

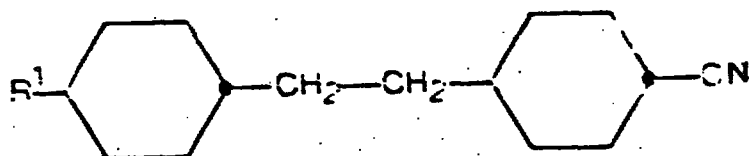
(10)

- 1 -

2102000

PRODUCTION OF 4-[2-(CYCLOHEXYL)ETHYL]CYCLO-HEXANECARBONITRILES
AND LIQUID CRYSTAL MIXTURES CONTAINING THEM.

The present invention is concerned with the manufacture of trans-
-4-[2-(trans-4-alkylcyclohexyl)ethyl]cyclohexanecarbo-
5 nitriles of the general formula



wherein R¹ signifies a straight-chain
alkyl group containing 1 to 12 carbon
atoms.

10

The invention is also concerned with liquid crystalline
mixtures containing these compounds as well as their use in
electro-optical devices.

The representation of the cyclohexane ring used in
15 formula I signifies in the scope of the present invention
trans-1,4-disubstituted cyclohexane.



The compounds in accordance with the invention are especially valuable as components of nematic and cholesteric liquid crystal mixtures with positive anisotropy of the dielectric constants ($\epsilon_{||} > \epsilon_{\perp}$, $\epsilon_{||}$ signifying the dielectric constant along the longitudinal molecular axis and $\epsilon_{\perp}$ signifying the dielectric constant perpendicular thereto).

Liquid crystals with positive dielectric anisotropy orientate themselves in an electric field with the direction of the largest dielectric constants (i.e. with the longitudinal molecular axes) parallel to the field direction. This effect is used, inter alia, in the interaction between embedded molecules and the liquid crystalline molecules (guest-host interaction) described by J.H. Heilmeyer and L.A. Zanoni [Appl. Phys. Lett. 13 (1968) 91] or D.L. White and G.N. Taylor [J. Appl. Phys. 45 (1974) 4718]. A further interesting application of the dielectric field device lies in the rotation cell discovered by M. Schadt and W. Helfrich [Appl. Phys. Lett. 18 (1971) 127].

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 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 polarized 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 (phase-change effect). By suitable choice of the cholesteric additives such mixtures can also be used to improve the electro-optical properties of rotation cell indicators.

It has now surprisingly been found that the compounds in accordance with the invention are low-viscous liquid crystals with positive anisotropy of the dielectric constants and very small optical anisotropy. Further, the compounds in accordance with the invention have an excellent chemical and photochemical stability and small electrical conductivity.

Furthermore, they are miscible with all known classes of liquid crystals and can be used in mixtures in high concentrations.

The following compounds can be manufactured by means of the present invention:

- Trans-4-[2-(trans-4-methylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- trans-4-[2-(trans-4-ethylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- 10 trans-4-[2-(trans-4-propylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- trans-4-[2-(trans-4-butylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- trans-4-[2-(trans-4-pentylcyclohexyl)ethyl]cyclo-
- 15 hexanecarbonitrile,
- trans-4-[2-(trans-4-hexylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- trans-4-[2-(trans-4-heptylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- 20 trans-4-[2-(trans-4-octylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- trans-4-[2-(trans-4-nonylcyclohexyl)ethyl]cyclohexanecarbonitrile,
- trans-4-[2-(trans-4-decylcyclohexyl)ethyl]cyclo-
- 25 hexanecarbonitrile,

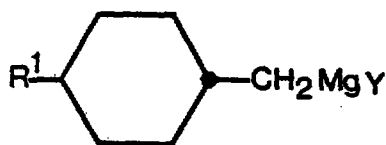
trans-4-[2-(trans-4-undecylcyclohexyl)ethyl]cyclohexanecarbonitrile,

trans-4-[2-(trans-4-dodecylcyclohexyl)ethyl]cyclohexanecarbonitrile.

5 Preferred compounds of formula I are those in which the straight-chain alkyl group R^1 contains 2 to 9, especially 3 to 7, carbon atoms. The compounds of formula I in which R^1 signifies propyl or pentyl are especially preferred.

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

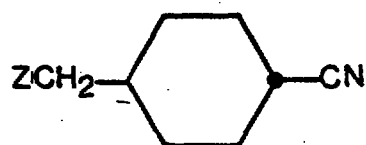
(a) reacting a compound of the general formula



II

15 wherein Y represents chlorine, bromine, or iodine and R^1 has the significance given earlier,
and a compound of the general formula

(15)

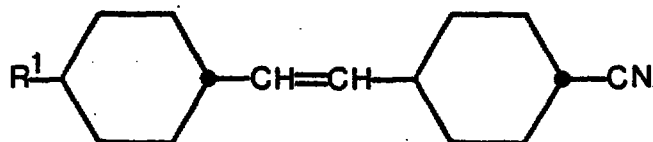


III

wherein Z signifies bromine, iodine,
an alkylsulphonyloxy group or an
arylsulphonyloxy group,

- 5 in the presence of dilithium tetrachlorocuprate or dilithium
tetrabromocuprate,
or

(b) catalytically hydrogenating a compound of the general
formula



IV

10

wherein R¹ has the significance given
earlier.

The reaction of a compound of formula II with a
compound of formula III can be carried out in a manner known

16
per se. As the catalyst there is used dilithium tetrachlorocuprate or dilithium tetrabromocuprate, preferably dilithium tetrachlorocuprate. As alkylsulphonyloxy and arylsulphonyloxy groups Z there come into consideration
5 all sulphonyloxy groups which are usually used as leaving groups in such reactions such as, for example, methane-sulphonyloxy, benzenesulphonyloxy, tosyloxy, naphthalene-sulphonyloxy and the like. Y in formula II preferably stands for bromine and Z in formula III preferably stands for
10 bromine or tosyloxy. The reaction is conveniently carried out in an ether such as dimethoxyethane, diethylene glycol dimethyl ether, tetrahydrofuran, dioxan, diethyl ether and the like. The preferred solvent is tetrahydrofuran or a mixture of tetrahydrofuran and diethyl ether. Temperature
15 and pressure can be held in wide limits. However, the reaction is generally carried out at atmospheric pressure and a temperature between about -80°C and room temperature. A reaction temperature of below about 0°C and especially about -15°C is preferred.

