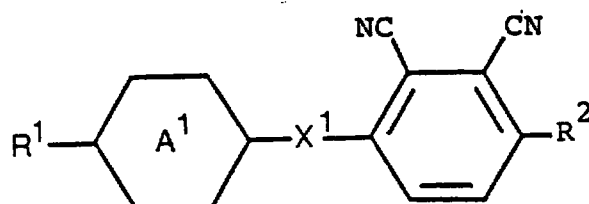


RAN 6220/O34

5 The present invention is concerned with novel liquid crystalline mixtures according to claim 12 containing dicyanobenzenes of the general formula

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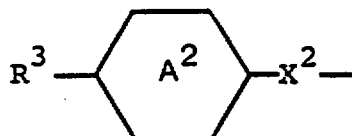


I

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wherein R^1 and R^2 signify straight-chain C_1 - C_{12} -alkyl or on an aromatic ring also straight-chain C_1 - C_{12} -alkoxy, or one of R^1 and R^2 also signifies a group of the general formula

20



II;

25

x^1 and x^2 denote single covalent bonds or one of x^1 and x^2 also denotes an ethylene group $-CH_2CH_2-$; rings A^1 and A^2 represent 1,4-phenylene or, insofar as x^1 or x^2 denotes an ethylene group $-CH_2CH_2-$, also trans-1,4-cyclohexylene;

and R^3 signifies straight-chain

C_1-C_{12} -alkyl or on an aromatic ring

A^2 also straight-chain C_1-C_{12} -alkoxy.

and liquid crystalline mixtures according to claims 11 and 13
5 containing compounds of formula I with an ethylene group X^1
or X^2 .

The invention is also concerned with the manufacture of
the compounds of formula I defined in claim 11 in accordance
10 with the process of claim 14 as well as with the novel
dicyanobenzenes according to claim 1 and their use for
electro-optical purposes.

15 As used herein, the term "straight-chain C_1-C_{12} -
-alkyl" embraces methyl, ethyl, propyl, butyl, pentyl,
hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl
and the term "straight-chain C_1-C_{12} -alkoxy" embraces methoxy,
20 ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy, heptyl-
oxy, octyloxy, nonyloxy, decyloxy, undecyloxy and dodecyl-
oxy.

25 Unless indicated otherwise, the terms "dielectric
anisotropy" or "anisotropy of the dielectric constants"
signify in the scope of the present invention the low-fre-
30 quency ("static") dielectric anisotropy.

Nematic and cholesteric liquid crystals with negative
anisotropy of the dielectric constants ($\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$
35 < 0 , $\epsilon_{||}$ signifying the dielectric constant along the long-
itudinal molecular axis and $\epsilon_{\perp}$ signifying the dielectric
constant perpendicular thereto) are orientated in an

electric field with their longitudinal molecular axes perpendicular to the field direction. This effect is known and is used for the control of the optical transmissivity in various liquid crystal indicators, for example in liquid crystal cells of the light scattering type (dynamic scattering), of the so-called DAP type (deformation of aligned phases) or of the guest/host type (guest host interaction).

10

The "guest/host cell" comprises essentially a condenser, at least one electrode being transparent and the dielectric being formed from a nematic or cholesteric liquid crystal which contains one or more dichroic colouring substances. Since the colouring substances used mainly have positive dichroism, i.e. the transition moment of the absorption of visible light lies approximately in the direction of the longitudinal molecular axis, the orientation of the liquid crystal with the molecular axes parallel to the surface of the plates generally corresponds to the coloured state and the homeotropic orientation (longitudinal molecular axes perpendicular to the surface of the plates) generally corresponds to the colourless state of the cell. When a liquid crystal with positive dielectric anisotropy is used, its homogeneous orientation (which is achieved by treating the surface of the plates) is arranged homeotropic by the application of a voltage, i.e. the cell is switched from "coloured" to "colourless". In this manner

25

colourless symbols are shown on a coloured background. On the other hand, when a liquid crystal with negative dielectric anisotropy is used, its homeotropic orientation (by treating the surface of the plates) is arranged parallel to the electrode surfaces by the application of a voltage, whereby the reading of coloured image elements on a colourless background is made possible.

Further, for the improvement of the multiplex ratio in the multiplex control of liquid crystal indicators, especially of rotation cells and guest/host cells, there has been proposed a two-frequency matrix addressing (e.g. German Offenlegungsschriften 2 856 134 and 2 907 940). In this case use is made of the fact that the dielectric anisotropy of liquid crystals, which upon application of a low frequency voltage have a positive anisotropy of the dielectric constants, is negative in the case of high frequencies. In order to maintain the capacitative loss low, the "cross-over frequency" f_c (dielectric relaxation frequency at which $\epsilon_{||} = \epsilon_{\perp}$) of such liquid crystals should be as low as possible and should not lie above about 20 kHz. Further, the absolute value of the dielectric anisotropy should be as large as possible not only below but also above the cross-over frequency. It has, however, been found that the substances, which are especially suitable for the two-frequency procedure, at frequencies above the cross-over frequency generally have a smaller absolute dielectric anisotropy than below the cross-over frequency. This dis-

advantage can be eliminated by adding compounds with negative dielectric anisotropy and suitable relaxation behaviour.

