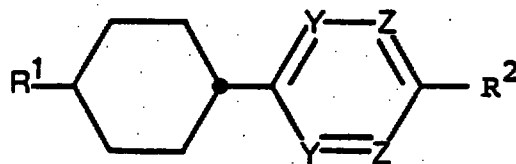


Liquid Crystal Trans-(4-Alkyl Cyclohexyl), Pyrimidines

5 The present invention is concerned with novel
trans-(4-alkylcyclohexyl)pyrimidines of the general
formula



I

wherein the symbols Y stand for
nitrogen and the symbols Z stand for
10 =CH- or the symbols Z stand for
nitrogen and the symbols Y stand for =CH-,
R¹ represents alkyl and R² represents
cyano, alkyl, p-alkylphenyl or trans-4-
-alkylcyclohexyl, the term alkyl signifies
15 straight-chain alkyl containing 1 to 12
carbon atoms or in one of the residues R¹
or R² also signifies a branched-chain
alkyl group C₂H₅-CH(CH₃)-(CH₂)_n-, n is an
integer of 1 to 3, and the sum of the

carbon atoms in the alkyl groups
present amounts to at most 14.

The invention is also concerned with the manufacture
of the compounds of formula I hereinbefore, liquid crystalline
5 mixtures which contain these compounds as well as their use
in electro-optical devices.

In the scope of the present invention, the term "alkyl"
signifies not only straight-chain alkyl groups such as methyl,
ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl,
10 decyl, undecyl and dodecyl, but also branched-chain alkyl
groups such as isopropyl, isobutyl, sec-butyl, tert-butyl,
2-methylbutyl, isopentyl and the like. In formula I,
however, a branched-chain alkyl group present can, in
accordance with the definition, only be 2-methylbutyl, 3-
15 -methylpentyl or 4-methylhexyl. Further, in those compounds
of formula I which contain two alkyl groups at least one of
the groups is straight-chain alkyl and the sum of the carbon
atoms in the two alkyl groups is at most 14. The term
"alkoxy" used hereinafter denotes alkyloxy groups in which
20 alkyl can have the above significance.

The compounds in accordance with the invention are
especially valuable as components of liquid crystalline
mixtures and most of them have themselves liquid crystalline
properties, the optically active compounds containing a
25 branched-chain alkyl group generally exhibiting a cholesteric

and/or smectic phase and the remaining compounds of formula I exhibiting a nematic and/or smectic phase.

Those compounds of formula I in which the symbols Y stand for =CH-, the symbols Z stand for nitrogen and R² stands
5 for cyano possess a high positive anisotropy of the dielectric constants ($\epsilon_{||} > \epsilon_{\perp}$, $\epsilon_{||}$ signifying the dielectric constant along the longitudinal axis of the molecule and $\epsilon_{\perp}$ signi-
fying the dielectric constant perpendicular thereto). The
remaining compounds of formula I possess a smaller anisotropy
10 of the dielectric constants.

The compounds in accordance with the invention are miscible with all known liquid crystals and can be used
in all customary electro-optical devices, the choice of the
components of the mixture generally depending on the special
15 purpose of use. However, the compounds in accordance with
the invention are preferably used for the manufacture of
nematic and cholesteric mixtures with positive anisotropy
of the dielectric constants.

Such mixtures (and compounds with positive dielectric
20 anisotropy) orientate themselves in an electric field with
the direction of their largest dielectric constants (i.e.
with their longitudinal axes) parallel to the field direction.
This effect is used, inter alia, in the interaction between
embedded molecules and the liquid crystalline molecules
25 (guest-host interaction) described by J.H.Heilmeyer and

L.A. Zanoni [Applied Physics Letters 13, 91 (1968)]. A further interesting application of the dielectric field orientation lies in the rotation cell discovered by M.Schadt and W. Helfrich [Applied Physics Letters 18, (1971)] as well as in the Kerr cell described in Molecular Crystals and Liquid Crystals 17, 355 (1972),

These electro-optical rotation cells comprise essentially a condenser with transparent electrodes, the dielectric of which is formed from a nematic crystal with $\epsilon_{||} > \epsilon_{\perp}$. The longitudinal molecular axes of the liquid crystals are arranged in twisted form between the condenser plates in the fieldless state, the twisting structure being determined by the given wall orientation of the molecules. After the application of an electric potential to the condenser plates, the molecules adjust themselves with their longitudinal axes in the field direction (i.e. perpendicular to the surface of the plates), whereby linear polarised light is no longer rotated in the dielectric (the liquid crystal is uniaxially perpendicular to the surface of the plates). This effect is reversible and can be used to electrically control the optical transmissivity of the condenser.

Further, it is known that the addition of cholesteric substances (or generally soluble, optically active substances as long as the total mixture remains liquid crystalline) to a matrix of nematic liquid crystals with positive anisotropy

of the dielectric constants leads to a cholesteric mixture which undergoes a cholesteric-nematic phase transition upon application of an electric field. This phase transition is reversible and makes possible high switching speeds of electro-optical devices operated with such mixtures.

It has now been found that the compounds in accordance with the invention, especially those in which R^2 signifies alkyl, have low viscosity. They are therefore suitable for improving the response times of mixtures. Further, the compounds of formula I in which the symbols Y stand for =CH-, the symbols Z stand for nitrogen and R^2 stands for cyano can be used to reduce the threshold potentials of mixtures. Moreover, some of the compounds in accordance with the invention have a large mesophase range, especially compared with known dialkyl compounds. They are colourless and exhibit a high stability towards chemical influences and UV-radiation.

Of the compounds of formula I there are preferred those in which the symbols Y stand for =CH-, the symbols Z stand for nitrogen and R^2 stands either for p-alkylphenyl or for cyano and those in which the symbols Y stand for nitrogen, the symbols Z stand for =CH- and R^2 stands for alkyl. Preferred alkyl groups are the straight-chain alkyl groups containing 2 to 7 carbon atoms.

The following are examples of preferred compounds of formula I:

- Trans-5-(4-methylcyclohexyl)-2-pyrimidinecarbonitrile,
trans-5-(4-ethylcyclohexyl)-2-pyrimidinecarbonitrile,
5 trans-5-(4-propylcyclohexyl)-2-pyrimidinecarbonitrile,
trans-5-(4-butylcyclohexyl)-2-pyrimidinecarbonitrile,
trans-5-(4-pentylcyclohexyl)-2-pyrimidinecarbonitrile,
trans-5-(4-hexylcyclohexyl)-2-pyrimidinecarbonitrile,
trans-5-(4-heptylcyclohexyl)-2-pyrimidinecarbonitrile,
10 trans-2-(4-methylcyclohexyl)-5-pyrimidinecarbonitrile,
trans-2-(4-ethylcyclohexyl)-5-pyrimidinecarbonitrile,
trans-2-(4-propylcyclohexyl)-5-pyrimidinecarbonitrile,
trans-2-(4-butylcyclohexyl)-5-pyrimidinecarbonitrile,
trans-2-(4-pentylcyclohexyl)-5-pyrimidinecarbonitrile,
15 trans-2-(4-hexylcyclohexyl)-5-pyrimidinecarbonitrile,
trans-2-(4-heptylcyclohexyl)-5-pyrimidinecarbonitrile,
trans-2-(4-ethylcyclohexyl)-5-pentylpyrimidine,
trans-2-(4-propylcyclohexyl)-5-propylpyrimidine,
trans-2-(4-propylcyclohexyl)-5-butylpyrimidine,
20 trans-2-(4-propylcyclohexyl)-5-pentylpyrimidine,
trans-2-(4-propylcyclohexyl)-5-heptylpyrimidine,
trans-2-(4-butylcyclohexyl)-5-propylpyrimidine,
trans-2-(4-butylcyclohexyl)-5-pentylpyrimidine,
trans-2-(4-butylcyclohexyl)-5-heptylpyrimidine,
25 trans-2-(4-pentylcyclohexyl)-5-propylpyrimidine,
trans-2-(4-pentylcyclohexyl)-5-butylpyrimidine,

- trans-2-(4-pentylcyclohexyl)-5-pentylpyrimidine,
- trans-2-(4-pentylcyclohexyl)-5-hexylpyrimidine,
- trans-2-(4-pentylcyclohexyl)-5-heptylpyrimidine,
- trans-2-(4-hexylcyclohexyl)-5-propylpyrimidine,
- 5 trans-2-(4-hexylcyclohexyl)-5-butylpyrimidine,
- trans-2-(4-hexylcyclohexyl)-5-pentylpyrimidine,
- trans-2-(4-heptylcyclohexyl)-5-ethylpyrimidine,
- trans-2-(4-heptylcyclohexyl)-5-propylpyrimidine,
- trans-2-(4-heptylcyclohexyl)-5-pentylpyrimidine,
- 10 trans-2-(4-heptylcyclohexyl)-5-heptylpyrimidine,
- trans-5-(4-ethylcyclohexyl)-2-pentylpyrimidine,
- trans-5-(4-propylcyclohexyl)-2-propylpyrimidine,
- trans-5-(4-propylcyclohexyl)-2-butylpyrimidine,
- trans-5-(4-propylcyclohexyl)-2-pentylpyrimidine,
- 15 trans-5-(4-propylcyclohexyl)-2-heptylpyrimidine,
- trans-5-(4-butylcyclohexyl)-2-pentylpyrimidine,
- trans-5-(4-pentylcyclohexyl)-2-propylpyrimidine,
- trans-5-(4-pentylcyclohexyl)-2-butylpyrimidine,
- trans-5-(4-pentylcyclohexyl)-2-pentylpyrimidine,
- 20 trans-5-(4-hexylcyclohexyl)-2-propylpyrimidine,
- trans-5-(4-hexylcyclohexyl)-2-pentylpyrimidine,
- trans-5-(4-heptylcyclohexyl)-2-ethylpyrimidine,
- trans-5-(4-heptylcyclohexyl)-2-propylpyrimidine,
- trans-5-(4-heptylcyclohexyl)-2-butylpyrimidine,
- 25 trans-5-(4-heptylcyclohexyl)-2-pentylpyrimidine,
- trans-5-(4-methylcyclohexyl)-2-(p-propylphenyl)-
pyrimidine,

trans-5-(4-methylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine,

trans-5-(4-ethylcyclohexyl)-2-(p-propylphenyl)-
pyrimidine,

5 trans-5-(4-ethylcyclohexyl)-2-(p-butylphenyl)-
pyrimidine,

trans-5-(4-ethylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine,

10 trans-5-(4-ethylcyclohexyl)-2-(p-heptylphenyl)-
pyrimidine,

trans-5-(4-propylcyclohexyl)-2-(p-propylphenyl)-
pyrimidine,

trans-5-(4-propylcyclohexyl)-2-(p-butylphenyl)-
pyrimidine,

15 trans-5-(4-propylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine,

trans-5-(4-butylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine,

20 trans-5-(4-pentylcyclohexyl)-2-(p-propylphenyl)-
pyrimidine,

trans-5-(4-pentylcyclohexyl)-2-(p-butylphenyl)-
pyrimidine,

trans-5-(4-pentylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine,

25 trans-5-(4-hexylcyclohexyl)-2-(p-propylphenyl)-
pyrimidine,

- trans-5-(4-heptylcyclohexyl)-2-(p-ethylphenyl)-
pyrimidine,
- trans-5-(4-heptylcyclohexyl)-2-(p-propylphenyl)-
pyrimidine,
- 5 trans-5-(4-heptylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine,
- trans-2-(4-ethylcyclohexyl)-5-(p-propylphenyl)-
pyrimidine,
- trans-2-(4-ethylcyclohexyl)-5-(p-pentylphenyl)-
10 pyrimidine,
- trans-2-(4-propylcyclohexyl)-5-(p-propylphenyl)-
pyrimidine,
- trans-2-(4-propylcyclohexyl)-5-(p-butylphenyl)-
pyrimidine,
- 15 trans-2-(4-propylcyclohexyl)-5-(p-pentylphenyl)-
pyrimidine,
- trans-2-(4-butylcyclohexyl)-5-(p-propylphenyl)-
pyrimidine,
- trans-2-(4-pentylcyclohexyl)-5-(p-propylphenyl)-
20 pyrimidine,
- trans-2-(4-pentylcyclohexyl)-5-(p-butylphenyl)-
pyrimidine,
- trans-2-(4-pentylcyclohexyl)-5-(p-pentylphenyl)-
pyrimidine,
- 25 2,5-bis(trans-4-propylcyclohexyl)pyrimidine,
5-(trans-4-propylcyclohexyl)-2-(trans-4-pentylcyclo-
hexyl)pyrimidine,

5-(trans-4-propylcyclohexyl)-2-(trans-4-heptyl-
cyclohexyl)pyrimidine,

5-(trans-4-pentylcyclohexyl)-2-(trans-4-propyl-
cyclohexyl)pyrimidine,

5 5-(trans-4-pentylcyclohexyl)-2-(trans-4-pentyl-
cyclohexyl)pyrimidine,

5-(trans-4-heptylcyclohexyl)-2-(trans-4-propyl-
- cyclohexyl)pyrimidine,

10 5-(trans-4-heptylcyclohexyl)-2-(trans-4-pentyl-
cyclohexyl)pyrimidine,

(+)-trans-5-[4-(2-methylbutyl)cyclohexyl]-2-
-pyrimidine carbonitrile,

(+)-trans-5-[4-(3-methylpentyl)cyclohexyl]-2-
-pyrimidine carbonitrile,

15 (+)-trans-5-[4-(4-methylhexyl)cyclohexyl]-2-
-pyrimidine carbonitrile,

(+)-trans-2-[4-(2-methylbutyl)cyclohexyl]-5-
-pyrimidine carbonitrile,

20 (+)-trans-2-[4-(2-methylbutyl)cyclohexyl]-5-
-butylpyrimidine,

(+)-trans-2-[4-(2-methylbutyl)cyclohexyl]-5-
-pentylpyrimidine,

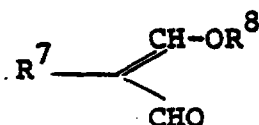
as well as the antipodes of the optically active compounds.