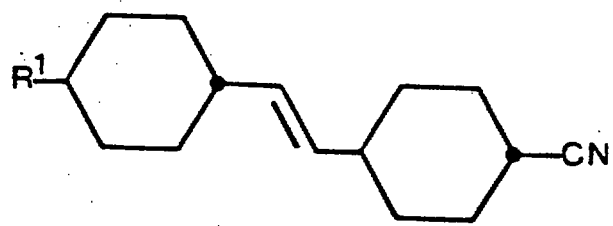
20 The catalytic hydrogenation of the compounds of formula IV can be carried out in a manner known per se using any usual hydrogenation catalyst such as palladium, platinum, Raney-nickel and the like (optionally on an inert carrier material such as carbon). Palladium and platinum are the
25 preferred catalysts. As solvents there can be used any inert organic solvent such as saturated alcohols, ethers,

(17)

esters, carboxylic acids, aromatic hydrocarbons and the like; for example, ethanol, dioxan, ethyl acetate, glacial acetic acid and toluene. Temperature and pressure are not critical aspects in this catalytic hydrogenation. The catalytic hydrogenation is, however, conveniently carried out at a temperature between room temperature and the boiling point of the mixture and under a pressure of about 1 to about 5 atmospheres.

10

The liquid crystalline trans-1,2-dicyclohexyl-ethenes of the general formula



V

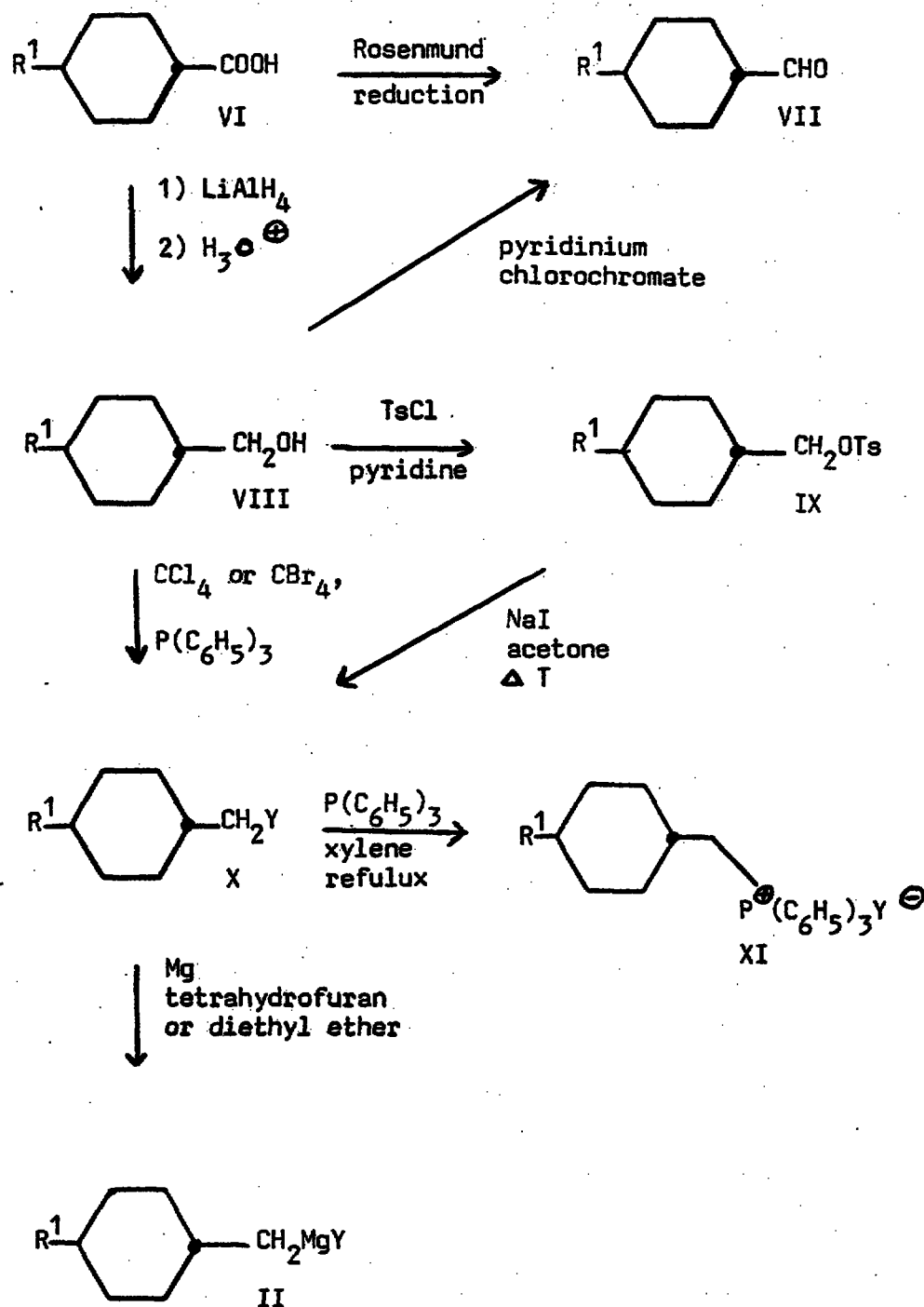
wherein R¹ has the significance given earlier, are novel and also form objects of the present invention.

15

The compounds of formulae II to IV can be prepared as illustrated in the following Schemes A-C in which R¹, Y and Z have the significances given earlier and Ts denotes a tosyl group.