5

A series of liquid crystalline compounds with weakly negative dielectric anisotropy has already been synthesized. On the other hand, still relatively few liquid crystal
10 components with large negative anisotropy of the dielectric constants are known. Moreover, the latter generally have disadvantages such as, for example, poor solubility in mixtures, high viscosity, high melting points, strong
15 smectic tendencies and chemical instability. There accordingly exists a need for further compounds with negative dielectric anisotropy which allow the properties of
20 mixtures for the widest variety of electro-optical uses to be improved further.

Liquid crystal compounds with negative dielectric anisotropy which possess two or three rings linked via
25 carboxyl groups of covalent bonds and one of more lateral groups such as halogen, cyano or nitro groups, are known from DE-AS 2240864, DE-OS 2613293, DE-OS 2835662, DE-OS 2836086 and EP-A-0023728. EP-A-0023728 describes inter alia also
30 compounds with a 2,3-dicyano-1,4-phenylene group, e.g. 2,3-dicyano-4-propylphenyl-4'-alkylcyclohexanes wherein alkyl signifies propyl, pentyl or heptyl. In contrast to the
35 compounds of the above formula I these 2,3-dicyanobenzenes possess at least one cyclohexane ring and the rings are linked via single covalent bonds and/or carboxyl or oxocarbonyl groups.

It has now been found that the compounds of the above
formula I have a large negative anisotropy of the di-
electric constants, a good solubility in known liquid
crystal mixtures and a relatively low viscosity. They are
5 colourless and have a very good chemical and photochemical
stability. Further, with the compounds of the above formula I
there can be manufactured mixtures which have
10 an improved melting behaviour and no smectic tendencies
or only slight smectic tendencies. They are accordingly

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especially suitable for improving the properties of liquid crystal mixtures with negative anisotropy of the dielectric constants or of liquid crystal mixtures which are suitable for the two-frequency matrix addressing. They can, however, also be used in mixtures with positive dielectric anisotropy, for example in order to adapt the threshold potential of the electro-optical cell which is used.

10

Compounds of formula I in which R^1 and R^2 signify straight-chain C_1 - C_{12} -alkyl or on an aromatic ring also straight-chain C_1 - C_{12} -alkoxy are preferred. In the case of these bicyclic compounds either X^1 denotes a single covalent bond and ring A^1 denotes 1,4-phenylene, or X^1 denotes an ethylene group and ring A^1 denotes 1,4-phenylene, or, preferably, X^1 denotes an ethylene group and ring A^1 denotes trans-1,4-cyclohexylene.

20

In principle, there are preferred those compounds of formula I in which at least one of the two side-chains (R^1 , R^2 or R^3), preferably both, signifies C_1 - C_{12} -alkyl. Accordingly, there are especially preferred those compounds of formula I in which R^1 and R^2 signify straight-chain alkyl and particularly those in which additionally X^1 denotes an ethylene group and ring A^1 denotes trans-1,4-cyclohexylene.

25

Further, there are preferred in principle those compounds of formula I in which the alkyl groups contain 3 to 7 carbon atoms and the alkoxy groups contain 2 to 6 carbon atoms.

5 Examples of preferred compounds of formula I are those in which R^1 , ring A^1 , X^1 and R^2 have the significances given in Table 1 (C_6H_4 denotes 1,4-phenylene, C_6H_{10} denotes trans-1,4-cyclohexylene and a single dash (-) for X^1 denotes a single
10 covalent bond), as well as the compounds of formula I named in the Examples hereinafter.

Table 1

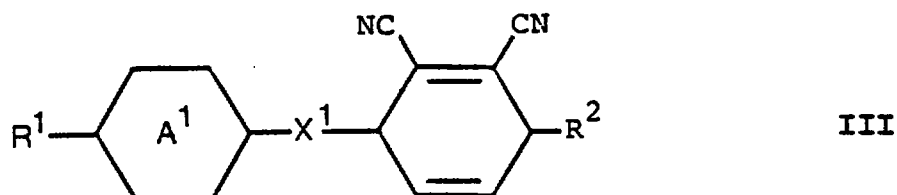
	R^1	A^1	X^1	R^2
15	C_3H_7	C_6H_4	-	C_3H_7
	C_3H_7	C_6H_4	-	C_5H_{11}
	C_3H_7	C_6H_4	-	C_7H_{15}
	C_5H_{11}	C_6H_4	-	C_3H_7
	C_5H_{11}	C_6H_4	-	C_5H_{11}
20	C_5H_{11}	C_6H_4	-	C_7H_{15}
	C_7H_{15}	C_6H_4	-	C_3H_7
	C_7H_{15}	C_6H_4	-	C_5H_{11}
	C_4H_9O	C_6H_4	-	C_3H_7
	C_4H_9O	C_6H_4	-	C_5H_{11}
	C_4H_9O	C_6H_4	-	C_6H_{13}
	C_3H_7	C_6H_4	-	C_4H_9O
25	C_5H_{11}	C_6H_4	-	C_4H_9O
	C_3H_7	C_6H_4	$-CH_2CH_2-$	C_7H_{15}
	C_5H_{11}	C_6H_4	$-CH_2CH_2-$	C_3H_7
	C_5H_{11}	C_6H_4	$-CH_2CH_2-$	C_5H_{11}
	C_5H_{11}	C_6H_4	$-CH_2CH_2-$	C_7H_{15}
	C_7H_{15}	C_6H_4	$-CH_2CH_2-$	C_3H_7