The compounds of formula I can be manufactured in
25 accordance with the invention by

- 11 -

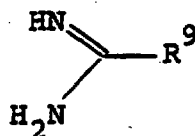
(a) for the manufacture of the compounds of formula I in which R^2 represents alkyl, p-alkylphenyl or trans-4-alkylcyclohexyl, reacting a compound of the general formula

5



IX

with an acid addition salt, preferably the hydrochloride, of a compound of the general formula

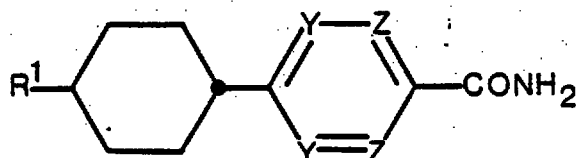


X

10 wherein one of R^7 and R^9 represents trans-4-alkylcyclohexyl and the other represents alkyl, p-alkylphenyl or trans-4-alkylcyclohexyl and R^8 signifies lower alkyl,

in the presence of a base, preferably an alcoholate,

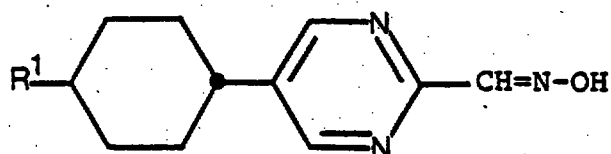
15 (b) for the manufacture of the compounds of formula I in which R^2 signifies cyano, dehydrating a compound of the general formula



XI

wherein R^1 , Y and Z have the significance given earlier,

- (c) for the manufacture of the compounds of formula I in which the symbols Y stand for =CH-, the symbols Z stand for nitrogen and R^2 represents cyano, dehydrating a compound of the general formula



XII

wherein R^1 has the significance given earlier.

The reaction of a compound of formula IX with an acid addition salt of a compound of formula X is conveniently

carried out in water or an organic solvent, for example an alcohol such as methanol, ethanol, ethyleneglycol and the like, in the presence of a base. Methanol and ethanol are preferred solvents. The acid addition salts of the compounds of formula X can be salts of hydrochloric acid, hydrobromic acid, sulphuric acid, p-toluenesulphonic acid and the like. However, the hydrochloride of the compounds of formula X is preferably used. Alkali metal alcoholates, especially sodium methylate and sodium ethylate, are the preferred bases. The lower alkyl group R^8 is conveniently an alkyl group containing 1 to 5 carbon atoms such as methyl, ethyl, propyl, isopropyl and the like, and is preferably methyl and ethyl. The temperature and pressure at which this reaction is carried out are not critical. Conveniently, the reaction is carried out at atmospheric pressure and a temperature between room temperature and the reflux temperature, preferably at room temperature.

The dehydration of a compound of formula XI can be carried out using any suitable dehydrating agent such as, for example, phosphorus oxychloride, phosphorus pentoxide, thionyl chloride, acetic anhydride or, especially, benzenesulphonyl chloride and the like. The dehydration can be carried out in an inert organic solvent such as, for example, a hydrocarbon or halogenated hydrocarbon, if necessary in the presence of a base such as sodium acetate, pyridine or triethylamine. It can, however, also be

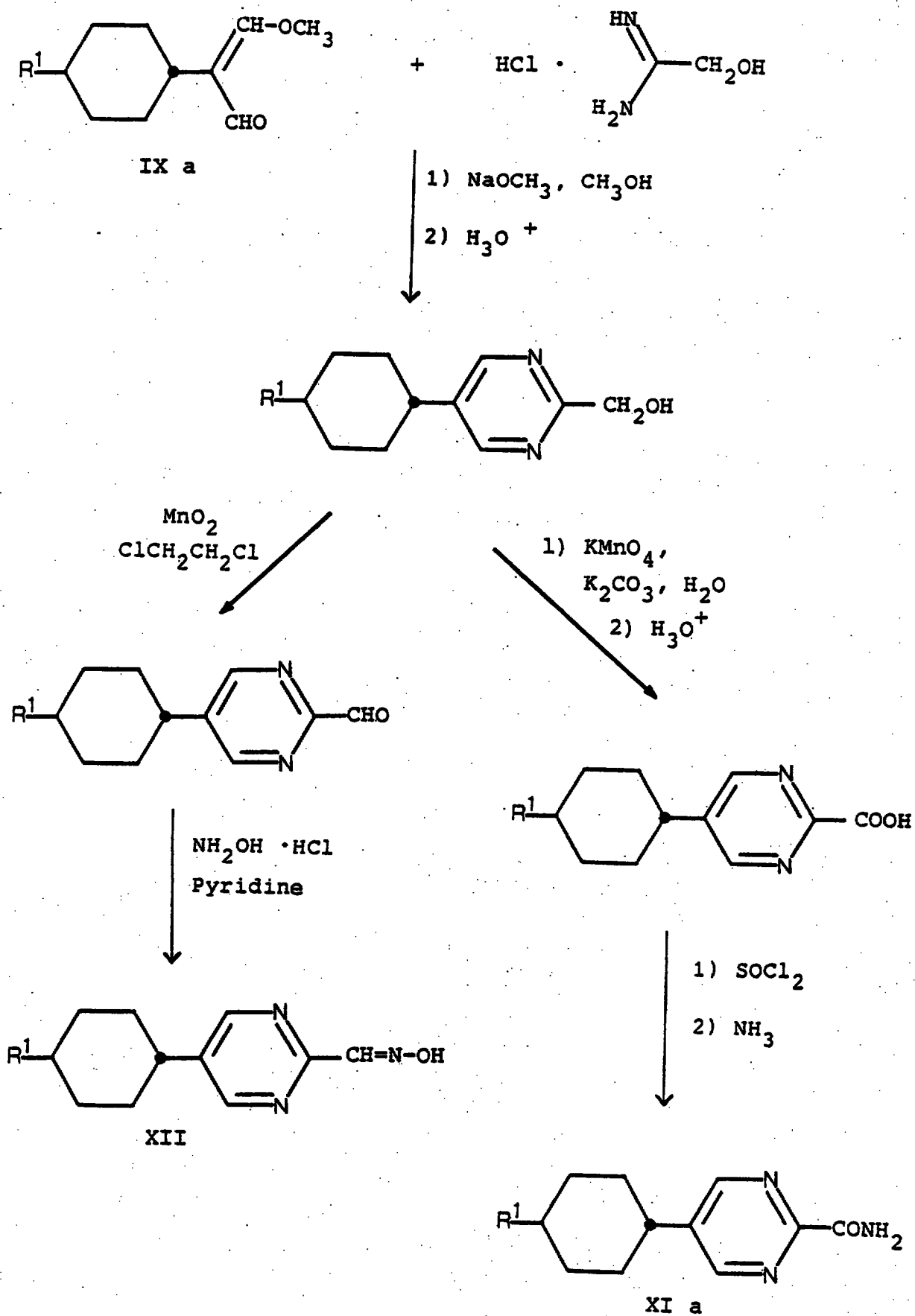
carried out in the absence of an organic solvent. If desired, the base, insofar as it is liquid at the reaction temperature, can also serve as the solvent. The reaction temperature preferably lies between about 50°C and the
5 reflux temperature of the reaction mixture. The pressure is not critical and the reaction is advantageously carried out at atmospheric pressure.

The dehydration of a compound of formula XII can be carried out in an analogous manner to the dehydration of a
10 compound of formula XI using a suitable dehydrating agent and, if desired, using an inert organic solvent and/or a base. The reaction can be carried out, for example, using phosphorus oxychloride, acetic anhydride and anhydrous sodium acetate in glacial acetic acid or, preferably,
15 benzenesulphonyl chloride in pyridine. The reaction is preferably carried out at a temperature between about 50°C and the reflux temperature of the reaction mixture. The pressure is not critical and the reaction is advantageously carried out at atmospheric pressure.

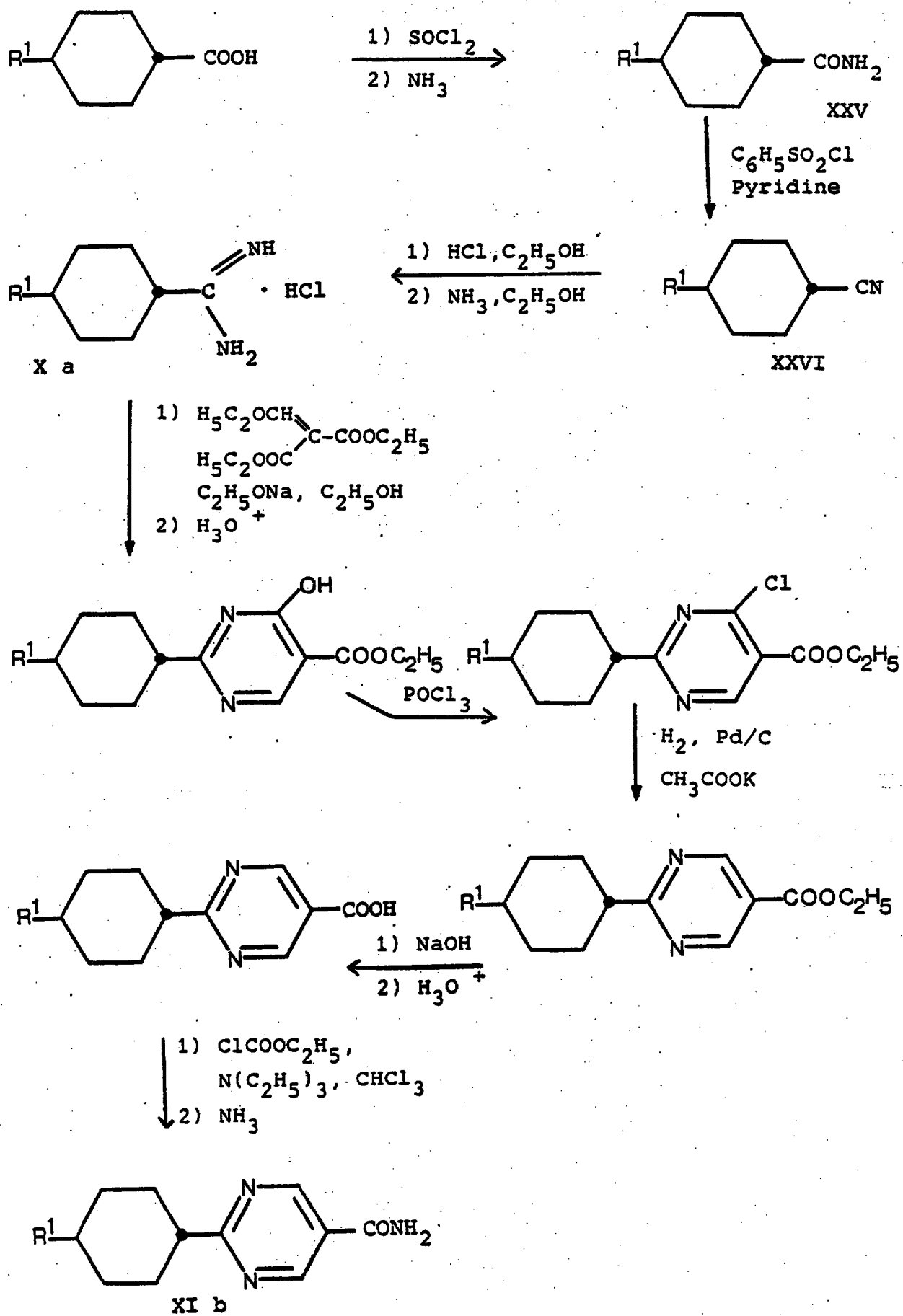
20 The compounds of formula IX and X are known or are analogues of known compounds [Z.Naturforsch. 33 b, 433 (1978) and 34 b, 1535 (1979)].

The preparation of the starting materials of formulae XI and XII is illustrated by the following Reaction Schemes
25 1 and 2 in which R^1 has the significance given earlier.

Scheme 1



Scheme 2

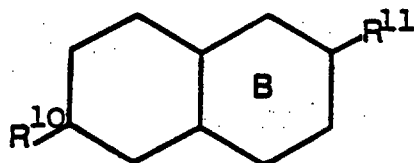


The starting materials used in Schemes 1 and 2 or analogues of these compounds are described, for example, in Z.Naturforsch, 34 b, 1535 (1979) and in Mol. Cryst. Liq. Cryst. 37, 189 (1976) or 42, 215 (1977).

5 The compounds of formula XXVI are novel, ~~and also form an object of the present invention.~~ They can be used, for example, as doping agents in liquid crystal mixtures. They can be prepared by dehydrating a compound of formula XXV in an analogous manner to the dehydration of a compound
10 of formula XI described earlier.