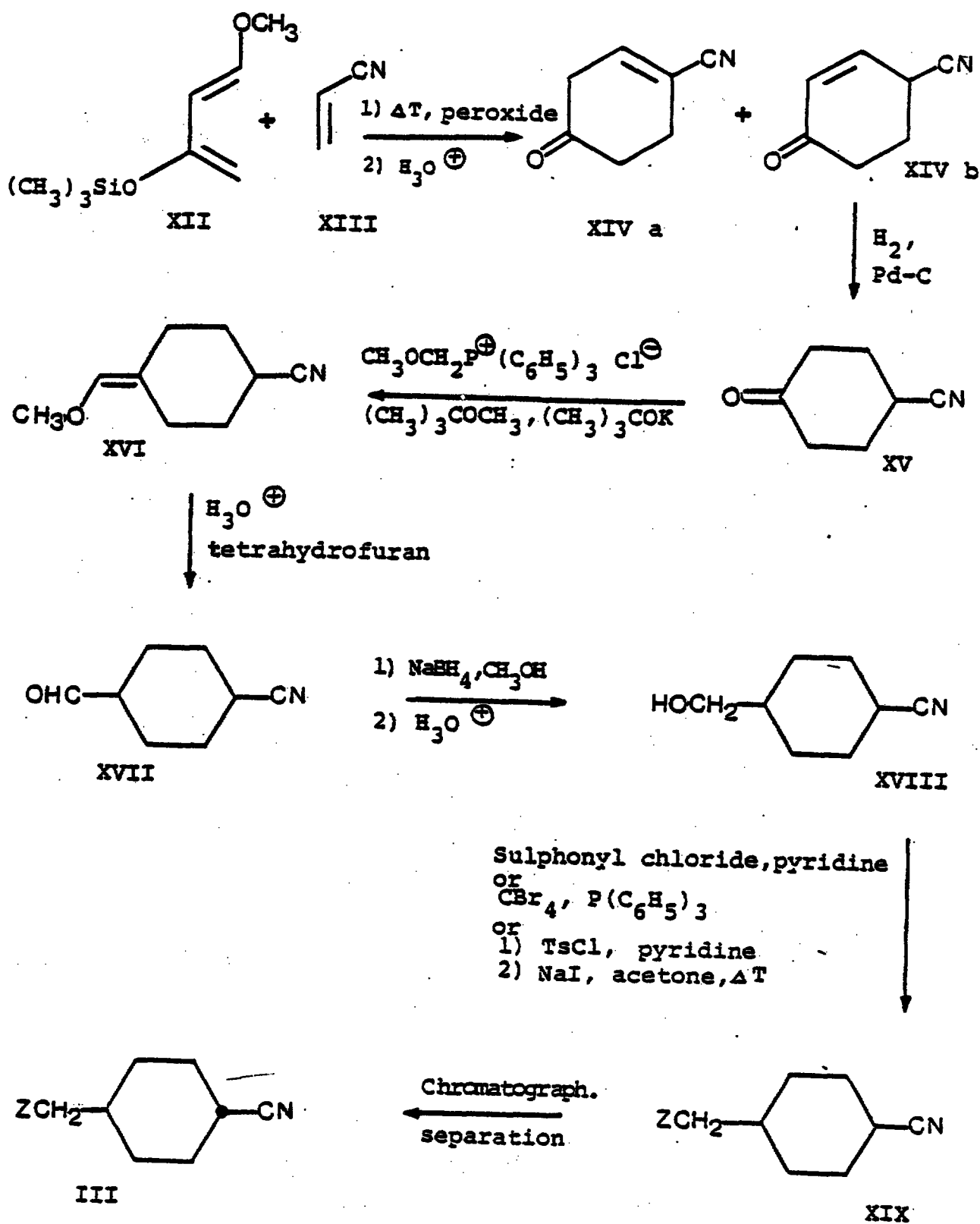
20

Scheme A

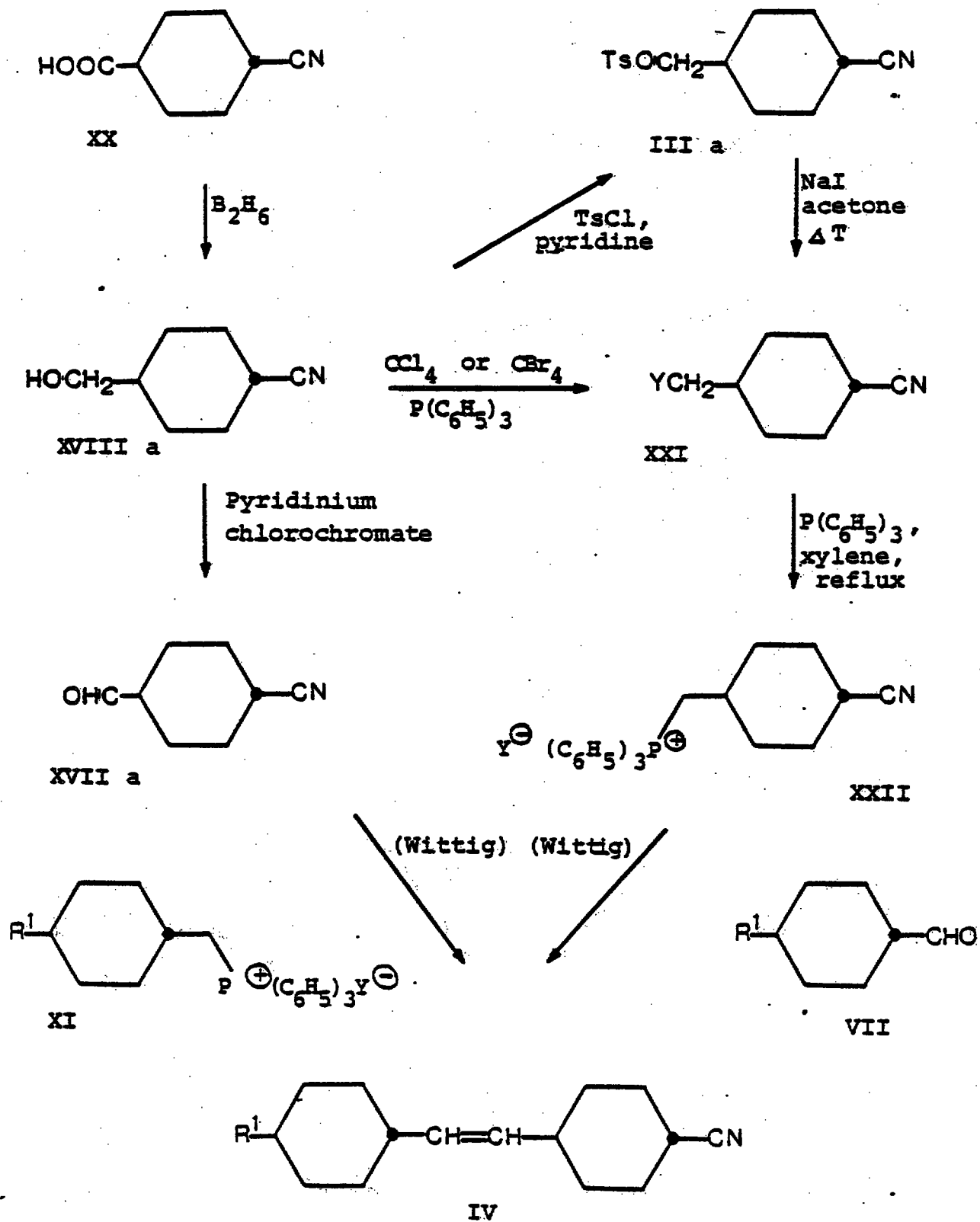


19

Scheme B



Scheme C



The compounds of formulae XVII-XIX in Scheme B are generally obtained as cis/trans mixtures which can subsequently be separated by chromatography. Starting from trans-4-cyanocyclohexanecarboxylic acid of formula XX (known from Chem. Abstr. 85: 123431 d) there can, however, as shown in Scheme C for some examples, also be obtained directly the corresponding trans compounds.