5	C_4H_9O	C_6H_4	$-CH_2CH_2-$	C_3H_7
	C_4H_9O	C_6H_4	$-CH_2CH_2-$	C_5H_{11}
	C_5H_{11}	C_6H_4	$-CH_2CH_2-$	C_4H_9O
	C_2H_5	C_6H_{10}	$-CH_2CH_2-$	C_3H_7
	C_3H_7	C_6H_{10}	$-CH_2CH_2-$	C_6H_{13}
	C_3H_7	C_6H_{10}	$-CH_2CH_2-$	C_7H_{15}
	C_5H_{11}	C_6H_{10}	$-CH_2CH_2-$	C_3H_7
	C_5H_{11}	C_6H_{10}	$-CH_2CH_2-$	C_4H_9
	C_5H_{11}	C_6H_{10}	$-CH_2CH_2-$	C_5H_{11}
	C_5H_{11}	C_6H_{10}	$-CH_2CH_2-$	C_7H_{15}
10	C_7H_{15}	C_6H_{10}	$-CH_2CH_2-$	C_3H_7
	C_5H_{11}	C_6H_{10}	$-CH_2CH_2-$	C_4H_9O
	C_3H_7	C_6H_4	-	$C_5H_{11}-C_6H_4$
	C_3H_7	C_6H_4	-	$C_7H_{15}-C_6H_4$
	C_5H_{11}	C_6H_4	-	$C_3H_7-C_6H_4$
	C_5H_{11}	C_6H_4	-	$C_5H_{11}-C_6H_4$
	C_5H_{11}	C_6H_4	-	$C_7H_{15}-C_6H_4$
	C_7H_{15}	C_6H_4	-	$C_3H_7-C_6H_4$
	C_7H_{15}	C_6H_4	-	$C_5H_{11}-C_6H_4$
	C_4H_9O	C_6H_4	-	$C_5H_{11}-C_6H_4$
15	C_5H_{11}	C_6H_4	-	$C_4H_9O-C_6H_4$
	$C_3H_7-C_6H_4$	C_6H_4	-	C_5H_{11}
	$C_5H_{11}-C_6H_4$	C_6H_4	-	C_3H_7
	$C_5H_{11}-C_6H_4$	C_6H_4	-	C_5H_{11}
	$C_7H_{15}-C_6H_4$	C_6H_4	-	C_3H_7
	$C_4H_9O-C_6H_4$	C_6H_4	-	C_5H_{11}
	$C_5H_{11}-C_6H_4$	C_6H_4	-	C_4H_9O
	$C_5H_{11}-C_6H_{10}-CH_2CH_2-$	C_6H_4	-	C_3H_7
	$C_5H_{11}-C_6H_{10}-CH_2CH_2-$	C_6H_4	-	C_5H_{11}
	$C_7H_{15}-C_6H_{10}-CH_2CH_2-$	C_6H_4	-	C_3H_7
20	$C_4H_9O-C_6H_4$	C_6H_4	-	
	$C_5H_{11}-C_6H_4$	C_6H_4	-	
	$C_5H_{11}-C_6H_{10}-CH_2CH_2-$	C_6H_4	-	
	$C_5H_{11}-C_6H_{10}-CH_2CH_2-$	C_6H_4	-	
	$C_7H_{15}-C_6H_{10}-CH_2CH_2-$	C_6H_4	-	
25				

The compounds of formula I can be manufactured
by

(a) for the manufacture of the compounds of formula I
in which R^2 signifies straight-chain C_1 - C_{12} -alkyl or a group
of formula II, oxidizing a compound of the general formula

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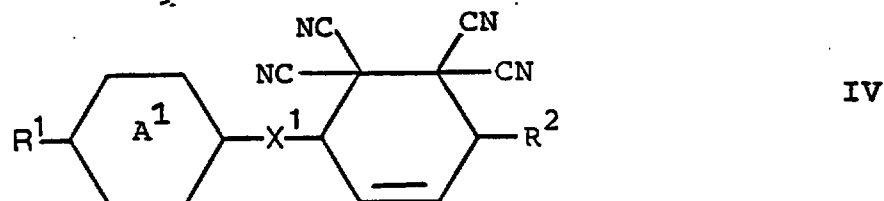
wherein R^2 represents straight-chain
 C_1 - C_{12} -alkyl or a group of formula II and
 R^1 , X^1 and ring A^1 have the significances
given above,