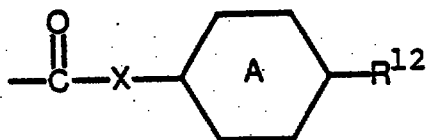
 The compounds of formula I can be used in the form of mixtures with other liquid crystalline or non-liquid crystalline substances such as, for example, with substances from the classes of Schiff's bases, azobenzenes, azoxybenzenes,
15 phenyl benzoates, cyclohexanecarboxylic acid phenyl esters, biphenyls, terphenyls, phenylcyclohexanes, cinnamic acid derivatives, phenylpyrimidines, diphenylpyrimidines, phenyldioxanes, cyclohexylphenylpyrimidines and the like. Such compounds are familiar and known to persons skilled in
20 the art; for example, from German Offenlegungsschriften 2 306 738, 2 306 739, 2 429 093, 2 356 085, 2 636 684, 2 459 374, 2 547 737, 2 641 724, 2 708 276, 2 811 001, from East German Patent Specifications 139 852 and 139 867, and from European Patent Application published under Number
25 0014885. Many of such substances are, moreover, commercially available.

The mixtures in accordance with the invention can contain, in addition, hydrogenated naphthalenes of the general formula



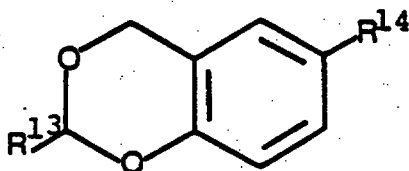
XIII

5 wherein ring B is saturated or aromatic
and a saturated ring B which may be
present is trans-linked with the second
ring; R^{10} denotes a straight-chain
alkyl or alkoxy group containing 1 to 11
10 carbon atoms; R^{11} signifies cyano, a
straight-chain alkyl group containing
1 to 11 carbon atoms, an ester group of
the general formula



XIV

or, when ring B is saturated,
additionally a straight-chain alkoxy
group containing 1 to 11 carbon
atoms; in the ester group of formula
5 XIV ring A is either aromatic and X
represents oxygen or sulphur and R^{12}
represents cyano or a straight-chain
alkyl or alkoxy group containing
1 to 10 carbon atoms, or ring A
10 signifies a trans-1,4-disubstituted
cyclohexane ring and X signifies
oxygen and R^{12} signifies cyano or a
straight-chain alkyl group containing
1 to 10 carbon atoms; and the total
15 number of carbon atoms in the alkyl
and/or alkoxy groups present amounts
to at most 12,
and/or benzodioxanes of the general formula



XV

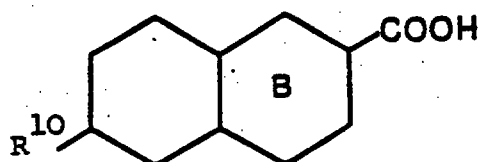
wherein R^{13} denotes a straight-chain alkyl group containing 1 to 11 carbon atoms; R^{14} represents cyano, a straight-chain alkyl group containing 1 to 11 carbon atoms or an ester group of formula XIV hereinbefore in which X, A and R^{12} have the significance given earlier; and the total number of carbon atoms in the alkyl and alkoxy groups present amounts to at most 12.

The compounds of formulae XIII and XV are novel and those in which R^{11} or R^{14} signifies an ester group of formula XIV are to a large extent themselves liquid crystalline. The remaining compounds, i.e. the compounds of formula XIII in which R^{11} signifies cyano, straight-chain alkyl or straight-chain alkoxy and the compounds of formula XV in which R^{14} signifies cyano or straight-chain alkyl, are above all suitable as doping agents in liquid crystal mixtures and in general are not liquid crystalline themselves. In the case of mixtures which contain such doping agents, care must accordingly be taken that they contain in addition at least one compound having liquid crystalline properties in sufficient amount so that the total mixture also has liquid crystalline properties.

32

The compounds of formula XIII can be manufactured by

(a) for the manufacture of the compounds of formula XIII in which R^{11} signifies an ester group of formula XIV, esterifying a compound of the general formula



XVII

5

wherein R^{10} and B have the significance given earlier,

or a reactive derivative thereof, for example the corresponding acid chloride, with a compound of the general

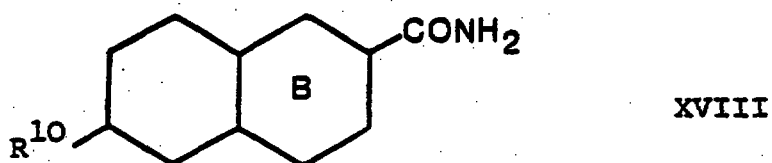
10 formula



XVI

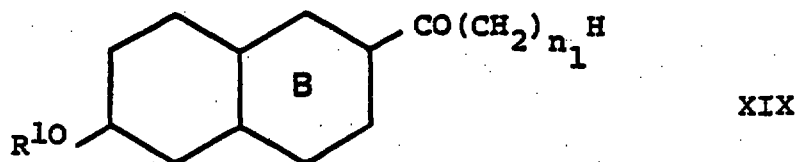
wherein X, A and R^{12} have the significance given earlier,

(b) for the manufacture of the compounds of formula XIII in which R^{11} signifies cyano, dehydrating a compound of the general formula



5 wherein R^{10} and B have the significance given earlier,

(c) for the manufacture of the compounds of formula XIII in which R^{11} signifies a straight-chain alkyl group, reacting a compound of the general formula

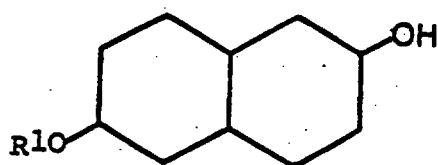


10

wherein n_1 denotes an integer of 0 to 10 and R^{10} and B have the significance given earlier,

with hydrazine in the presence of a base,

(d) for the manufacture of the compounds of formula XIII in which ring B is saturated and R^{11} represents a straight-chain alkoxy group, etherifying a compound of the general
5 formula

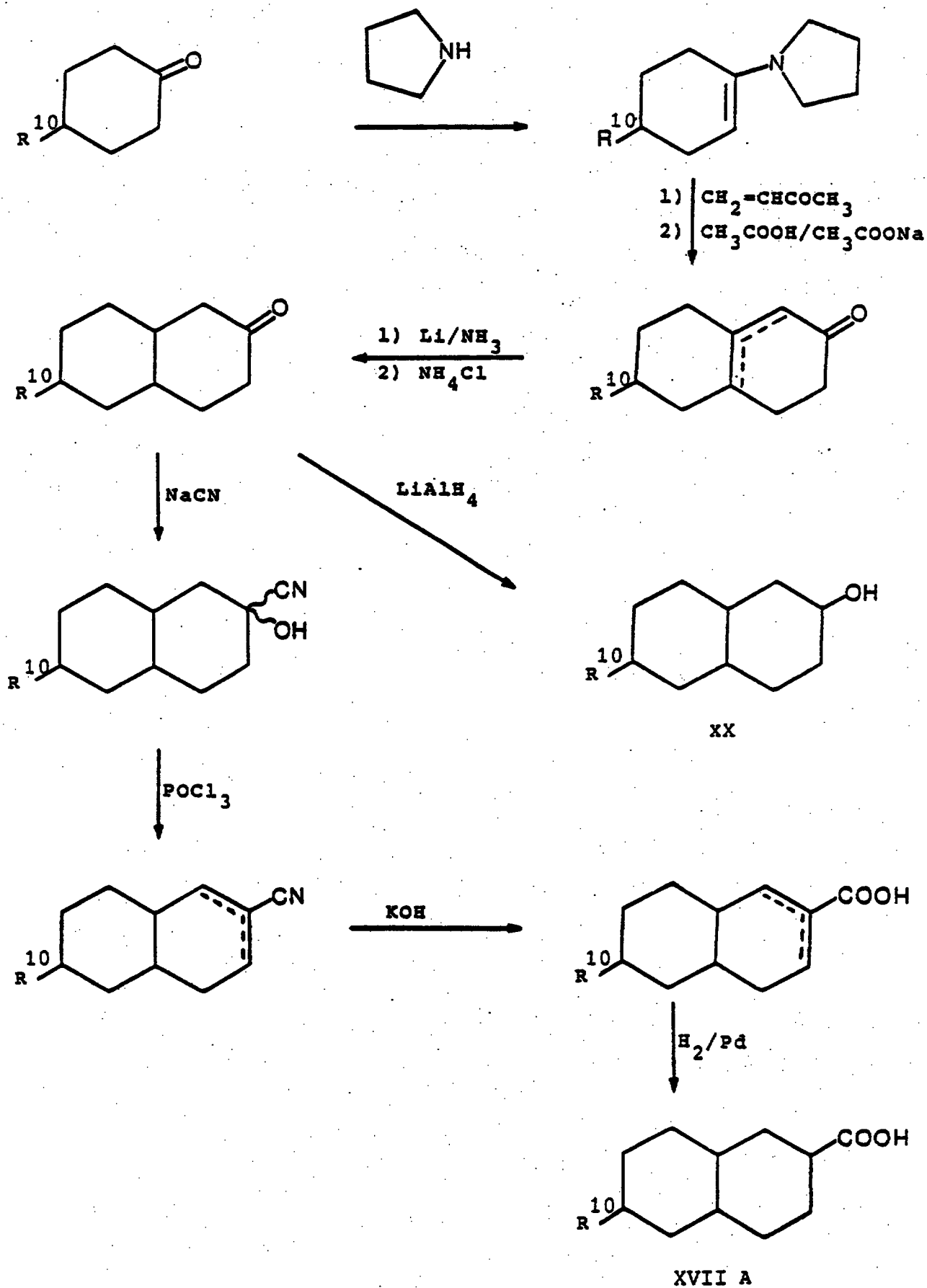


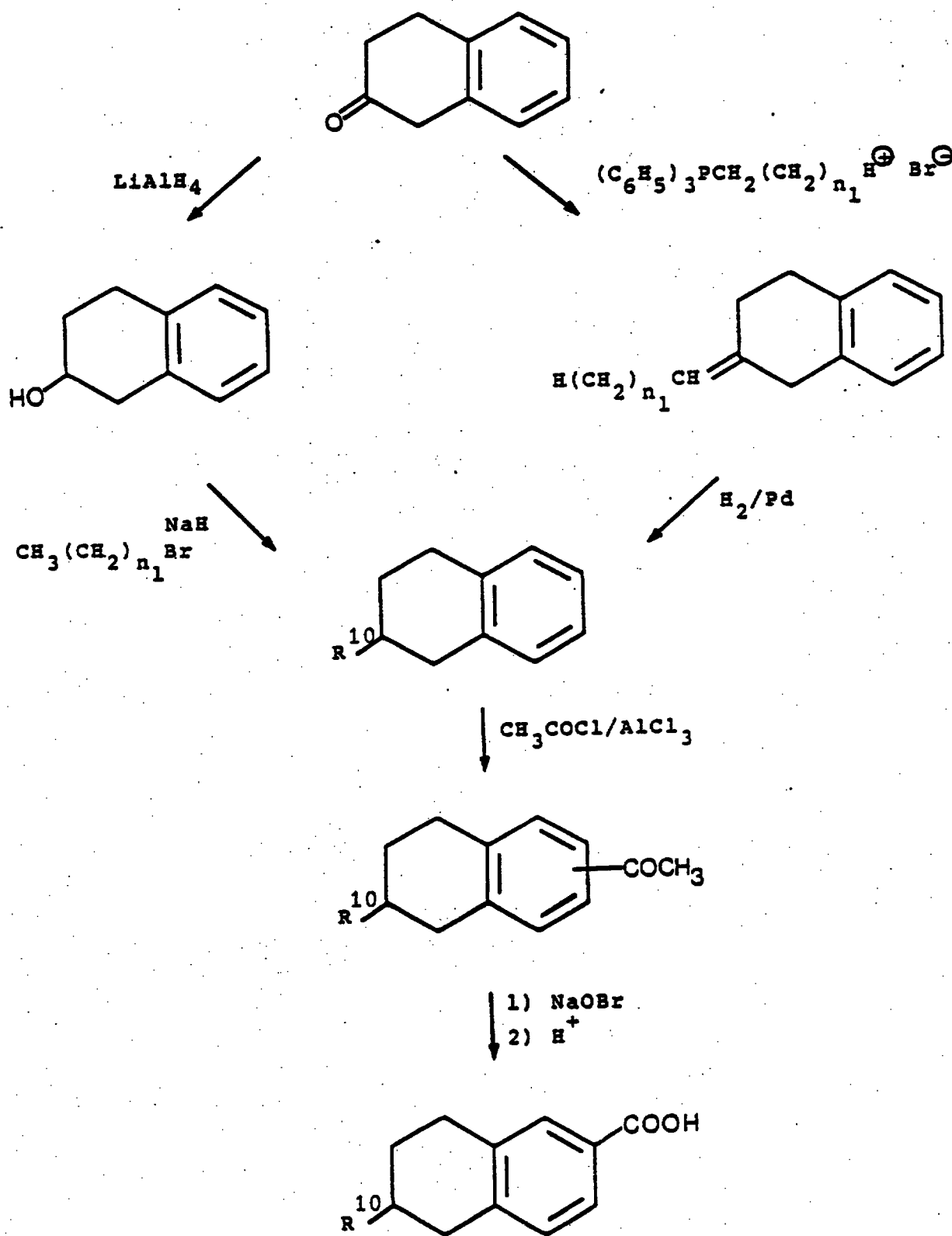
XX

wherein R^{10} has the significance given earlier.