The Wittig reactions for the preparation of the compounds of formula IV can be carried out in a manner known per se in the presence of a base, for example butyl lithium, phenyl lithium, sodium hydride, potassium hydride, sodium amide, potassium t-butyrate, sodium ethylate, sodium hexamethyldisilazide, lithium diisopropylamide and the like, in an inert organic solvent such as an alkane, a chlorinated or aromatic hydrocarbon, an ether, an alcohol, an aprotic polar solvent and the like. Hexane, methylene chloride, benzene, toluene, diethyl ether, t-butyl methyl ether, ethanol, t-butanol, dimethyl sulphoxide and hexamethylphosphoric acid triamide are examples of preferred solvents. If sodium amide is used as the base, liquid ammonia can also be used as the solvent. Temperature and pressure are not critical. The reaction is conveniently carried out at atmospheric pressure and a temperature between about -40°C and about +65°C. The reaction in t-butyl methyl ether in the presence of potassium t-butyrate at about 0°C is especially preferred. Y in the compounds of formulae XI,

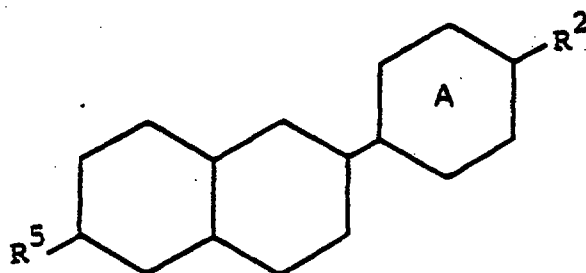
22

XXI and XXII preferably signifies bromine.

The compounds of formula IV are generally obtained as mixtures of the corresponding cis- and trans-1,2-dicyclohexylethenes which can subsequently be converted directly
5 into compounds of formula I by catalytic hydrogenation. However, if desired, the compounds of formula V can also be obtained in pure form from these mixtures, for example by chromatographic separation and recrystallization.

The compounds of formula I can be used in the form of
10 mixtures consisting only of compounds of formula I or 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, phenyl benzoates, cyclohexanecarboxylic acid
15 phenyl esters, cyclohexanecarboxylic acid cyclohexyl esters, biphenyls, terphenyls, phenylcyclohexanes, cinnamic acid derivatives, phenylpyrimidines, diphenylpyrimidines, cyclohexylphenylpyrimidines, phenyldioxanes and the like. Such substances are known to the person skilled in the art and
20 many of them are, moreover commercially available.

The mixtures in accordance with the invention can contain, in addition, equatorially substituted trans-decalins of the general formula

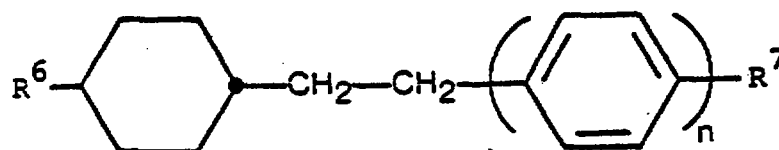


XXIII

wherein ring A is aromatic or represents
a trans-1,4-disubstituted cyclohexane
ring; R^2 denotes methyl or one of the
5 groups $-CH_2R'$, $-OR'$, $-CO-R'$, $-CN$, $-COOH$,
 $-CO-OR'$, $-CO-SR'$ or $-O-CO-R'$; R^5 sig-
nifies hydrogen, methyl or one of the
groups $-CH_2R$, $-OR$, $-CH_2OR$ or, when R^2
denotes methyl or one of the groups
10 $-CH_2R'$, $-OR'$ or $-CO-R'$, R^5 also sig-
nifies $-CN$, $-COOH$, $-CO-OR$, $-CO-SR$ or
 $-O-CO-R$; R and R' stand for straight-
-chain or branched-chain alkyl groups;
 R^2 and R^5 have the same significance
15 or different significances; and R^2 and
 R^5 individually contain up to 12 carbon
atoms and together contain at most 14
carbon atoms,

and/or (trans-4-alkylcyclohexyl)ethanes of the general
20 formula

24



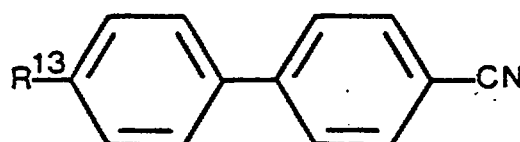
XXIV

5 wherein R^7 represents one of the groups $-R^8$, $-OR^8$, $-CO-R^8$, $-CO-OR^8$ or $-O-CO-R^8$, R^6 and R^8 signify straight-chain alkyl groups containing 1 to 12 carbon atoms and n stands for one of the numbers 1 or 2.

The preparation of compounds of formulae XXIII and ⁵⁸XXIV are disclosed in published Applications Nos: 2090593 and 2092146 respectively.

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:

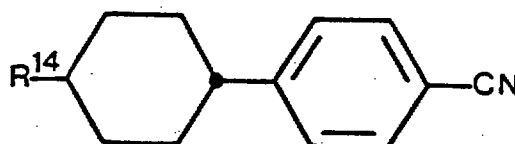
- 10 4-Cyanobiphenyls of the general formula



VLIII

wherein R^{13} signifies a straight-chain alkyl or alkoxy group containing 2 to 7 carbon atoms,

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

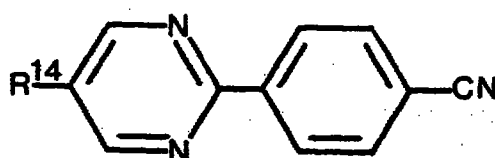


IL

26

wherein R^{14} signifies a straight-chain alkyl group containing 2 to 7 carbon atoms,

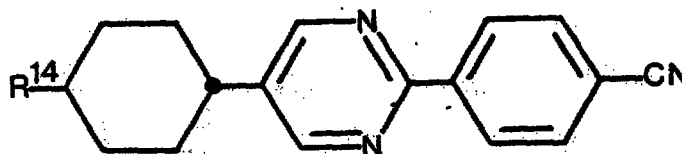
5 p-(5-alkyl-2-pyrimidinyl)benzonitriles of the general formula



L

wherein R^{14} has the significance given earlier,

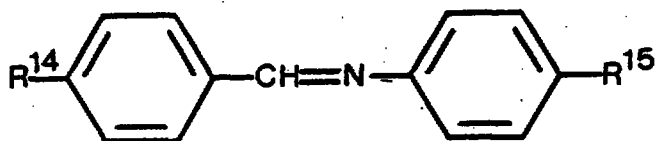
10 p-[5-(trans-4-alkylcyclohexyl)-2-pyrimidinyl]benzonitriles of the general formula



LI

wherein R^{14} has the significance given earlier,
Schiff's bases of the general formula

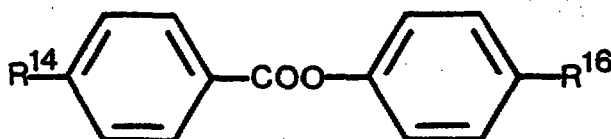
(27)