15

or

(b) for the manufacture of the compounds of formula I
in which R^2 signifies straight-chain C_1 - C_{12} -alkyl or a group
of formula II, cleaving off hydrogen cyanide from a compound
of the general formula

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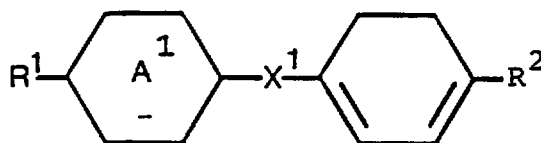


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wherein R^2 represents straight-chain
 C_1-C_{12} -alkyl or a group of formula II and
 R^1 , X^1 and ring A^1 have the significances
 5 given above,

or

(c) for the manufacture of the compounds of formula I
 in which R^2 signifies straight-chain C_1-C_{12} -alkoxy, reacting
 10 a compound of the general formula



V

15

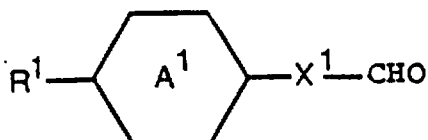
wherein R^2 represents straight-chain
 C_1-C_{12} -alkoxy and R^1 , X^1 and ring A^1
 20 have the significances given above,
 with dicyanoacetylene and subsequently cleaving off ethylene.

These reactions can be carried out according to
 methods known per se. The oxidation of a compound of formula
 25 III is preferably carried out with 2,3-dichloro-5,6-dicyano-
 -p-benzoquinone in dioxan or by catalytic dehydrogenation
 (preferably in the presence of a palladium catalyst). The
 cleavage of hydrogen cyanide from the compounds of formula
 IV is preferably carried out with caesium fluoride in di-

methylformamide. The reaction of a compound of formula V with dicyanoacetylene can be carried out according to the methods of the Diels-Alder reaction, preferably in an ether (e.g. tetrahydrofuran); the subsequent cleavage of ethylene from the Diels-Alder primary adduct obtained is preferably carried out by heating.

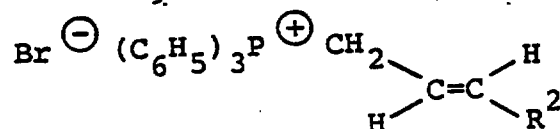
The compounds of the above formulae are novel.

The compounds of formula III can be obtained, for example, by reacting an aldehyde of the general formula



VI

with a phosphonium salt of the general formula



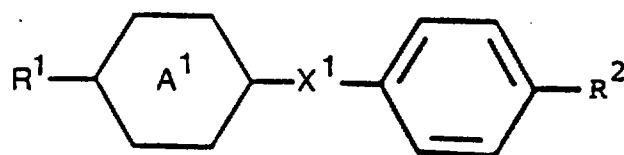
VII

wherein R^1 , R^2 , X^1 and ring A^1 have the significances given in formula III,

in diethyl ether in the presence of butyl lithium and converting the diene obtained into a compound of formula III by Diels-Alder reaction with dicyanoacetylene in tetrahydrofuran. The compounds of formula VII and the compounds of formula VI in which X^1 denotes a single covalent bond are known or are analogues of known compounds. The compounds of formula VI in which X^1 denotes an ethylene group can be prepared, for example, by heating a corresponding compound of formula VI in which X^1 denotes a single covalent bond with $(C_6H_5)_3P=CH-COOC_2H_5$ to reflux in benzene, catalytically hydrogenating the resulting α,β -unsaturated ester in ethanol in the presence of a palladium catalyst, reducing the ester obtained with lithium aluminium hydride in diethyl ether and oxidizing the alcohol obtained to the desired aldehyde with pyridinium chlorochromate in methylene chloride.

The compounds of formula IV can be prepared, for example, by reacting an aldehyde of formula VI with a phosphonium salt of formula VII in absolute diethyl ether in the presence of butyl lithium and converting the diene obtained into a compound of formula IV by Diels-Alder reaction with tetracyanoethylene in diethyl ether.

The compounds of formula V can be prepared, for example, by reducing a compound of the general formula



VIII

5

wherein R^2 denotes straight-chain
 C_1-C_{12} -alkoxy and R^1 , X^1 and ring A^1
 10 have the significances given in formula I,
 with lithium and liquid ammonia (preferably in a diethyl
 ether/ethanol mixture). In this case there is generally ob-
 tained the 1,4-diene of a mixture of the 1,3-diene (a com-
 pound of formula V) and the 1,4-diene. The isomerization
 15 to the 1,3-diene can be carried out, for example, using
 2,3-dichloromaleic anhydride. This is preferably carried
 out by using the product obtained in the above reaction
 directly for the subsequent Diels-Alder reaction [variant
 (c)] and adding 2,3-dichloromaleic anhydride to the reaction
 20 mixture. The compounds of formula VIII above are known or
 are analogues of known compounds.