The compounds of formula XVI are known or are analogues
10 of known compounds. The preparation of the compounds of formulae XVII-XX hereinbefore is illustrated by the following Reaction Schemes A-C in which R^{10} , B and n_1 have the significance given earlier, n_2 denotes an integer of 1 to 10, the symbol ($\sim$) indicates that the substituent
15 in question can stand in the α - or β -position (below or above the plane of the formula) and the dotted line (----) indicates that one of the bonds denoted thereby is a double bond.

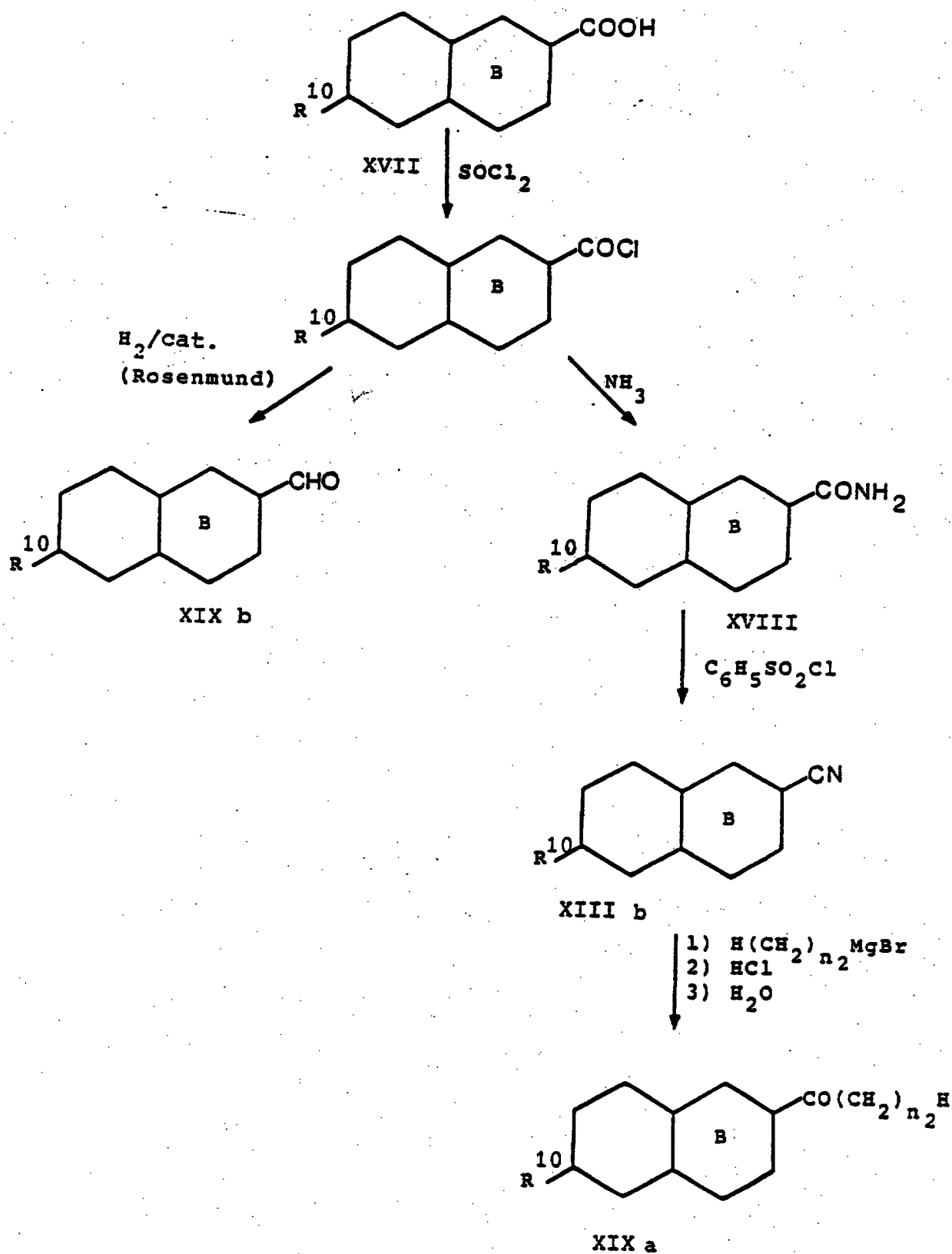
Scheme A



Scheme B

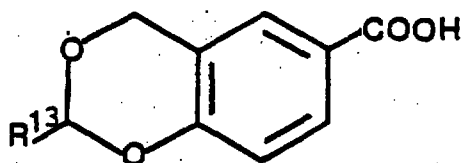
XVII B

Scheme C



The compounds of formula XV can be manufactured by

- (a) for the manufacture of the compounds of formula XV in which R^{14} signifies an ester group of formula XIV, esterifying a compound of the general formula

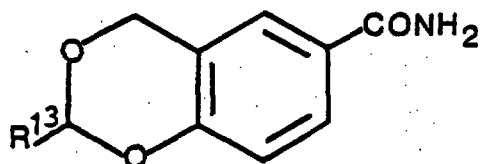


XXI

5

wherein R^{13} has the significance given earlier,
with a compound of formula XVI hereinbefore,

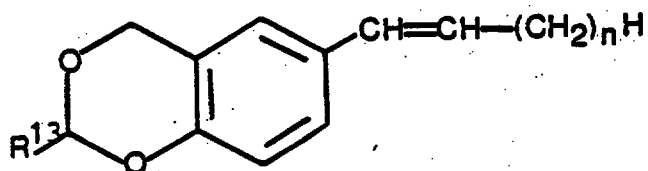
- (b) for the manufacture of the compounds of formula XV
10 in which R^{14} signifies cyano, dehydrating a compound of the general formula



XXII

wherein R^{13} has the significance
given earlier,

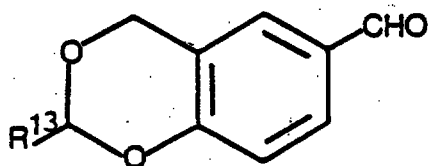
- (c) for the manufacture of the compounds of formula XV
in which R^{14} signifies a straight-chain alkyl group con-
5 taining 2 to 11 carbon atoms, catalytically hydrogenating a
compound of the general formula



XXIII

wherein n denotes an integer of
0 to 9 and R^{13} has the significance
10 given earlier,

- (d) for the manufacture of the compounds of formula XV
in which R^{14} signifies methyl, reacting a compound of the
general formula

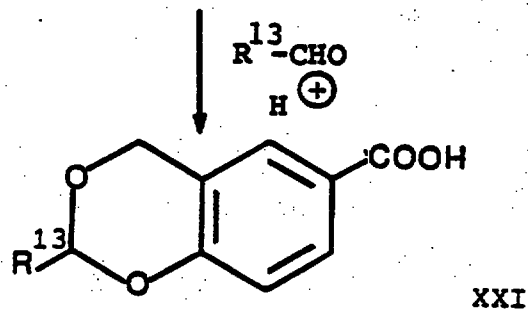
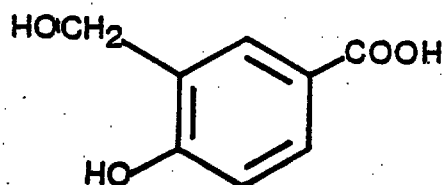


XXIV

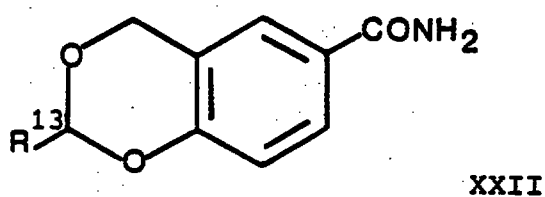
wherein R^{13} has the significance
given earlier,
with hydrazine in the presence of a base.

The compounds of formulae XXI-XXIV used as the starting
5 materials can be prepared according to the following Scheme
D in which R^{13} and n have the significance given earlier.

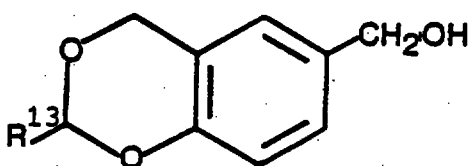
Scheme D



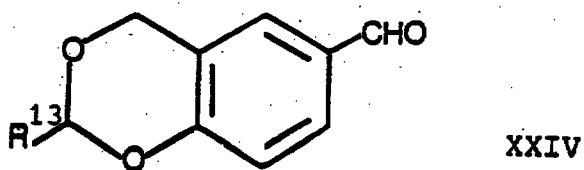
1) $\text{ClCOOC}_2\text{H}_5$,
 $\text{N}(\text{C}_2\text{H}_5)_3$
 2) NH_3



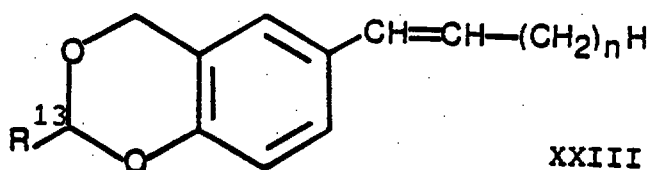
LiAlH_4



MnO_2
 Toluene



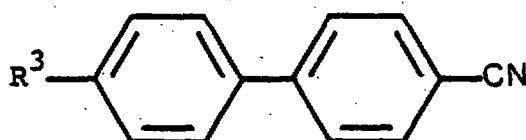
$(\text{C}_6\text{H}_5)_3\text{PCH}_2(\text{CH}_2)_n\text{H}^+ \text{Br}^-$



40

The liquid crystal mixtures in accordance with the invention contain, in addition to one or more compounds of formula I, preferably one or more of the following compounds:

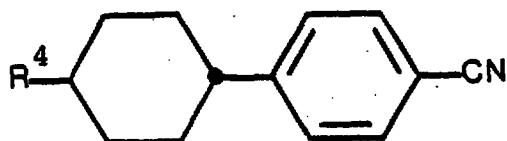
5 4-Cyanobiphenyls of the general formula



II

wherein R^3 signifies a straight-chain alkyl or alkoxy group containing 2 to 7 carbon atoms,

10 trans-p-(4-alkylcyclohexyl)benzonitriles of the general formula

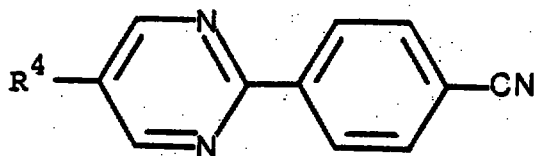


III

wherein R^4 signifies a straight-chain alkyl group containing 3 to 7 carbon atoms,

15

p-(5-alkyl-2-pyrimidinyl)benzonitriles of the general formula

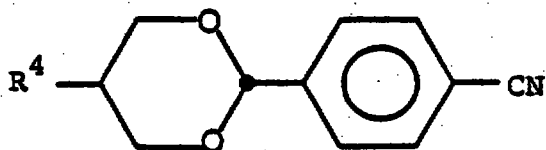


IV

wherein R^4 has the significance
given earlier,

p-(trans-5-alkyl-m-dioxan-2-yl)benzonitriles of the

5 general formula

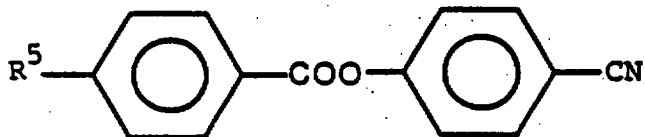


V

wherein R^4 has the significance
given earlier,

p-alkylbenzoic acid p'-cyanophenyl esters of the general

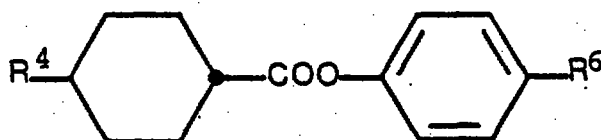
10 formula



VI

wherein R^5 signifies a straight-chain alkyl group containing 2 to 7 carbon atoms,

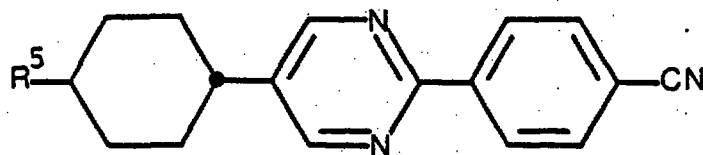
trans-4-alkylcyclohexanecarboxylic acid phenyl esters of the general formula



VII

wherein R^4 has the significance given earlier and R^6 signifies cyano or a straight-chain alkoxy group containing 1 to 3 carbon atoms,

and trans-p-[5-(4-alkylcyclohexyl)-2-pyrimidinyl]benzonitriles of the general formula



VIII

wherein R^5 has the significance given earlier.

The weight ratio of the components of the mixture preferably corresponds to the eutectic composition. In this case it is, however, to be observed that when large amounts of compounds of formula I are used the total mixture can possibly be smectic. The amount of the compounds of formula I in the liquid crystal mixtures in accordance with the invention can, in general, amount to about 1 to about 40 mol percent, preferably about 5 to about 30 mol percent. In mixtures which contain compounds of formula I in which R^2 signifies p-alkylphenyl or trans-4-alkylcyclohexyl the amount of these compounds generally lies, however, between about 1 and about 20 mol percent, preferably between about 3 and about 10 mol percent, of the total mixture.