LII

wherein R^{15} denotes the cyano group or a
straight-chain alkyl or alkoxy group con-
taining 1 to 5 carbon atoms and R^{14} has
the significance given earlier,

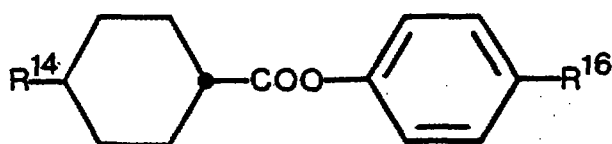
p-alkylbenzoic acid phenyl esters of the general formula



LIII

wherein R^{16} denotes the cyano group or
a straight-chain alkoxy group containing
1 to 6 carbon atoms and R^{14} has the
significance given earlier,

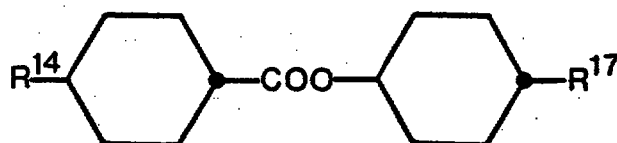
trans-4-alkylcyclohexanecarboxylic acid phenyl esters of
the general formula



LIV

wherein R^{14} and R^{16} have the significances given earlier,
trans-4-alkylcyclohexanecarboxylic acid cyclohexyl esters
of the general formula

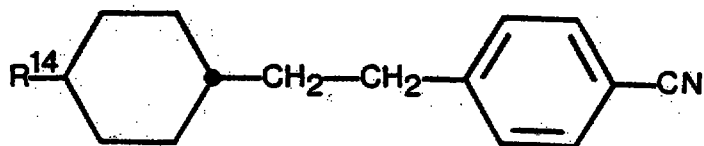
5



LV

wherein R^{17} denotes the cyano group or
a straight-chain alkyl group containing
1 to 6 carbon atoms and R^{14} has the sig-
nificance given earlier,

10 p-[2-(trans-4-alkylcyclohexyl)ethyl]benzonitriles of the
general formula



LVI

wherein R^{14} has the significance given
earlier,

15 equatorially substituted trans-decalins of formula XXIII

29

hereinbefore in which R and R' signify straight-chain alkyl groups and, preferably, R⁵ denotes methyl or one of the groups -CH₂R or -OR and R² denotes methyl or one of the groups -CH₂R', -OR', -CO-R', -CN, -CO-OR' or -O-CO-R',
5 and (trans-4-alkylcyclohexyl)ethanes of formula XXIV hereinbefore in which n stands for the number 1 and R⁷ preferably represents one of the groups -R⁸ or -OR⁸.

The amount of the compounds of formula I present in the mixtures in accordance with the invention can generally
10 be chosen at will; for example, mixtures which consist of two or more compounds of formula I can also be used. However, there are preferred mixtures which contain about 1 wt.% to about 80 wt.% of compounds of formula I and there are especially preferred those mixtures which contain about
15 10 wt.% to about 60 wt.% of compounds of formula I.

Further, the mixtures in accordance with the invention can contain suitable optically active compounds, for example optically active biphenyls, and/or dichroic colouring substances, for example azo, azoxy and anthraquinone colouring
20 substances. The amount of such compounds present is determined by the solubility, the desired pitch, colour, extinction and the like. The amount of optically active compounds preferably amounts to at most about 4 weight percent and the amount of dichroic colouring substance preferably
25 amounts to at most about 10 weight percent.

The manufacture of the liquid crystalline mixtures in accordance with the invention 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
5 and subsequently cooling down.

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

The following mixtures are examples of preferred
15 mixtures in accordance with the invention. η denotes the viscosity (bulk viscosity).

Mixture Example 1

40.4 wt.% of 4'-pentyl-4-cyanobiphenyl,
59.6 wt.% of trans-4-[2-(trans-4-pentylcyclohexyl)ethyl]-
20 cyclohexanecarbonitrile,
m.p. -10°C, cl.p. 56.5°C, nematic.

(31)

Mixture Example 2

- 34.5 wt.% of 4'-pentyl-4-cyanobiphenyl,
10.6 wt.% of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,
5 54.9 wt.% of trans-4-[2-(trans-4-pentylcyclohexyl)ethyl]-
cyclohexanecarbonitrile,
m.p. -10°C, cl.p. 70°C, nematic.

Mixture Example 3

- 16.8 wt.% of 4'-pentyl-4-cyanobiphenyl,
10 6.2 wt.% of p-[5-(trans-4-ethylcyclohexyl)-2-pyrimidinyl]-
benzonitrile,
16.6 wt.% of 2-(trans-4-propylcyclohexyl)-1-(p-ethoxyphenyl)-
ethane,
19.3 wt.% of 2-(trans-4-pentylcyclohexyl)-1-(p-ethoxyphenyl)-
15 ethane,
41.1 wt.% of trans-4-[2-(trans-4-pentylcyclohexyl)ethyl]-
cyclohexanecarbonitrile,
m.p. <-10°C, cl.p. 58°C, nematic; η = 27.2 cp.

The manufacture of the compounds of formula I in accordance with the invention is illustrated on the basis of the following Examples:

Example 1

- 5 121 mg of magnesium shavings were covered with 3 ml of absolute tetrahydrofuran while gassing with argon, treated with a crystal of iodine and then treated at reflux temperature with a solution of 989 mg of trans-1-(bromomethyl)-4-pentylcyclohexane in 7 ml of absolute tetrahydrofuran.
- 10 After completion of the addition, the mixture was heated to reflux for a further 45 minutes.

- Subsequently, the mixture, cooled to -78°C , was treated with 0.7 ml of a 0.1N solution of dilithium tetrachlorocuprate (prepared in accordance with M. Tamura et al, 15 Synthesis 1971, 303) in tetrahydrofuran and treated with a solution of 587 mg of trans-4-(tosyloxymethyl)cyclohexane-carbonitrile in 9 ml of absolute tetrahydrofuran. The mixture, warmed to -15°C , was stirred for a further 21 hours, then treated with about 10 ml of saturated ammonium chloride 20 solution and extracted three times with 50 ml of diethyl ether each time. The organic phases were washed with 50 ml of saturated sodium chloride solution, dried over magnesium sulphate and concentrated. Low-pressure chromatography

(0.5 bar) of the residue on silica gel with 3% ethyl acetate/petroleum ether gave, besides a large amount of coupling product of trans-1-(bromomethyl)-4-pentylcyclohexane, 164 mg (28.5%) of trans-4-[2-(trans-4-pentylcyclohexyl)ethyl]cyclohexanecarbonitrile [353 mg of trans-4-(tosyloxymethyl)cyclohexanecarbonitrile could be recovered with 30% ethyl acetate/petroleum ether]. A single recrystallization from 5 ml of methanol yielded 96 mg of trans-4-[2-(trans-4-pentylcyclohexyl)ethyl]cyclohexanecarbonitrile as colourless crystals (purity 99.98%); solid-solid transition 39.3°C, m.p. 56.5°C, c.l.p. 72.7°C (nematic).

