (*m*, 4 H); 1.90 (*m*, $\Sigma J = 42$, H_{ax}–C(3)); 2,11 (*m*, $\Sigma J = 30$, H_{eq}–C(3)); 2.54 (*t*, $J = 7$, C_6H_5–CH_2); 2.57 (*t*, $J = 7$, C_6H_5–CH_2); 2.79–3.05 (*m*, 2H–C(1), H–C(2), 2H–C(4)); 6.94 (*d*×*d*, $J = 8$ and 2, H–C(7)); 6.95 (*d*, $J = 2$, H–C(5)); 7.01 (*d*, $J = 8$, H–C(8)); 7.14 and 7.20 (centres of *AA'BB'* spectrum, 4 H). – MS.: 320 (45, M^+), 277 (6), 249 (11), 200 (16), 174 (100), 117 (44), 91 (23).

$C_{24}H_{32}$ (320.52) Calc. C 89.94 H 10.06% Found C 89.94 H 9.96%

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