Further, the mixtures in accordance with the invention can contain optically active compounds, for example optically active biphenyls, and/or dichroic colouring substances, for example azo, azoxy and anthraquinone colouring substances. The amount of such compounds is determined by the desired pitch, colour, extinction, solubility and the like.

The manufacture of mixtures containing, inter alia, compounds of formula I as well as other liquid crystalline and/or non-liquid crystalline compounds can be carried out in a manner known per se; for example, by heating a mixture of the components to a temperature barely above

the clearing point and subsequently cooling down.

The manufacture of an electro-optical device containing one or more compounds of formula I can be carried out in a manner known per se; for example, by
5 evacuating a suitable cell and introducing the corresponding compound or mixture into the evacuated cell.



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The trans-5-(4-pentylcyclohexyl)-2-pyrimidine-carboxaldehyde used as the starting material can be prepared as follows:

- (a) 9.1 g of 2-hydroxyacetamidine hydrochloride are
- 5 suspended under a nitrogen atmosphere in a solution of 17.8 g of 3-methoxy-2-(trans-4-pentylcyclohexyl)acrolein [prepared analogously to the 3-ethoxy compound described in Z. Naturforsch, 34 b, 1535 (1979)] in 150 ml of absolute methanol. Subsequently, a sodium methylate solution,
- 10 freshly prepared from 3.1 g of sodium in 75 ml of absolute methanol, is added dropwise, the mixture is stirred overnight at room temperature and then adjusted to pH 4 by adding about 3 ml of concentrated hydrochloric acid. There-
- 15 after, the precipitate is filtered off, the filtrate is evaporated and the residue is treated with water and ether. The product is present in the organic phase and this is washed with water, dried over sodium sulphate, filtered and evaporated. The crude product obtained is chromat-
- 20 graphed on a column of 425 g of silica gel with toluene/10% acetone. The pure fractions (in accordance with thin-layer chromatography) of trans-5-(4-pentylcyclohexyl)-2-pyrimidinecarbinol are combined and evaporated. Yield: 6.8 g.

(b) A solution of 12.0 g of trans-5-(4-pentylcyclohexyl)-2-pyrimidinecarbinol in 300 ml of ethylene chloride is treated with 21.7 g of activated manganese dioxide. The mixture is heated to boiling until starting material can no longer be observed in the thin-layer chromatogram (about 4 hours) and filtered. After evaporating the filtrate, there are obtained 9.0 g of oily, almost pure (in accordance with thin-layer chromatography) trans-5-(4-pentylcyclohexyl)-2-pyrimidinecarboxaldehyde.

10 The following compounds can be manufactured in an analogous manner:

Trans-5-(4-heptylcyclohexyl)-2-pyrimidinecarbonitrile;
m.p. 81°C,

(+)-trans-5-[4-(2-methylbutyl)cyclohexyl]-2-pyrimidine-
15 carbonitrile; m.p. 47.5°C.

Example 2

20.3 g of benzenesulphonyl chloride are added while stirring to a mixture of 9.45 g of trans-2-(4-propylcyclohexyl)-5-pyrimidinecarboxamide and 55 ml of pyridine. After 2 hours, the solution is poured into a mixture of 100 g of ice and 0.9 ml of half-concentrated hydrochloric acid. The precipitated product is taken up in ether and

the ether extract is washed neutral with water, dried and evaporated. The crude product is purified by chromatography on 200 g of silica gel with hexane/benzene (1:1) and subsequent bulb-tube distillation at 135°C/0.05 mmHg. There is obtained trans-2-(4-propylcyclohexyl)-5-pyrimidinecarbonitrile; m.p. 74°C, cl.p 89.5°C, smectic-nematic phase transition 71.5°C (monotropic).

The trans-2-(4-propylcyclohexyl)-5-pyrimidine-carboxamide used as the starting material can be prepared as follows:

(a) A mixture of 52.1 g of trans-4-propylcyclohexanecarboxylic acid and 200 ml of thionyl chloride is heated to boiling for 2 hours. The excess thionyl chloride is distilled off and the residue is evaporated twice with 100 ml of benzene each time. The oily acid chloride formed is dissolved in 200 ml of methylene chloride and added to 500 ml of methylene chloride into which ammonia is conducted. Ammonia is conducted into the resulting suspension for a further 3 hours and then the mixture is evaporated in vacuo. The residue is treated with water and methylene chloride, the organic phase is separated and the aqueous phase is back-extracted. The organic extracts are dried over sodium sulphate and concentrated. The crude trans-4-propylcyclohexanecarboxamide is recrystallised from

acetone (m.p. 189-191°C). This product can be purified further by sublimation at 150°C/0.1 mmHg; m.p. 195.6-195.9°C.

(b) 22.3 g of trans-4-propylcyclohexanecarboxamide are dissolved partly in 275 ml of pyridine. 27 g of benzenesulphonyl chloride are added dropwise within 15 minutes while stirring. Subsequently, the mixture is warmed at 55°C for 4 hours, then cooled, poured into ice/water and subsequently extracted with ether. The extract is washed several times with 3N hydrochloric acid, then washed neutral with water, dried over sodium sulphate and concentrated. There are obtained 19.6 g of liquid trans-4-propylcyclohexanecarbonitrile; b.p. 125°C/13 mmHg (bulb-tube distillation).

(c) Dry hydrogen chloride is conducted for several hours into a solution, cooled to 0-5°C, of 18.3 g of trans-4-propylcyclohexanecarbonitrile in 150 ml of benzene. The closed vessel is left to stand at room temperature overnight and then the contents are evaporated in vacuo. The resulting foam is treated with 300 ml of absolute ether and this suspension is stirred in a closed vessel for 1.5 hours in an ice-bath. Subsequently, the mixture is suction filtered and the residue is back-washed with a small amount of absolute ether and dried in vacuo. The very hydrolysis-

-sensitive imino ester hydrochloride obtained (28 g) is dissolved in 60 ml of absolute ethanol and treated while stirring with 63.7 g of a solution of ammonia in ethanol (containing 11.3 g of ammonia). The precipitate which results immediately again passes into solution after about 10 minutes. The mixture is left to stand overnight and is then evaporated. The residue is suspended in 170 ml of ether, left to stand at 0°C for 4 hours and then suction filtered and dried. There are obtained 25.7 g of crude trans-4-propylcyclohexanecarboxamide hydrochloride (m.p. 210-211°C). For purification it is recrystallized from ethanol/ether; yield 24.0 g, m.p. 214-215°C.

(d) 23.9 g of trans-4-propylcyclohexanecarboxamide hydrochloride and 25.2 g of diethyl ethoxymethylene-malonate are added to a sodium ethylate solution prepared from 5.4 g of sodium and 210 ml of ethanol and the mixture is diluted with 150 ml of ethanol. The mixture is stirred at room temperature for 50 minutes and at boiling temperature for 50 minutes and, after cooling, evaporated in vacuo. The viscid residue is suspended in 600 ml of water and acidified with 60 ml of glacial acetic acid. Subsequently, the suspension is stirred for 1.5 hours in an ice-bath and suction filtered. The material on the suction filter is washed with water and dried at 50°C in vacuo over potassium hydroxide. There are obtained 33 g of ethyl trans-4-hydroxy-

-2-(4-propylcyclohexyl)-5-pyrimidinecarboxylate; m.p.
156-157°C.

(e) 32.85 g of ethyl trans-4-hydroxy-2-(4-propylcyclohexyl)-5-pyrimidinecarboxylate are boiled under reflux
5 for 3.5 hours with 210 ml of phosphorus oxychloride.
After cooling, the mixture is concentrated in vacuo and
evaporated a further twice with 100 ml of toluene each
time. The residue is chromatographed with methylene
chloride on a column of 300 g of silica gel. There are
10 obtained 31.3 g of crude ethyl trans-4-chloro-2-(4-
-propylcyclohexyl)-5-pyrimidinecarboxylate as a yellow oil.

(f) 31.1 g of ethyl trans-4-chloro-2-(4-propylcyclohexyl)-
-5-pyrimidinecarboxylate are dissolved in 350 ml of ethanol
and, after adding 14.1 g of potassium acetate and 2.56 g of
15 palladium/carbon (5%), the mixture is hydrogenated at
room temperature until 0.10-0.11 mol of hydrogen have been
taken up. The mixture is suction filtered, back-washed
with methylene chloride and evaporated in vacuo. Thereby,
there are obtained 35.6 g of crude, partly crystalline ethyl
20 trans-2-(4-propylcyclohexyl)-5-pyrimidinecarboxylate which
is used in the next step without further purification.

(g) 35.6 g of crude ethyl trans-2-(4-propylcyclohexyl)-5-
-pyrimidinecarboxylate are treated with 62 ml of ethanol

and a solution of 46.6 g of sodium hydroxide in 312 ml of water and heated to boiling for 1 hour. After cooling, the mixture is acidified with 220 ml of half-concentrated hydrochloric acid, left to stand for 1 hour in an ice-bath and then suction filtered. The material on the suction filter is washed with water and dried in vacuo at 50°C over potassium hydroxide. For purification, the crude product is recrystallized from dioxan/water. There is obtained trans-2-(4-propylcyclohexyl)-5-pyrimidinecarboxylic acid; m.p. 184-185.5°C.

(h) A solution of 13.85 g of trans-2-(4-propylcyclohexyl)-5-pyrimidinecarboxylic acid, 260 ml of chloroform and 7.8 ml of triethylamine is cooled to 2°C and treated with 5.32 ml of ethyl chloroformate. The mixture is stirred at 2°C for 15 minutes and then a strong stream of ammonia gas is conducted in for 10 minutes (while cooling with an ice-bath). The resulting suspension is stirred at 20°C for a further 1 hour and then evaporated in vacuo. The solid residue is stirred up with 210 ml of water for 45 minutes and then filtered off under suction and dried. There are obtained 9.6 g of crude trans-2-(4-propylcyclohexyl)-5-pyrimidinecarboxamide (m.p. 234-235°C) which can be purified by sublimation at 175°C/0.05 mmHg; m.p. 249.3-250.5°C.

The following compounds can be manufactured in an analogous manner:

- Trans-2-(4-methylcyclohexyl)-5-pyrimidinecarbonitrile;
m.p. 86°C,
5 trans-2-(4-ethylcyclohexyl)-5-pyrimidinecarbonitrile;
m.p. 82°C,
trans-2-(4-butylcyclohexyl)-5-pyrimidinecarbonitrile;
m.p. 60°C, smectic-nematic phase transition 85°C, cl.p. 91°C,
trans-2-(4-pentylcyclohexyl)-5-pyrimidinecarbonitrile;
10 m.p. 70°C, smectic-nematic phase transition 94°C, cl.p. 98°C,
trans-4-methylcyclohexanecarbonitrile; b.p. 85-90°C/
12 mmHg,
trans-4-ethylcyclohexanecarbonitrile; b.p. 105-110°C/
13 mmHg,
15 trans-4-butylcyclohexanecarbonitrile; b.p. 80°C/0.02
mmHg.

Example 3

6.8 g of caproic acid amidine hydrochloride are
suspended in a solution of 7.4 g of 3-methoxy-2-(trans-4-
20 -propylcyclohexyl)acrolein in 50 ml of absolute methanol.
Subsequently, a sodium methylate solution, freshly prepared
from 1.2 g of sodium in 40 ml of absolute methanol, is
added dropwise thereto. The mixture is stirred at room

temperature for a further 20 hours and then adjusted to pH 5 by adding about 2 ml of concentrated hydrochloric acid. The mixture is evaporated in vacuo and the residue is treated with water and extracted with ether. The extract is washed neutral with water, dried over sodium sulphate, filtered and evaporated. The crude product is chromatographed on a column of 250 g of silica gel with hexane/20% ether. The pure fractions (in accordance with thin-layer chromatography) are combined and recrystallized from 50 ml of acetonitrile at about -20°C. There is obtained analytically pure trans-5-(4-propylcyclohexyl)-2-pentylpyrimidine; m.p. 33°C, cl.p. 48°C (smectic).

The following compounds can be manufactured in an analogous manner:

- 15 Trans-5-(4-ethylcyclohexyl)-2-pentylpyrimidine;
m.p. 24°C, cl.p. 16.5°C (monotropic smectic),
trans-5-(4-propylcyclohexyl)-2-propylpyrimidine;
m.p. 28°C, cl.p. 20°C (monotropic smectic),
trans-5-(4-propylcyclohexyl)-2-butylpyrimidine;
20 m.p. 29.5°C, cl.p. 31.5°C (smectic),
trans-5-(4-pentylcyclohexyl)-2-propylpyrimidine;
m.p. 34°C, cl.p. 29.5°C (monotropic smectic),
trans-5-(4-pentylcyclohexyl)-2-butylpyrimidine;
m.p. 19°C, cl.p. 40.5°C (smectic),

trans-5-(4-pentylcyclohexyl)-2-pentylpyrimidine;
m.p. 33.5°C, cl.p. 60°C (smectic),

trans-5-(4-heptylcyclohexyl)-2-propylpyrimidine;
m.p. 29.5°C, cl.p. 30°C (smectic), monotropic nematic-
5 -isotropic phase transition 29.2°C,

trans-5-(4-heptylcyclohexyl)-2-butylpyrimidine;
m.p. 32.5°C, cl.p. 40.5°C (smectic),

trans-5-(4-heptylcyclohexyl)-2-pentylpyrimidine;
m.p. 34°C, cl.p. 60°C (smectic).