The trans-1-(bromomethyl)-4-pentylcyclohexane used as the starting material was prepared as follows:

(a) 3.79 g of lithium aluminium hydride were placed in 100 ml of absolute tetrahydrofuran while gassing with argon and treated within 30 minutes with a solution of 19.83 g of trans-4-pentylcyclohexanecarboxylic acid in 100 ml of absolute tetrahydrofuran. After completion of the addition, the mixture was heated to reflux for 1 hour, then cautiously added to 200 ml of 2N hydrochloric acid and extracted three times with 100 ml of diethyl ether each time. The organic phases were washed with 100 ml of saturated sodium carbonate solution, dried over potassium carbonate and concentrated. Distillation of the residue (19.2 g) gave in the main run

17.7 g (96%) of (trans-4-pentylcyclohexyl)methanol as a colourless oil (purity 99.9%); b.p. 89°C/0.2 mmHg.

(b) A solution of 3.69 g of (trans-4-pentylcyclohexyl)-methanol and 5.51 g of triphenylphosphine in 70 ml of methylene chloride at -30°C was placed under argon gasification and treated portionwise within 15 minutes with 7.30 g of solid tetrabromomethane in such a manner that the internal temperature did not exceed -20°C. After completion of the addition, the cooling bath was removed and the mixture was stirred for a further 18 hours with gradual warming to room temperature. The mixture was then concentrated on a rotary evaporator and the semi-crystalline residue obtained was triturated with 200 ml of warm hexane, filtered and the concentrated filtrate was chromatographed with hexane on a column of silica gel. There were obtained 4.79 g (97%) of trans-1-(bromomethyl)-4-pentylcyclohexane as a colourless liquid which was purified further by distillation; b.p. 82°C/0.08 mmHg.

The trans-4-(tosyloxymethyl)cyclohexanecarbonitrile also used as the starting material was prepared as follows:

(c) A mixture of 18.9 g of 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene [S. Danishefsky et al, J. Amer. Chem. Soc. 96, (1974) 7807], 6.4 g of acrylonitrile, 100 mg of

dibenzoyl peroxide and 50 ml of benzene was heated to reflux for 23 hours while gassing with argon. After cooling, the volatile constituents (benzene and excess acrylonitrile) were removed on a rotary evaporator and the residue was

5 heated to reflux for 2 hours in 100 ml of tetrahydrofuran/1N hydrochloric acid (4:1). The cooled mixture was subsequently extracted three times with 100 ml of methylene chloride each time. The organic phases were washed twice with 100 ml of water each time and once with 100 ml of

10 saturated sodium chloride solution, dried over magnesium sulphate and concentrated. There were obtained 10.3 g of yellow oil which consisted of 87.9% of 4-cyano-3-cyclohexen-1-one, of 4.1% of 4-cyano-2-cyclohexen-1-one and of 2.7% of trans-4-cyano-3-methoxycyclohexanone (an intermediately

15 occurring hydrolysis product). Bulb-tube distillation (130-140°C/0.27-0.15 mmHg) of the oil obtained gave 7.64 g of a mixture of 4-cyano-3-cyclohexen-1-one and 4-cyano-2-cyclohexen-1-one as an orange, crystallizing oil. This was dissolved in 70 ml of ethanol and hydrogenated at

20 normal pressure in the presence of 764 mg of 10% palladium/carbon (hydrogen uptake 1425 ml). After filtration of the catalyst, washing with methylene chloride, concentration of the filtrate and bulb-tube distillation (130-150°C/0.11 mmHg), there were obtained 5.45 g (70%) of 4-cyanocyclohexanone as

25 a colourless oil; Rf-value (toluene/ethyl acetate 3:1): 0.25.

(d) 9.6 g of triphenyl(methoxymethyl)phosphonium chloride were suspended in 50 ml of t-butyl methyl ether while gassing with argon and treated portionwise at -10°C with 3.39 g of solid potassium t-butyrate. After completion of the addition, the mixture was stirred at 0 to 5°C for a further 30 minutes and then the deep orange, partially heterogeneous mixture was treated dropwise within 10 minutes with a solution of 2.30 g of 4-cyanocyclohexanone in 20 ml of t-butyl methyl ether. In so doing the internal temperature should not exceed 5°C . After completion of the addition, the now yellow-orange mixture was warmed to 25°C and stirred for a further 2 hours. 50 ml of a 2% sodium hydrogen carbonate solution were subsequently added and the separated, aqueous phase was extracted twice with 50 ml of diethyl ether each time. The organic phases were washed with 50 ml of saturated sodium chloride solution, dried over potassium carbonate and concentrated. The residual, semi-crystalline, orange oil was triturated with 400 ml of hexane, cooled to -20°C and freed from precipitated triphenylphosphine oxide by filtration (rinsing with cold hexane). Low-pressure chromatography (0.4 bar) of the concentrated residue on silica gel using 10% ethyl acetate/petroleum ether as the elution agent gave 1.60 g (56%) of 4-(methoxymethylene)cyclohexanecarbonitrile as a colourless oil (purity 97%).

(e) The 4-(methoxymethylene)cyclohexanecarbonitrile obtained was heated to reflux for 1.5 hours in 100 ml of tetrahydrofuran/0.2N hydrochloric acid (4:1). The cooled mixture was then poured into 50 ml of water and extracted
5 three times with 50 ml of diethyl ether each time. The organic phases were washed with 50 ml of water and 50 ml of saturated sodium hydrogen carbonate solution, dried over magnesium sulphate and concentrated. There were obtained 1.35 g (94%) of a colourless oil which, in accordance with
10 gas chromatographical analysis, contained 92% of a mixture of the cis- and trans-4-cyanocyclohexanecarboxaldehydes (in the ratio of about 1:1). This material was used in the following reduction without additional purification. Rf-values (toluene/ethyl acetate 3:1): cis-4-cyanocyclo-
15 hexanecarboxaldehyde 0.36, trans-4-cyanocyclohexanecarboxaldehyde 0.32.