The compounds of the above formula I can be used
 in the form of mixtures with liquid crystalline substances
 25 such as, for example, with substances from the classes of
 Schiff's bases, azobenzenes, azoxybenzenes, phenylbenzoates,
 cyclohexanecarboxylic acid phenyl esters and cyclohexyl

esters, biphenyls, terphenyls, phenylcyclohexanes, cyclohexylbiphenyls, phenylpyrimidines, diphenylpyrimidines, cyclohexyl-phenylpyrimidines, phenyldioxanes and the like.

5 Such substances are known to the person skilled in the art and many of them are, moreover, commercially available.

The mixtures provided by the invention conveniently contain about 1-40 wt.% and preferably about 3-25 wt.%
10 of compounds of formula I.

In principle, the compounds of the above formula I can be used in any liquid crystalline mixtures,

for example, even in mixtures with positive dielectric
15 anisotropy in order to adjust the dielectric anisotropies to the cell which is used. The compounds of the above formula I are, however, preferably used in mixtures with negative dielectric anisotropy or in mixtures which are suitable for the two-frequency control. Such mixtures can
20 be manufactured in a manner known per se.

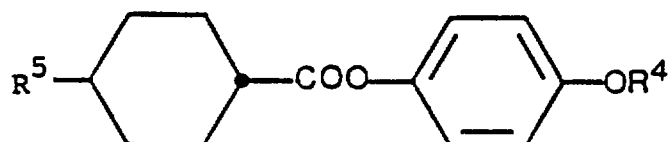
However, the mixtures for the two-frequency matrix addressing preferably consist of three components A, B and C, each of which contains one
25 or more compounds, with component A having a viscosity of at most 40 cp, a clearing point of at least 40°C and a dielectric anisotropy between -2 and +1, component B having a dielectric anisotropy below -2 and containing at least one compound of formula I, and

component C having a dielectric anisotropy above +10, a clearing point of at least 100°C and a cross-over frequency in the total mixture of at most 15
5 kHz at 20°C.

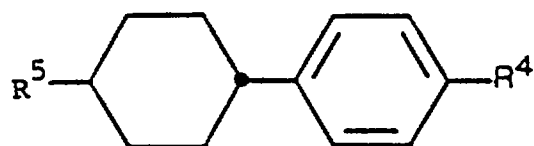
Such mixtures preferably consist of at least about 30 wt.% of component A, about 3-50 wt.% of component B and about 5-40 wt.% of component C and particularly of about
10 30-87 wt.% of component A, about 3-40 wt.% of component B and 10-30 wt.% of component C.

Compounds and mixtures having the above properties required for the components A, B and C are in principle
15 known to the person skilled in the art. The total mixture must have nematic or cholesteric properties. Component A can be nematic or cholesteric and component C can be nematic, cholesteric or, provided that the total mixture is not smectic, also smectic. Components A and C must have at
20 least monotropic liquid crystalline properties. However, there are preferred those mixtures in which at least component C is enantiotropic liquid crystalline and there are especially preferred those mixtures in which components A and C are enantiotropic liquid crystalline. Individual
25 compounds in the mixtures provided by the invention and component B can, however, be liquid crystalline or non-liquid crystalline, but in the latter case care should be taken that the mesophase range of the total mixture is not restricted too severely.

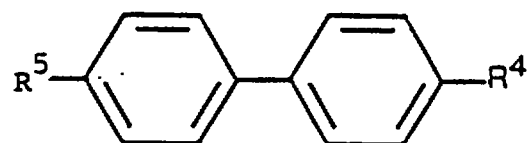
Compounds and mixtures which are suitable as component A are to a large extent known and many of them are also commercially available. The following compounds or their mixtures are especially suitable:



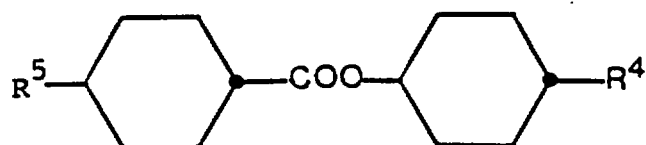
IX



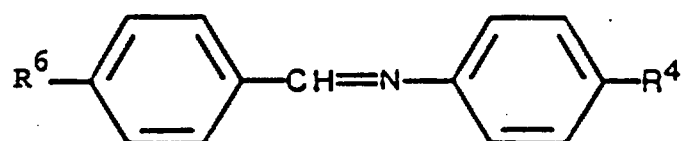
X



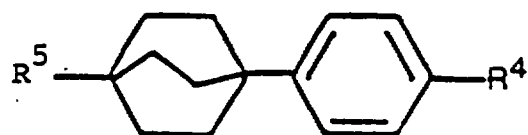
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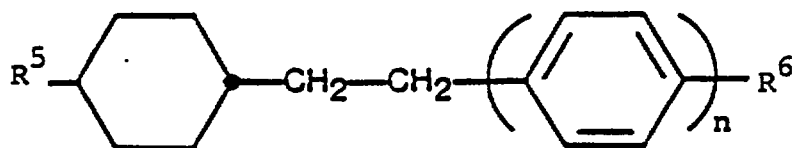
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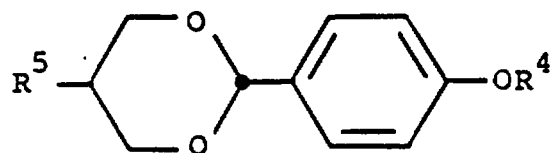
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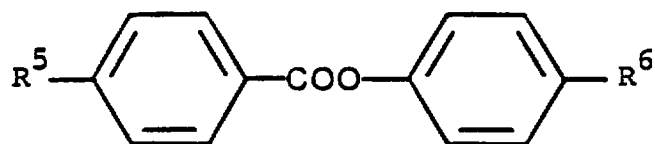
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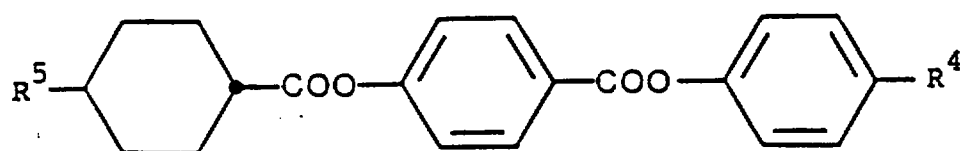
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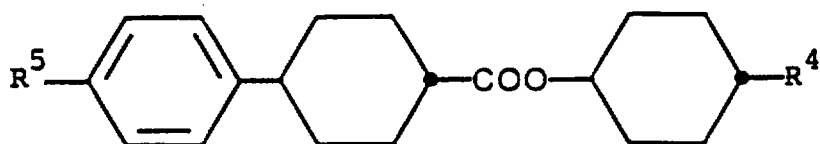
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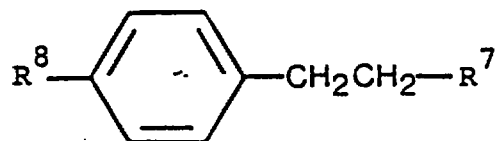
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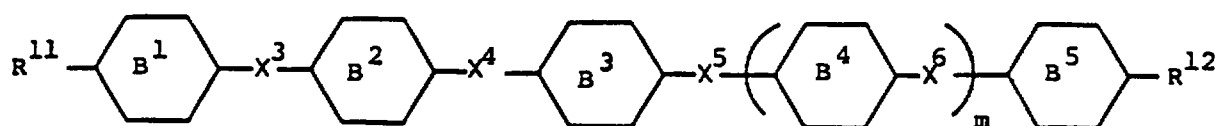
XVIII



XIX

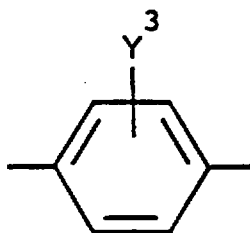


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XXI

wherein R^4 and R^5 signify straight-chain alkyl groups containing 1 to 8 carbon atoms, R^6 denotes a straight-chain alkyl or alkoxy group containing 1 to 8 carbon atoms and n is 1 or 2; R^8 represents trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenyl, p-(trans-4-alkylcyclohexyl)phenyl, 2-(trans-4-alkylcyclohexyl)ethyl or p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl and R^7 represents trans-4-alkylcyclohexyl, or R^8 represents trans-4-alkylcyclohexyl and R^7 represents p-(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl or 4'-(trans-4-alkylcyclohexyl)-4-biphenyl, or R^8 represents p-alkylphenyl and R^7 represents p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl, and the alkyl groups in the substituents R^7 and R^8 denote straight-chain groups containing 1 to 7 carbon atoms; m stands for the number 0 or 1; one of the symbols X^3 and X^4 signifies an ester group -COO- or -OOC- and the remainder of the symbols X^3 , X^4 , X^5 and X^6 signify a single covalent bond, or one of these symbols also signifies the ethylene group -CH₂CH₂-; rings B^1 and B^5 denote a group of the formula



XXII

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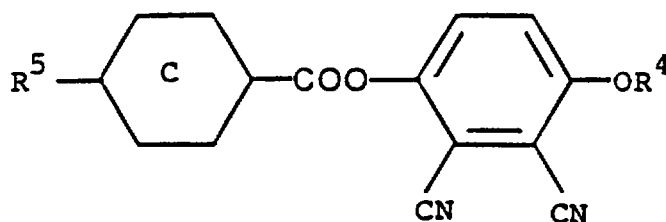
or trans-1,4-cyclohexylene; rings B², B³ and B⁴ represent a group of formula XXII or, insofar as they are not linked with at least one of the other two of these rings by a single covalent bond, also trans-1,4-cyclohexylene; Y³ signifies hydrogen or on a ring of formula XXII which is not linked with a further ring via a single covalent bond also fluorine, chlorine or methyl; and R¹¹ and R¹² denote straight-chain alkyl containing 1 to 7 carbon atoms or on a ring of formula XXII also straight-chain alkoxy containing 1 to 7 carbon atoms.

In an especially preferred embodiment the compounds of formulae IX-XII, XV, XX and XXI are used.