10

Example 4

In an analogous manner to that described in Example 3,
a mixture of 3.8 g of 3-ethoxy-2-heptylacrolein, 4.7 g of
trans-4-pentylcyclohexanecarboxamide hydrochloride and
40 ml of absolute methanol is treated with a sodium
15 methyrate solution prepared from 0.8 g of sodium in 25 ml
of absolute methanol. The reaction duration, working-up
and chromatography are as in Example 3. The pure fractions
eluted in the chromatography are combined and recrystallised
twice from acetonitrile at about -20°C. There is obtained
20 analytically pure trans-2-(4-pentylcyclohexyl)-5-heptyl-
pyrimidine; m.p. 22°C, cl.p. 40.5°C (smectic).

The following compounds can be manufactured in an
analogous manner:

- Trans-2-(4-propylcyclohexyl)-5-propylpyrimidine;
m.p. 25°C,
trans-2-(4-propylcyclohexyl)-5-butylpyrimidine;
m.p. 9°C,
5 trans-2-(4-pentylcyclohexyl)-5-propylpyrimidine;
m.p. 26°C,
trans-2-(4-pentylcyclohexyl)-5-butylpyrimidine;
m.p. 3.5°C, cl.p. -7°C (monotropic nematic),
trans-2-(4-pentylcyclohexyl)-5-pentylpyrimidine;
10 m.p. 17°C, cl.p. 10°C (monotropic nematic),
trans-2-(4-heptylcyclohexyl)-5-heptylpyrimidine;
m.p. 19°C, cl.p. 45°C (smectic).

Example 5

- In an analogous manner to that described in Example 3,
15 a mixture of 3.0 g of 3-methoxy-2-(trans-4-propylcyclohexyl)-
acrolein, 3.75 g of p-pentylbenzoic acid amidine hydro-
chloride and 50 ml of absolute methanol is treated with a
sodium methylate solution prepared from 0.5 g of sodium in
20 ml of absolute methanol. The reaction duration, working-
20 -up and chromatography are as in Example 3. The pure
fractions resulting in the chromatography are combined and
recrystallised from hexane. There is obtained analytically
pure trans-5-(4-propylcyclohexyl)-2-(p-pentylphenyl)-
pyrimidine; m.p. 93.5°C, smectic-nematic phase transition
25 178-179°C, cl.p. 190°C.

The following compounds can be manufactured in an analogous manner:

Trans-5-(4-ethylcyclohexyl)-2-(p-propylphenyl)-pyrimidine; m.p. 125.5°C, smectic-nematic phase

5 transition 128.5°C, cl.p. 167°C,

trans-5-(4-ethylcyclohexyl)-2-(p-butylphenyl)-pyrimidine; m.p. 108.5°C, smectic-nematic phase transition 140°C, cl.p. 163.5°C,

10 trans-5-(4-ethylcyclohexyl)-2-(p-pentylphenyl)-pyrimidine; m.p. 101°C, smectic-nematic phase transition 139°C, cl.p. 167°C,

trans-5-(4-ethylcyclohexyl)-2-(p-heptylphenyl)-pyrimidine; m.p. 80°C, smectic-nematic phase transition 138.5°C, cl.p. 157°C,

15 trans-5-(4-propylcyclohexyl)-2-(p-propylphenyl)-pyrimidine; m.p. 116.5°C, smectic-nematic phase transition 175°C, cl.p. 194.5°C,

trans-5-(4-pentylcyclohexyl)-2-(p-propylphenyl)-pyrimidine; m.p. 51°C, cl.p. 190°C (smectic),

20 trans-5-(4-pentylcyclohexyl)-2-(p-butylphenyl)-pyrimidine; m.p. 37.5°C, cl.p. 187°C (smectic),

trans-5-(4-heptylcyclohexyl)-2-(p-ethylphenyl)-pyrimidine; m.p. 68°C, smectic-nematic phase transition 179°C, cl.p. 182°C,

25 trans-5-(4-heptylcyclohexyl)-2-(p-pentylphenyl)-pyrimidine; m.p. 122.5°C, cl.p. 186.5°C (smectic).

Example 6

In an analogous manner to that described in Example 3, a mixture of 6.3 g of 3-ethoxy-2-(p-butylphenyl)acrolein, 6.6 g of trans-4-pentylcyclohexanecarboxamide hydrochloride and 60 ml of absolute methanol is treated with a sodium methylate solution prepared from 1.1 g of sodium in 25 ml of absolute methanol. The reaction duration, working-up and chromatography are as in Example 3. The pure fractions (in accordance with thin-layer chromatography) resulting in the chromatography are combined and recrystallized twice from hexane. There is obtained analytically pure trans-2-(4-pentylcyclohexyl)-5-(p-butylphenyl)pyrimidine; m.p. 87°C, smectic-nematic phase transition 136.5°C, cl.p. 146.5°C.

The following compound can be manufactured in an analogous manner:

Trans-2-(4-propylcyclohexyl)-5-(p-butylphenyl)-pyrimidine; m.p. 98°C, smectic-nematic phase transition 130°C, cl.p. 145°C.

Example 7

In an analogous manner to that described in Example 3, a mixture of 3.2 g of 3-methoxy-2-(trans-4-propylcyclohexyl)-

acrolein, 4.1 g of trans-4-pentylcyclohexanecarboxamidine hydrochloride and 50 ml of absolute methanol is treated with a sodium methylate solution prepared from 0.53 g of sodium in 20 ml of absolute methanol. The reaction
5 duration, working-up and chromatography are as in Example 3. The pure fractions (in accordance with thin-layer chromatography) resulting in the chromatography are combined and recrystallized twice from hexane. There is
10 obtained pure 5-(trans-4-propylcyclohexyl)-2-(trans-4-pentylcyclohexyl)pyrimidine; m.p. 98°C, cl.p. 178°C (smectic).

The following compound can be manufactured in an analogous manner:

5-(Trans-4-heptylcyclohexyl)-2-(trans-4-pentyl-
15 cyclohexyl)pyrimidine; m.p. 193°C, cl.p. 190°C (monotropic smectic).

Example 8

6.16 g (25 mmol) of 2-pentyl-1,2,3,4-tetrahydro-
naphthalene-6-carboxylic acid are boiled at reflux with
20 62.5 ml of thionyl chloride while excluding moisture for 2 hours. After removing the excess thionyl chloride, the acid chloride is obtained as a yellowish oil.

The acid chloride, diluted with 10 ml of absolute benzene, is added dropwise while stirring at 3-7°C to a solution, cooled to 3°C, of 2.99 g (25 mmol) of p-cyanophenyl in 15 ml of absolute pyridine, the mixture is
5 left to stand overnight, then poured into a mixture of 30 g of ice and 30 ml of hydrochloric acid (1:1), exhaustively extracted with ether and the organic phases are washed once with 35 ml of ice-cold 1N sodium hydroxide and water. After drying with sodium sulphate and removing
10 the solvent in vacuo, there is obtained a crystalline residue (8.6 g) of p-cyanophenyl 2-pentyl-1,2,3,4-tetrahydro-6-naphthoate which, for purification, is chromatographed on 230 g of silica gel. Elution with benzene/hexane (1:1) and benzene yields 8.1 g of substance which is
15 recrystallized from acetone/hexane up to constant melting point and clearing point and dried up to constant weight in a high vacuum (0.01 mbar). There are obtained colourless crystals of p-cyanophenyl 2-pentyl-1,2,3,4-tetrahydro-6-naphthoate; m.p. 72.7-73.3°C; cl.p. 127.7°C.

20 The 2-pentyl-1,2,3,4-tetrahydro-naphthalene-6-carboxylic acid used as the starting material can be prepared as follows:

(a) 51.6 g (0.456 mol) of potassium tert-butyrate are added to a suspension of 178 g (0.431 mol) of n-pentyl-triphenylphosphonium bromide in 1560 ml of absolute toluene, the mixture is stirred at room temperature for 5 45 minutes, a solution of 41.9 g (0.287 mol) of 2-tetralone in 300 ml of absolute toluene is added drop-wise thereto within 50 minutes and the mixture is heated at 75-80°C for 3 hours. The mixture is left to cool down and poured into 1500 ml of ice/water. The organic phase 10 is separated, the aqueous phase is extracted twice more with toluene and the combined toluene phases are washed with water. After drying over sodium sulphate and removing the solvent in vacuo, there are obtained 175 g of a brownish suspension which, for purification, is filtered through a 15 column of 450 g of silica gel. Elution with hexane and benzene/hexane (1:1) yields 53.2 g of 2-pentylidene-1,2,3,4-tetrahydronaphthalene as a yellowish oil.

(b) A mixture of 53.2 g (0.268 mol) of 2-pentylidene-1,2,3,4-tetrahydronaphthalene, 275 ml of rectified alcohol, 20 1.4 ml of triethylamine and 1.44 g of palladium/carbon (5%) is shaken at room temperature in a hydrogen atmosphere until the hydrogenation is complete (24 hours). Subsequently, the catalyst is filtered off and the solvent is removed in vacuo. The 49.4 g of 2-pentyl-1,2,3,4-tetra- 25 hydronaphthalene remaining as the residue are purified by

distillation in a high vacuum; 47.3 g of a colourless liquid; b.p. 106-110°C (0.5 mbar).

(c) 37.6 g (0.282 mol) of anhydrous aluminium chloride are added portionwise while stirring at room temperature within 1 hour to a mixture of 47.3 g (0.234 mol) of 2-pentyl-1,2,3,4-tetrahydronaphthalene, 22.1 g (0.281 mol) of acetyl chloride and 380 ml of absolute dichloromethane, the yellow-brown mixture is boiled under reflux for 3 hours, left to stand overnight and then poured into a mixture of 500 ml of ice/water and 165 ml of concentrated hydrochloric acid. The organic layer is separated, the aqueous phase is extracted twice more with dichloromethane, the organic phases are washed with 230 ml of 3N sodium hydroxide and with water, dried over sodium sulphate and the solvent is removed in vacuo. There are obtained 57.8 g of a mixture of 2-pentyl-6-acetyl-1,2,3,4-tetrahydronaphthalene and 2-pentyl-7-acetyl-1,2,3,4-tetrahydronaphthalene as a brownish liquid which is reacted directly.

(d) A solution of 54.6 g (0.223 mol) of the mixture of 2-pentyl-6-acetyl-1,2,3,4-tetrahydronaphthalene and 2-pentyl-7-acetyl-1,2,3,4-tetrahydronaphthalene in 450 ml of dioxan is warmed to 60°C and allowed to flow while stirring within 30 minutes into a solution of sodium hypobromite (prepared from 261 ml of 28% sodium hydroxide, 202 g of

ice and 112 ml of water by the dropwise addition of 51.5 ml of bromine at 0°C within 35 minutes). The brownish mixture is subsequently warmed to 30°C, an exothermic reaction occurring with decolourization. The mixture is left to react for a further 1 hour, the excess hypobromite is reduced by adding sodium hydrogen sulphite solution, 102 ml of concentrated hydrochloric acid are added thereto and the mixture is extracted with dichloromethane. After washing with water, drying with sodium sulphate and evaporating the solvent in vacuo, there are obtained 57.9 g of a crude mixture of 2-pentyl-1,2,3,4-tetrahydronaphthalene-6-carboxylic acid and 2-pentyl-1,2,3,4-tetrahydronaphthalene-7-carboxylic acid as a yellowish crystalline residue. The mixture of the two acids can be separated by repeated recrystallization from hexane, ethanol, isopropanol and the like. More successful, however, is the separation of the corresponding amides (prepared in accordance with Example 10) by recrystallization from suitable solvents (e.g. acetone) and subsequent hydrolysis (e.g. with potassium hydroxide in diethyleneglycol). 2-Pentyl-1,2,3,4-tetrahydronaphthalene-6-carboxamide melts at 166.4-167.8°C and 2-pentyl-1,2,3,4-tetrahydronaphthalene-7-carboxamide melts at 122.9-123.5°C. The liquid crystalline 2-pentyl-1,2,3,4-tetrahydronaphthalene-6-carboxylic acid has a melting point of 122.9-123.1°C and a clearing point of 174.9-177.6°C; the 2-pentyl-1,2,3,4-tetrahydronaphthalene-7-carboxylic acid melts at 103.6-105.5°C and is not liquid crystalline.

64

Example 9

1.893 g (7.50 mmol) of 6-pentyl-trans-decalin-2-carboxylic acid are boiled at reflux for 2 hours with 15 ml of thionyl chloride while excluding moisture.
5 After removing the excess thionyl chloride in vacuo, the acid chloride is obtained as a brownish liquid.

The acid chloride, diluted with 10 ml of absolute benzene, is added dropwise while stirring at 3-7°C to a solution, cooled to 3°C, of 0.893 g (7.497 mmol) of
10 p-cyanophenol in 7.5 ml of absolute pyridine, the mixture is warmed at 50-55°C for 3.5 hours and left to stand at room temperature overnight. The mixture is then poured into a mixture of 15 g of ice and 15 ml of hydrochloric acid (1:1), exhaustively extracted with ether and the
15 organic phases are washed once with 11.5 ml of ice-cold 1N sodium hydroxide and with water. The crystalline residue (2.6 g) of 6-pentyl-trans-decalin-2-carboxylic acid p-cyanophenyl ester obtained after drying with sodium sulphate and removing the solvent in vacuo is, for
20 purification, chromatographed on 90 g of silica gel. Elution with hexane/toluene and toluene yields 2.5 g of substance which is recrystallized from hexane up to constant melting point and clearing point and dried up to constant weight in a high vacuum (0.01 mbar). There
25 are obtained colourless crystals of the 6-pentyl-trans-

-decalin-2-carboxylic acid p-cyanophenyl ester; m.p. 79.9°C, cl.p. 148.0°C.