(f) A solution of 1.34 g of 4-cyanocyclohexanecarboxaldehyde (cis/trans mixture) in 40 ml of 0.1N methanolic potassium hydroxide solution was treated portionwise at
20 0°C while gassing with argon with 378 mg of solid sodium borohydride. After completion of the addition, the mixture was stirred at 0°C for a further 20 minutes, then 50 ml of water were added and the mixture was extracted three times with 50 ml of methylene chloride each time. The organic
25 phases were washed twice with 50 ml of water each time,

- dried over magnesium sulphate and concentrated. Low-pressure chromatography (0.4 bar) of the residual oil on silica gel with chloroform/ethyl acetate (1:1) gave 1.22 g (90%) of 4-(hydroxymethyl)cyclohexanecarbonitrile (likewise as an about 1:1 mixture of the two epimers) as a colourless, viscous oil. This material was used in the following tosylation without further purification. Rf-value of 4-(hydroxymethyl)cyclohexanecarbonitrile [chloroform/ethyl acetate (1:1): 0.29 (longish spot).
- 10 (g) A solution of 1.20 g of the 4-(hydroxymethyl)cyclohexanecarbonitrile obtained in 5 ml of pyridine was treated portionwise at room temperature and while gassing with argon with 2.46 g of tosyl chloride. After stirring at room temperature for 3.5 hours (formation of a white precipitate),
- 15 the mixture, cooled to 0°C was treated with about 2 ml of water, cautiously made acid with about 7 ml of concentrated hydrochloric acid and extracted three times with 30 ml of diethyl ether each time. The organic phases were washed with 50 ml of water and 50 ml of saturated sodium chloride
- 20 solution, dried over magnesium sulphate and concentrated, 2.31 g of semi-crystalline oil remaining behind. Low-pressure chromatography (0.5 bar) on 480 g of silica gel using 30% ethyl acetate/petroleum ether as the elution agent gave 1.06 g (42%) of trans-4-(tosyloxymethyl)-
- 25 cyclohexanecarbonitrile as a colourless, crystallizing oil (m.p. 84-85°C) and 1.03 g (41%) of cis-4-(tosyloxymethyl)-

cyclohexanecarbonitrile as a colourless viscous oil. Rf-value (30% ethyl acetate/petroleum ether): trans product 0.25, cis product 0.20.

The following compounds can be manufactured in an analogous manner:

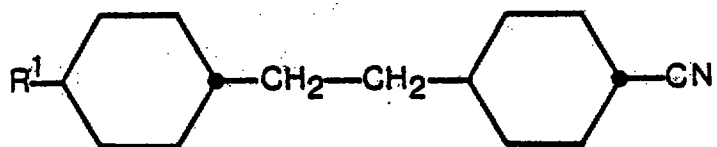
Trans-4-[2-(trans-4-ethylcyclohexyl)ethyl]cyclohexanecarbonitrile; m.p. 33.8°C, cl.p. 39.1°C (nematic);
trans-4-[2-(trans-4-propylcyclohexyl)ethyl]cyclohexanecarbonitrile; m.p. 47.5°C, cl.p. 64.3°C (nematic); and
10 trans-4-[2-(trans-4-butylcyclohexyl)ethyl]cyclohexanecarbonitrile; m.p. 60.1°C, cl.p. 64.5°C (nematic).



-31 -

CLAIMS

1. A process for the manufacture of trans-4-[2-(trans-4-alkylcyclohexyl)ethyl]cyclohexanecarbonitriles of the general formula

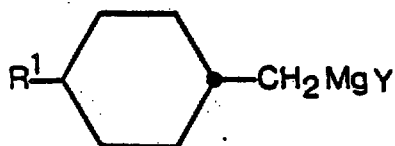


5 wherein R^1 signifies a straight-chain alkyl group containing 1 to 12 carbon atoms,

which process comprises

(a) reacting a compound of the general formula

10

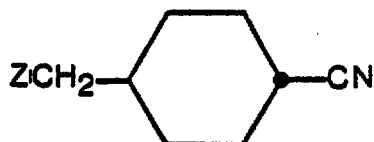


wherein Y represents chlorine, bromine or iodine and R^1 has the significance given earlier in this claim,



41

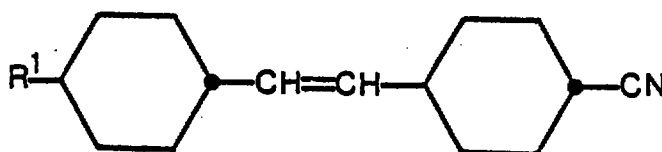
and a compound of the general formula



III

wherein Z signifies bromine, iodine,
 an alkylsulphonyloxy group or an
 5 arylsulphonyloxy group,
 in the presence of dilithium tetrachlorocuprate or di-
 lithium tetrabromocuprate,
 or

(b) catalytically hydrogenating a compound of the
 10 general formula



IV

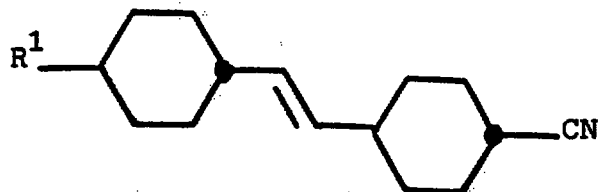
wherein R¹ has the significance
 given earlier in this claim.

42



- 3 2 -

2. Liquid crystalline trans 1,2 dicyclohexyl-ethanes of the general formula



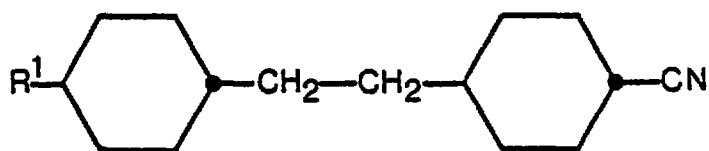
V

where R¹ is as defined in claim 1.



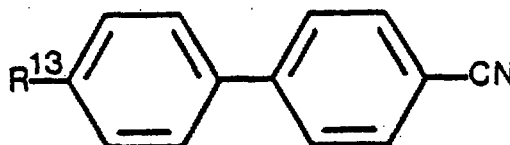
42

3. A liquid crystalline mixture containing at least one trans-4-[2-(trans-4-alkylcyclohexyl)ethyl]cyclohexane-carbonitrile of the general formula



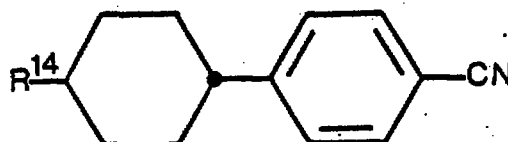
I

- 5 wherein R¹ signifies a straight-chain alkyl group containing 1 to 12 carbon atoms,
and at least one of the compounds of the general formulae



VLIII

- 10 wherein R¹³ signifies a straight-chain alkyl or alkoxy group containing 2 to 7 carbon atoms,