The compounds of formula I above have been found to be especially suitable compounds for component B. Other compounds suitable for component B which can be used in admixture with one or more compounds of formula I are, for example, the phenylpyridazines and diphenylpyridazines mentioned in Z. Chemie 17, 333 (1977), J. prakt, Chemie

151, 221 (1938), Z. Chemie 6, 467 (1966) and Mol. Cryst.
 Liq. Cryst. 25, 299 (1974) and the compounds which are
 described in German Offenlegungsschriften 2 933 563 and
 5 2 937 700 and which have two lateral cyano groups.

Especially suitable compounds which can be used in admixture
 with one or more compounds of formula I are, however,
 the dicyanophenyl esters of the general formula

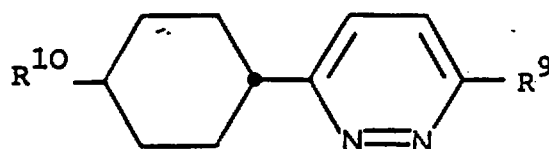


XXIII

15

wherein R^4 and R^5 signify straight-chain
 alkyl groups containing 1 to 8 carbon
 atoms and ring C denotes p-phenylene or a
 trans-1,4-disubstituted cyclohexane ring,

20 and especially the cyclohexylpyridazines of the general
 formula



XXIV

25

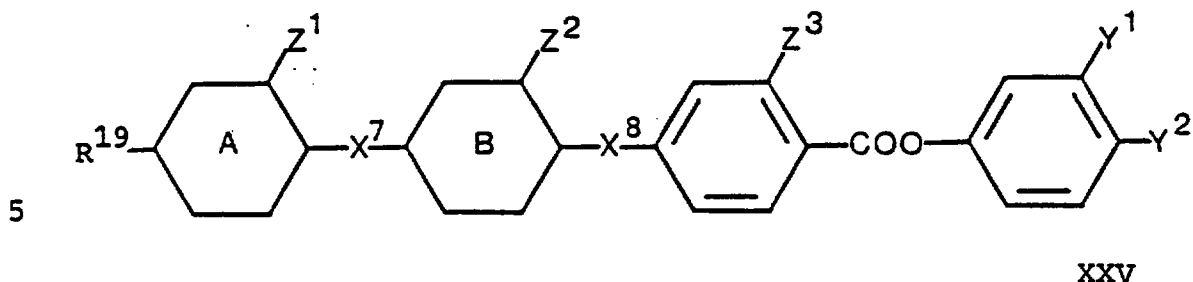
wherein R^{10} signifies a straight-chain
 alkyl group containing 1 to 12 carbon

atoms, R^9 represents an alkyl, 1-alkynyl, alkoxy, p-alkylphenyl, p-alkoxyphenyl or trans-4-alkylcyclohexyl group, the alkyl and alkoxy groups in R^9 are straight-chain groups containing 1 to 10 carbon atoms and the 1-alkynyl group in R^2 is a straight-chain group containing 2 to 10 carbon atoms.

Under the aforementioned "dielectric anisotropy" of component B there is to be understood in the case of non-liquid crystalline components the extrapolated value (from liquid crystalline mixtures which contain this component) of the dielectric anisotropy at a temperature which lies 10°C below the extrapolated (virtual) clearing point. For example, the compounds of formula I above have dielectric anisotropies of about -15 and the compounds of formula XXIV above have dielectric anisotropies of about -9.

For or as component C there are suitable, for example, compounds containing three or four p-phenylene or trans-1,4-cyclohexylene groups, a polar end group and optionally a lateral halogen or cyano substituent. Such compounds are partly known and are described, for example, in Mol. Cryst. Liq. Cryst. 63, 129 (1981) and German Offenlegungsschriften 2 736 772, 2 752 975 and 3 046 872.

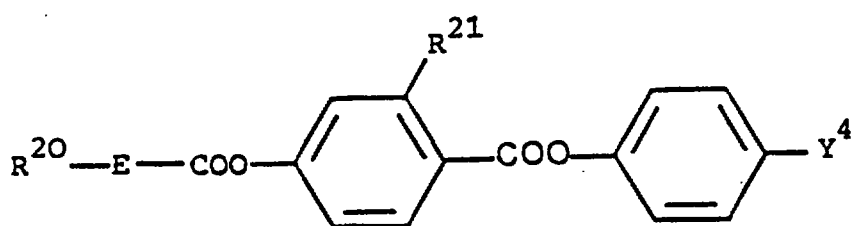
Especially suitable compounds for component C are the compounds of the general formula