The 6-pentyl-trans-decalin-2-carboxylic acid used as the starting material can be prepared as follows:

- 5 (a) A mixture of 84.1 g (0.5 mol) of 4-pentylcyclohexanone, 51.3 g (0.72 mol) of pyrrolidine, 120 ml of toluene and 0.62 g of p-toluenesulphonic acid is heated to boiling for 2 hours while connecting a water-separator and the pyrrolidine-containing water which separates is
- 10 separated off. The residue containing the 4-pentyl-1-pyrrolidinyl-1-cyclohexene is firstly freed from excess toluene in vacuo and subsequently distilled in a high vacuum; b.p. 107-113°C (0.16 mbar), yellowish liquid.
- 15 (b) While stirring and gassing with nitrogen there are added dropwise to a mixture of 98.4 g (0.444 mol) of 4-pentyl-1-pyrrolidinyl-1-cyclohexene and 315 ml of absolute toluene within 1 hour 35.9 g (0.512 mol) of methyl vinyl ketone (temperature increase to 42°C). The
- 20 mixture is left to stand overnight and then boiled under reflux for 3 hours. There is added to the boiling mixture a solution of 19.6 g (0.238 mol) of anhydrous sodium acetate and 39.1 ml of glacial acetic acid in 39.1 ml of water and the mixture is boiled under reflux for a further

8 hours. After cooling, the toluene layer is separated, the aqueous phases are extracted twice more with toluene and the organic phases are washed in sequence with water, 1N hydrochloric acid, water, saturated sodium hydrogen carbonate solution and water and then dried over sodium sulphate. After removing the solvent in vacuo, there is obtained a mixture of 6-pentyl-octahydro- $\Delta^{1,9}$ -naphthalen-2-one and 6-pentyl-octahydro- $\Delta^{9,10}$ -naphthalen-2-one as a brown liquid (106 g). For purification, the mixture is distilled in a high vacuum. Yield: 69.4 g of yellowish liquid; b.p. 127-132°C (0.22 mbar).

(c) A solution of 71.2 g (0.323 mol) of the aforementioned mixture of 6-pentyl-octahydro- $\Delta^{1,9}$ -naphthalen-2-one and 6-pentyl-octahydro- $\Delta^{9,10}$ -naphthalen-2-one in 450 ml of absolute ether is added dropwise while stirring to a solution of 17.2 g (2.479 g atoms) of lithium wire in 2 litres of liquid ammonia (dry-ice condenser), the mixture is left to react for a further 1 hour, diluted with 1 litre of absolute ether and there are added portionwise thereto 113 g (2.112 mol) of ammonium chloride until decolourization occurs. The ammonia is allowed to evaporate at room temperature overnight, the mixture is cooled with ice and made Congo-acid with concentrated hydrochloric acid. After adding water and an additional amount of ether, the ether layer is separated, the aqueous phase is extracted twice more with ether, the organic phases are washed with water and

dried over sodium sulphate. After removing the solvent in vacuo, there are obtained 69.4 g of a mixture of predominantly 6-pentyl-trans-decalin-2-one and 6-pentyl-cis-decalin-2-one as a brown liquid which is used in the crude state.

(d) A solution of 23.6 g (0.482 mol) of sodium cyanide in 54 ml of water is added while gassing with nitrogen to 69.4 g (0.312 mol) of the mixture of 6-pentyl-trans-decalin-2-one and 6-pentyl-cis-decalin-2-one dissolved in 350 ml of ether. The mixture is cooled to 0°C and there are added dropwise thereto while stirring within 2 hours 69.9 ml of 25% hydrochloric acid.

Subsequently, the mixture is stirred at room temperature for a further 1 hour, the organic phase is separated, the aqueous phase is extracted twice more with ether, the combined organic phases are washed with water and dried with sodium sulphate. The cyanohydrin mixture (75.6 g of a brown oil) obtained after removing the solvent in vacuo is used in the crude state.

(e) 75.6 g (0.303 mol) of the aforementioned crude cyanohydrin mixture are dissolved while stirring in 81 ml of absolute pyridine and 67 ml of absolute benzene, cooled to -2°C, treated dropwise within 20 minutes with a mixture of 42.0 ml (0.460 mol) of phosphorus oxychloride and 53.4 ml of absolute pyridine and subsequently boiled under reflux.

6.8

for 4 hours. The precipitate originally formed dissolves upon warming, but again forms upon cooling overnight. The mixture is poured on to 375 g of ice, diluted with ether, the ether layer is separated and the aqueous phase
5 is extracted twice more with ether. The ether phases are washed with water, dried over sodium sulphate and freed from solvent in vacuo. There are obtained 72.5 g of a dark brown oil which consists predominantly of 6-pentyl-trans-octahydro- Δ^1 -naphthalene-2-carbonitrile and 6-pentyl- Δ^2 -
10 -naphthalene-2-carbonitrile as well as, in addition, the corresponding 9,10-cis compounds. The mixture is used in the crude state.

(f) The foregoing nitrile mixture (72.5 g, 0.313 mol) is heated at 200°C (bath temperature) for 6.5 hours while
15 gassing with nitrogen with a hot solution of 35.1 g (0.625 mol) of potassium hydroxide in 355 ml of diethyleneglycol. After this time, the ammonia evolution is almost complete. The mixture is left to cool, the alkaline solution, diluted with 500 ml of water, is extracted three times with ether
20 and the organic phases are back-washed twice with water. The 17.2 g of dark brown oil obtained after drying with sodium sulphate and evaporating the ether are discarded. The aqueous phases (including water washings) are made Congo-acid with 3N sulphuric acid, a precipitate of a
25 turbidity occurring. The mixture is exhaustively extracted with ether and the organic phases are washed with water and dried with sodium sulphate. After evaporating in vacuo,

there are obtained 57.6 g of a brown, solid residue which consists predominantly of 6-pentyl-trans-octahydro- Δ^1 -naphthalene-2-carboxylic acid and 6-pentyl-trans-octahydro- Δ^2 -naphthalene-2-carboxylic acid as well as, in addition, the corresponding 9,10-cis compounds. For purification, this residue is dissolved in warm toluene and filtered through a column of 300 g of silica gel. Elution with toluene and toluene containing 1% or 2% acetone yields a total of 45.9 g of brownish, crystalline substance which is used directly.

(g) The aforementioned mixture of unsaturated acids (45.9 g) is dissolved while warming in 700 ml of rectified alcohol, cooled to room temperature and, after treatment with 4.3 g of palladium/carbon (5% palladium), shaken in a hydrogen atmosphere until the hydrogenation comes to a standstill (24 hours). Subsequently, the catalyst is filtered off and the solvent is evaporated in vacuo. There are obtained 45.9 g of a yellowish crystalline residue which consists predominantly of 6-pentyl-trans-decalin-2-carboxylic acid and, in addition, still contains the cis isomer. For purification the residue is recrystallized several times from ether/hexane or hexane, the purification being followed by gas chromatography, melting point and clearing point. After sublimation in a high vacuum (0.01 mbar), there are obtained 13.7 g of pure liquid crystalline 6-pentyl-trans-decalin-2-carboxylic acid as colourless

crystals; m.p. 113.5-114.3°C, cl.p. 165.8-167.1°C.

Example 10

8.95 g (35.60 mmol) of 6-pentyl-trans-decalin-2-
-carboxamide are suspended in 94 ml of absolute pyridine
5 and treated while stirring with 12.94 g (73.29 mmol) of
benzenesulphonyl chloride. The solution, which becomes
clear, is left to stand at room temperature overnight,
then poured into a mixture of 190 g of ice and 180 ml of
hydrochloric acid (1:1) and exhaustively extracted with
10 ether. The ether solutions are washed neutral with water,
dried over sodium sulphate and the solvent is evaporated off
in vacuo. There are obtained 11.0 g of crude 6-pentyl-
-trans-decalin-2-carbonitrile as a yellowish oil which
crystallizes later and which, for purification, is
15 chromatographed on 200 g of silica gel. Elution with
hexane/toluene mixtures containing 30%, 40% and 50% toluene
yields 8.1 g of substance which is recrystallized from
hexane up to constant melting point and subsequently
distilled in a high vacuum; b.p. 115-120°C (0.02 mbar).
20 There is obtained 6-pentyl-trans-decalin-2-carbonitrile as
colourless crystals; m.p. 41.9°C.

The 6-pentyl-trans-decalin-2-carboxyamide used
as the starting material can be prepared as follows:

31.0 g (0.123 mol) of the mother liquors acid obtained in Example 9, which still contains the cis isomer in addition to 6-pentyl-trans-decalin-2-carboxylic acid, are converted into the acid chloride with 133 ml of thionyl chloride analogously to Example 9. After removing the excess thionyl chloride, it is diluted with 100 ml of absolute dichloromethane and this solution is added dropwise while stirring and cooling to a solution of 465 ml of absolute dichloromethane which is saturated with ammonia gas. Ammonia gas is introduced for a further 2.5 hours, the mixture is evaporated to dryness in vacuo, treated with 530 ml of water and 500 ml of ether and stirred at room temperature for 30 minutes. The precipitate is filtered off under suction, washed with water and ether and dried. There are obtained 8.9 g of 6-pentyl-trans-decalin-2-carboxamide which, for purification, is recrystallized from dioxan and sublimed in a high vacuum (0.01 mbar); colourless crystals, m.p. 211.6-212.7°C. From the ether solutions there are obtained by repeated recrystallization (control by gas chromatography) a further 1.1 g of the trans amide and by recrystallization of the mother liquors from ether the 6-pentyl-cis-decalin-2-carboxamide as colourless crystals (m.p. 126.7-128.0°C).

Example 11

A mixture of 3.478 g (11.89 mmol) of 6-pentyl-2-valeryl-trans-decalin, 11.4 ml of absolute ethanol and 1.339 g (26.75 mmol) of hydrazine hydrate is dissolved
5 while warming and left to stand overnight. After adding 12.2 ml of diethyleneglycol and 1.8 g (32.08 mmol) of potassium hydroxide, the mixture is heated under a descending condenser for 2 hours at 200°C (bath temperature) and left at this temperature for 1.5 hours. The distillate
10 and residue are combined, treated with 25 ml of water and extracted with ether. The organic phases are washed with water and dried over sodium sulphate. After evaporating the solvent in vacuo, there are obtained 3.35 g of crude 2,6-dipentyl-trans-decalin which, for purification, is
15 chromatographed on 90 g of silica gel. Elution with hexane yields 1.74 g of substance which is distilled in a high vacuum at 145°C/0.03 mbar. There are obtained colourless crystals of 2,6-dipentyl-trans-decalin; m.p. 47.8°C.

The 6-pentyl-2-valeryl-trans-decalin used as the
20 starting material can be prepared as follows:

A Grignard solution is prepared by the dropwise addition of a mixture of 2.890 g (21.09 mmol) of n-butyl bromide and 3.5 ml of absolute ether to a suspension

of 0.513 g (21.10 mg atoms) of magnesium in 7 ml of absolute ether. After dissolution of the magnesium, there is added dropwise at 35-37°C while stirring a solution of 4.101 g (17.57 mmol) of 6-pentyl-trans-decalin-2-carbo-

5 nitrile (prepared according to Example 10) in 7 ml of absolute ether, the mixture is boiled under reflux for 7 hours and left to stand overnight. Then there are added dropwise 3.326 g (0.104 mol) of methanol and, after stirring for 30 minutes, the precipitate formed is

10 filtered off under suction and washed well with absolute ether. Subsequently, hydrogen chloride gas is introduced into the filtrate for 1 hour while cooling at 0°C and the mixture is concentrated to dryness. There are obtained 6.9 g of imine hydrochloride of 6-pentyl-2-valeryl-trans-

15 -decalin as a brownish, turbid oil. This is warmed at 50°C with 50 ml of water for 30 minutes, the 6-pentyl-2-valeryl-trans-decalin separating as an oil which later crystallizes. The mixture is extracted with ether, the organic phase is washed with water, dried over sodium

20 sulphate and the solvent is removed in vacuo. There remain 5.3 g of brownish, crystallizing oil which, for purification, can be recrystallized (e.g. from hexane). There are thus obtained colourless crystals of 6-pentyl-2-valeryl-trans-decalin; m.p. 47.0-48.5°C

Example 12

0.1 g of 4-(dimethylamino)pyridine and 1.6 g of p-propylphenol are added to a solution of 2.5 g of 2-pentyl-1,3-benzodioxan-6-carboxylic acid in 50 ml of methylene chloride. The mixture is treated portionwise at 0°C while stirring with 2.4 g of N,N'-dicyclohexylcarbodiimide. After completion of the addition, the mixture is stirred at 0°C for a further 10 minutes and then at room temperature for 3 hours. The precipitate is filtered off and the filtrate is evaporated. The residue is taken up in 40 ml of methylene chloride and again filtered. The filtrate is washed with saturated sodium carbonate solution and then with water, dried over sodium sulphate, filtered and evaporated. The crude product is dissolved in boiling hexane, filtered hot with active carbon and crystallized from the filtrate. The crystallizate is recrystallized twice more from hexane. There is obtained pure 2-pentyl-1,3-benzodioxan-6-carboxylic acid p-propylphenyl ester; m.p. 97.5°C, cl.p. 74.5°C (monotropic).