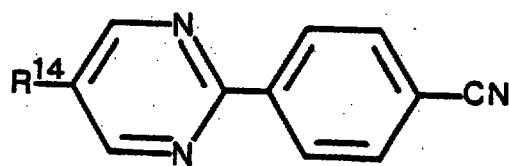
IL

- 15 wherein R¹⁴ signifies a straight-chain alkyl group containing 2 to 7 carbon atoms,

AA

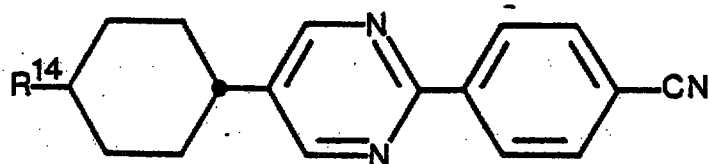


- 35 -



L

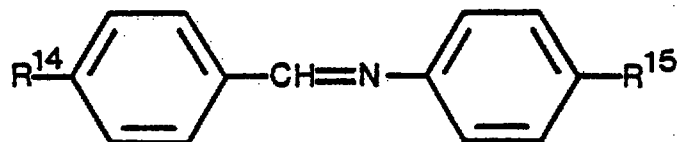
wherein R^{14} has the significance given earlier,



LI

5

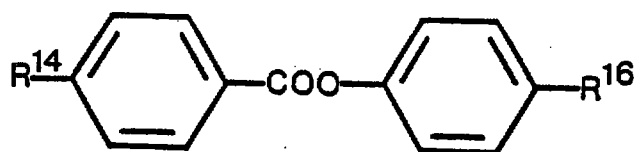
wherein R^{14} has the significance given earlier,



LII

wherein R^{15} denotes the cyano group or a straight-chain alkyl or alkoxy group containing 1 to 5 carbon atoms and R^{14} has the significance given earlier,

10



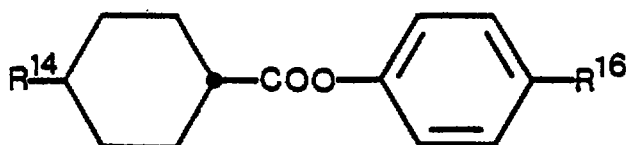
LIII



(45)

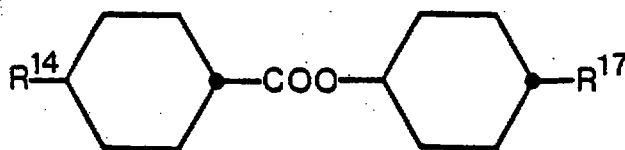
wherein R^{16} denotes the cyano group or a straight-chain alkoxy group containing 1 to 6 carbon atoms and R^{14} has the significance given earlier,

5



LIV

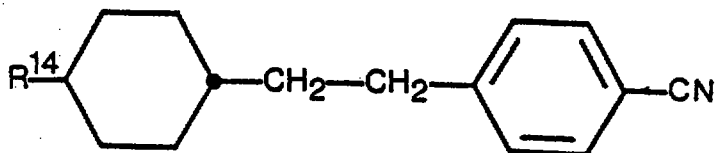
wherein R^{14} and R^{16} have the significances given earlier,



LV

10

wherein R^{17} denotes the cyano group or a straight-chain alkyl group containing 1 to 6 carbon atoms and R^{14} has the significance given earlier,

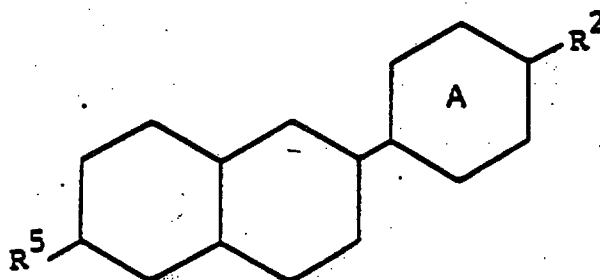


LVI

15

wherein R^{14} has the significance given earlier,

(46)

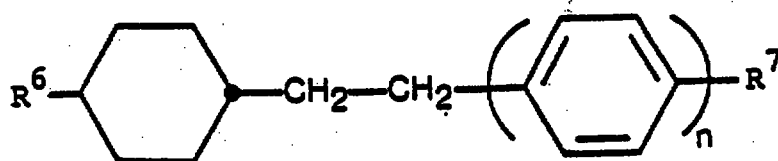


XXIII

wherein ring A is aromatic or represents
a trans-1,4-disubstituted cyclohexane
ring; R^2 denotes methyl or one of the
5 groups $-CH_2R'$, $-OR'$, $-CO-R'$, $-CN$, $-COOH$,
 $-CO-OR'$, $-CO-SR'$ or $-O-CO-R'$; R^5 sig-
nifies hydrogen, methyl or one of the
groups $-CH_2R$, $-OR$, $-CH_2OR$ or, when R^2
denotes methyl or one of the groups
10 $-CH_2R'$, $-OR'$ or $-CO-R'$, R^5 also sig-
nifies $-CN$, $-COOH$, $-CO-OR$, $-CO-SR$ or
 $-O-CO-R$; R and R' stand for straight-
chain or branched-chain alkyl groups;
 R^2 and R^5 have the same significance
15 or different significances; and R^2 and
 R^5 individually contain up to 12 carbon
atoms and together contain at most 14
carbon atoms,



47



XXIV

wherein R^7 represents one of the groups
 $-R^8$, $-OR^8$, $-CO-R^8$, $-CO-OR^8$ or $-O-CO-R^8$,
 R^6 and R^8 signify straight-chain alkyl
groups containing 1 to 12 carbon atoms
and n stands for one of the numbers 1 or
2.

4. A liquid crystalline mixture according to Claim 3,
wherein R^5 denotes methyl or one of the groups $-CH_2R$ or
10 $-OR$, R^2 denotes methyl or one of the groups $-CH_2R'$, $-OR'$,
 $-CN$, $-CO-OR'$ or $-O-CO-R'$, n stands for the number 1 and
 R^7 represents one of the groups $-R^8$ or $-OR^8$.

5. A liquid crystalline mixture according to Claim 3 or
4, wherein R^1 denotes propyl or pentyl.

15 6. A liquid crystalline mixture according to any one of
Claims 3 to 5, characterized in that it contains 1 wt% to
80 wt% of compounds of formula I.

7. A liquid crystalline mixture according to
Claim 6, characterized in that it contains 10 wt% to
20 60 wt% of compounds of formula I.



8. A liquid crystalline mixture according to any one of Claims 3 to 7, characterized in that it further contains suitable optically active compounds and/or dichroic colouring substances.

5. 9. The use of the liquid crystalline mixture defined in Claim 3 for electro-optical purposes.
-