20 The 2-pentyl-1,3-benzodioxan-6-carboxylic acid used as the starting material can be prepared as follows:

A mixture of 16.8 g of 4-hydroxy-3-(hydroxymethyl)-benzoic acid, 1000 ml of benzene, 15.0 g of caproaldehyde and 0.36 ml of concentrated sulphuric acid is boiled for

5 hours while stirring under a water separator. After cooling, the mixture is filtered. The filtrate is concentrated and the residue is boiled up with hexane. The insoluble material is dissolved in ether/hexane and stirred up in the cold with active carbon. The mixture is filtered, the filtrate is evaporated and the residue is boiled with isopropyl ether. There are obtained 11.7 g of beige coloured 2-pentyl-1,3-benzodioxan-6-carboxylic acid; m.p. 148°C.

10

Example 13

15

20

1.85 ml of benzenesulphonyl chloride are added dropwise while stirring to a suspension of 1.2 g of 2-pentyl-1,3-benzodioxan-6-carboxamide in 10 ml of pyridine. The mixture is left to stand overnight and then the solution is extracted with 15 ml of 1N sodium hydroxide and ether. The aqueous phase is separated and back-extracted with ether. The combined organic phase is washed with 1N sodium hydroxide and then with water, dried over sodium sulphate, filtered and concentrated. The residue is treated with hot hexane. The mixture is decanted off from insoluble material and the solution is evaporated. The crude product is recrystallized once from hexane and twice from isopropanol. There is obtained 2-pentyl-1,3-benzodioxan-6-carbonitrile; m.p. 40.5-41°C (not liquid crystalline).

The 2-pentyl-1,3-benzodioxan-6-carboxamide used as the starting material can be prepared as follows:

A mixture of 3.0 g of 2-pentyl-1,3-benzodioxan-6-carboxylic acid (prepared in accordance with Example 12), 60 ml of chloroform and 2.2 ml of triethylamine is cooled to 0°C. 1.5 ml of ethyl chloroformate are added dropwise while stirring. The mixture is stirred at 0°C for 1 hour and then ammonia gas is conducted in. The mixture is stirred at room temperature for 5 hours and then evaporated. The residue is stirred up with 100 ml of water and the suspension is suction filtered. The material on the suction filter is dried and boiled up with hexane. There is obtained 2-pentyl-1,3-benzodioxan-6-carboxamide as a beige powder; m.p. 162.5-163°C.

15

Example 14

2.5 g of crude 2-pentyl-6-propenyl-1,3-benzodioxan are dissolved in 75 ml of ethanol and hydrogenated with 0.25 g of palladium/carbon (5%) at room temperature until the hydrogen uptake comes to a standstill. The mixture is filtered and concentrated. The crude product is purified by chromatography on a column of 32 g of basic aluminium oxide with hexane/ether (9:1). Pure 2-pentyl-6-propyl-1,3-benzodioxan is obtained as a colourless oil.

The 2-pentyl-6-propenyl-1,3-benzodioxan used as the starting material can be prepared as follows:

(a) A solution of 10.0 g of 2-pentyl-1,3-benzodioxan-6-carboxylic acid (prepared in accordance with Example 12) in 400 ml of ether is added to a suspension of 1.6 g of lithium aluminium hydride in 400 ml of dry ether in such a manner that the hydrogen evolution can be held under control. The mixture is stirred at room temperature for a further 1 hour and then 50 ml of acetone and 100 ml of water are added thereto cautiously. The aqueous phase is separated and back-extracted with ether. The combined organic phase is washed with water, dried over sodium sulphate and evaporated. 8.7 g of 2-pentyl-1,3-benzodioxan-6-carbinol is obtained as a colourless oil.

(b) A solution of 8.5 g of 2-pentyl-1,3-benzodioxan-6-carbinol in 225 ml of toluene is added to 13 g of activated manganese dioxide. The mixture is heated to boiling overnight and then filtered. After rinsing with a small amount of toluene, the filtrate is concentrated at 50°C on a rotary evaporator. 8.0 g of crude 2-pentyl-1,3-benzodioxan-6-carboxaldehyde are obtained as a yellowish oil.

(c) A mixture of 4.8 g of 2-pentyl-1,3-benzodioxan-6-carboxaldehyde, 100 ml of dioxan, 5 g of finely powdered

potassium carbonate and 11.5 g of ethyltriphenylphosphonium bromide is heated to boiling under reflux for 24 hours. The inorganic salts are filtered off and back-washed with dioxan and the filtrate is evaporated. The residue is

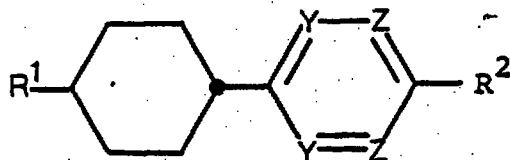
5 stirred up with hexane. Insoluble triphenylphosphine oxide is filtered off and the filtrate is evaporated. The residue is distilled at 210°C/11 mmHg in a bulb-tube. The turbid distillate is re-distilled at 130°C/0.1 mmHg in a bulb-tube. 2.5 g of not quite pure, oily 2-pentyl-6-

10 -propenyl-1,3-benzodioxan are obtained.



CLAIMS:

1. Compounds of the general formula



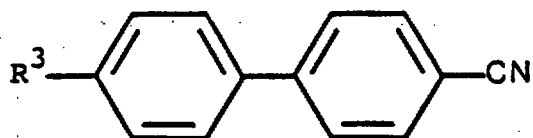
wherein the symbols Y stand for
 5 nitrogen and the symbols Z stand
 for =CH- or the symbols Z stand for
 nitrogen and the symbols Y stand
 for =CH-, R^1 represents alkyl and
 R^2 represents cyano, alkyl, p-alkyl-
 10 phenyl or trans-4-alkylcyclohexyl,
 the term alkyl signifies straight-
 -chain alkyl containing 1 to 12
 carbon atoms or in one of the residues
 R^1 or R^2 also signifies a branched-
 15 -chain alkyl group $C_2H_5-CH(CH_3)-(CH_2)_n-$,
 n is an integer of 1 to 3, and the sum
 of the carbon atoms in the alkyl groups
 present amounts to at most 14.

2. Compounds according to claim 1, wherein the symbols Y
 20 stand for =CH-, the symbols Z stand for nitrogen and R^2
 represents cyano.



3. Compounds according to claim 1, wherein the symbols Y stand for nitrogen, the symbols Z stand for =CH- and R² represents alkyl, preferably straight-chain alkyl containing 2 to 7 carbon atoms.
- 5 4. Compounds according to claim 1, wherein the symbols Y stand for =CH-, the symbols Z stand for nitrogen and R² represents a p-alkylphenyl group, whereby alkyl in the p-alkylphenyl group preferably signifies straight-chain alkyl containing 2 to 7 carbon atoms.
- 10 5. Compounds according to any one of claims 1 to 4, wherein R¹ signifies straight-chain alkyl containing 2 to 7 carbon atoms.
6. Compounds according to any one of claims 1 to 5 as components in liquid crystalline mixtures.
- 15 7. A liquid crystalline mixture containing at least two components, wherein at least one component is a compound of formula I in accordance with claim 1.
8. A liquid crystalline mixture according to claim 7, which contains one or more compounds of formula I defined
- 20 in claim 1 and one or more compounds of the general formula

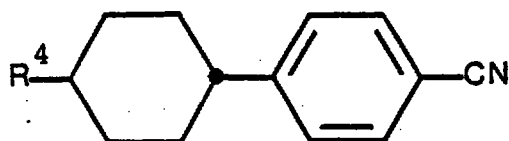
8



II

wherein R³ signifies a straight-chain
alkyl or alkoxy group containing 2 to
7 carbon atoms,

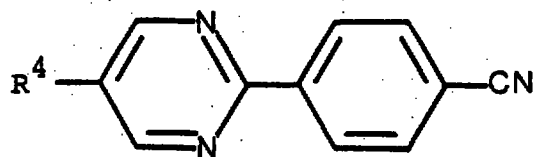
5 and/or



III

wherein R⁴ signifies a straight-chain
alkyl group containing 3 to 7 carbon
atoms,

10 and/or

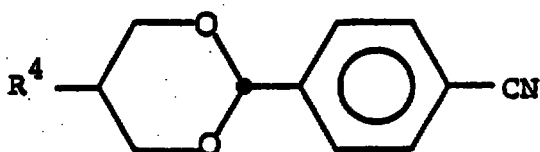


IV



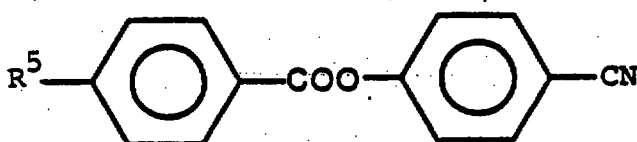
82

wherein R^4 has the significance
given earlier in this claim,
and/or



V

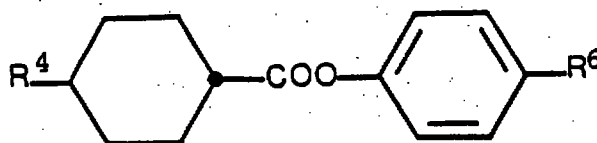
5 wherein R^4 has the significance
given earlier in this claim,
and/or



VI

10 wherein R^5 signifies a straight-chain
alkyl group containing 2 to 7 carbon
atoms,

and/or

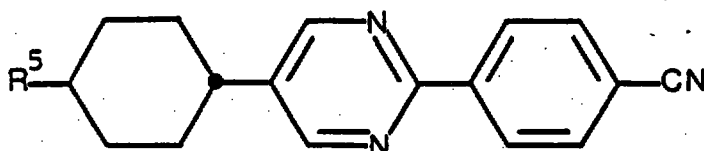


VII



wherein R^4 has the significance
 given earlier in this claim and R^6
 signifies cyano or a straight-chain
 alkoxy group containing 1 to 3 carbon
 atoms,

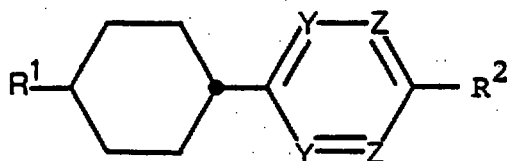
and/or



VIII

wherein R^5 has the significance given
 earlier in this claim.

- 10 9. A process for the manufacture of compounds of the
 general formula



I

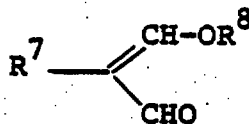
wherein the symbols Y stand for
 nitrogen and the symbols Z stand for
 =CH- or the symbols Z stand for



nitrogen and the symbols Y stand
for =CH-, R¹ represents alkyl and
R² represents cyano, alkyl, p-alkyl-
phenyl or trans-4-alkylcyclohexyl,
5 the term alkyl signifies straight-chain
alkyl containing 1 to 12 carbon atoms
or in one of the residues R¹ or R² also
signifies a branched-chain alkyl group
C₂H₅-CH(CH₃)-(CH₂)_n-, n is an integer
10 of 1 to 3, and the sum of the carbon
atoms in the alkyl groups present amounts
to at most 14,

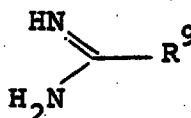
which process comprises

(a) for the manufacture of the compounds of formula I
15 in which R² represents alkyl, p-alkylphenyl or trans-4-
-alkylcyclohexyl, reacting a compound of the general formula



IX

with an acid addition salt, preferably the hydrochloride,
of a compound of the general formula

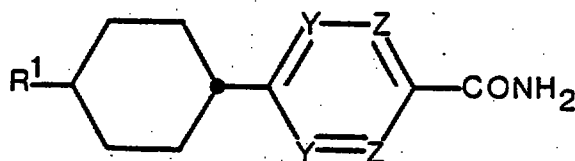


X



wherein one of R^7 and R^9 signifies
trans-4-alkylcyclohexyl and the other
signifies alkyl, p-alkylphenyl or
trans-4-alkylcyclohexyl and R^8
5 signifies lower alkyl,
in the presence of a base, preferably an alcoholate,

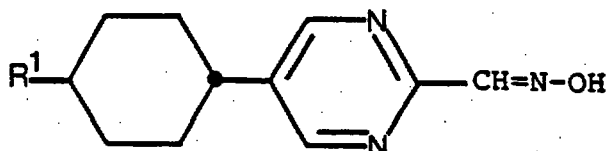
(b) for the manufacture of the compounds of formula I in
which R^2 signifies cyano, dehydrating a compound of the
general formula



XI

wherein R^1 , Y and Z have the significance
given earlier in this claim,

(c) for the manufacture of the compounds of formula I in
which the symbols Y stand for =CH-, the symbols Z stand for
15 nitrogen and R^2 represents cyano, dehydrating a compound
of the general formula



XII



wherein R^1 has the significance given
earlier in this claim.

10. The use of the compounds of formula I defined in claim 1
for electro-optical purposes.
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