wherein X^8 denotes a single covalent bond
 or the ester group $-COO-$; X^7 signifies
 10 a single covalent bond, the ester group
 $-COO-$, the ethylene group $-CH_2CH_2-$ or, in-
 sofar as X^8 denotes the ester group $-COO-$,
 also $p-C_6H_4-$, $p-C_6H_4-CH_2CH_2-$, $-CH_2CH_2-p-C_6H_4-$,
 $p-C_6H_4-COO-$ or $-COO-p-C_6H_4-$ ($p-C_6H_4-$ standing
 15 for p-phenylene); ring A stands for a benzene
 ring or for trans-1,4-cyclohexylene; ring B
 represents a benzene ring or, insofar as X^8
 denotes the ester group $-COO-$ and X^7 denotes
 a single covalent bond, the ester group $-COO-$
 20 or the ethylene group $-CH_2CH_2-$, also trans-
 -1,4-cyclohexylene; the symbols Z^1 , Z^2 and Z^3
 signify hydrogen or on a benzene ring which is
 not linked directly with a further ring via a
 single covalent bond also halogen, cyano or
 25 methyl; Y^2 represents cyano, nitro or 2,2-
 -dicyanovinyl or, insofar as Y^1 stands for
 hydrogen, also 2,2-dicyano-1-methylvinyl;

Y¹ denotes halogen, cyano, C₁-C₃-alkyl or, insofar as X⁷ has a benzene ring or an ester group or Y² stands for nitro or Z¹ and/or Z² are/is different from hydrogen, also hydrogen; and R¹⁹ signifies C₁-C₁₂-alkyl or on a benzene ring also C₁-C₁₂-alkoxy,

and the compounds of the general formula



XXVI

wherein R²¹ denotes hydrogen, fluorine, chlorine, bromine or the cyano group, Y⁴ represents 2,2-dicyanovinyl, 2,2-dicyano-1-methylvinyl or cyano, R²⁰ and E together signify p-R²⁰-phenyl, trans-4-R²⁰-cyclohexyl, 4'-R²⁰-4-biphenylyl, p-(trans-4-R²⁰-cyclohexyl)phenyl, p-(5-R²⁰-2-pyrimidinyl)phenyl, p-[2-(p'-R²⁰-phenyl)-ethyl]phenyl, p-[2-(trans-4-R²⁰-cyclohexyl)-ethyl]phenyl, trans-4-[2-(p-R²⁰-phenyl)-ethyl]cyclohexyl or trans-4-[2-(trans-4-R²⁰-cyclohexyl)ethyl]cyclohexyl, and R²⁰ denotes

a straight-chain alkyl group containing
1 to 12 carbon atoms or on a benzene ring
also a straight-chain alkoxy group con-
5 taining 1 to 12 carbon atoms.

These compounds have large nematic mesophase ranges, low
cross-over frequencies and large absolute dielectric aniso-
tropies. The term "halogen" above stands for fluorine,
chlorine or bromine, preferably for chlorine.

10

The mixtures with negative
dielectric anisotropy conveniently contain, in addition to
one or more compounds of formula I one or more additional
compounds with negative and/or small positive anisotropy
15 of the dielectric constants (compounds with positive
dielectric anisotropy should in the use discussed herein be
used in accordance with definition only in amounts which do
not leave the anisotropy of the total mixture positive). The
carrier material (remaining mixture without the compounds
20 of formula I) conveniently has a dielectric anisotropy of
at most about +1. Examples of preferred mixture components
are the compounds named above in connection with components
A and B and especially the compounds of formulae IX-XII, XV,
XX, XXI, XXIII and XXIV.

25

The mixtures provided by the invention can also con-
tain optically active compounds (e.g. optically active
biphenyls) and/or dichroic colouring substances (e.g. azo,

azoxy or anthraquinone colouring substances), in the case of the mixtures for the two-frequency addressing as ingredients of components A, B and C depending on properties.

5 The amount of such compounds is determined by the solubility, the desired pitch, colour, extinction and the like. Preferably, the amount of optically active compounds amounts to at most about 4 wt.% and the amount of dichroic colouring substance amounts to at most about 10 wt.%, these per-

10 centages being based on the total mixture.

The manufacture of the liquid crystalline mixtures provided by the invention can be carried out in a manner known per se; for example, by heating a mixture of the

15 ingredients to a temperature barely above the clearing point and subsequently cooling down.

The manufacture of an electro-optical device containing a mixture provided by the invention can also be

20 carried out in a manner known per se; for example, by evacuating a suitable cell and introducing the mixture into the evacuated cell.

The compounds of formula XX are novel. They can be

25 prepared as illustrated in the following Reaction Schemes 1 and 2 in which R^{15} represents trans-4-alkylcyclohexyl, 4'-alkyl-4-biphenyl, p-(trans-4-alkylcyclohexyl)phenyl or 2-(trans-4-alkylcyclohexyl)ethyl and R^{16} represents trans-

-4-alkylcyclohexyl, or R^{15} represents trans-4-alkylcyclohexyl and R^{16} represents p-(trans-4-alkylcyclohexyl)phenyl, p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl or 4'-(trans-
5 -4-alkylcyclohexyl)-4-biphenyl, or R^{15} represents p-alkylphenyl and R^{16} represents p-[2-(trans-4-alkylcyclohexyl)ethyl]phenyl, and R^{13} and R^{14} as well as the alkyl groups in the substituents R^{15} and R^{16} are straight-chain alkyl groups containing 1 to 7 carbon atoms.

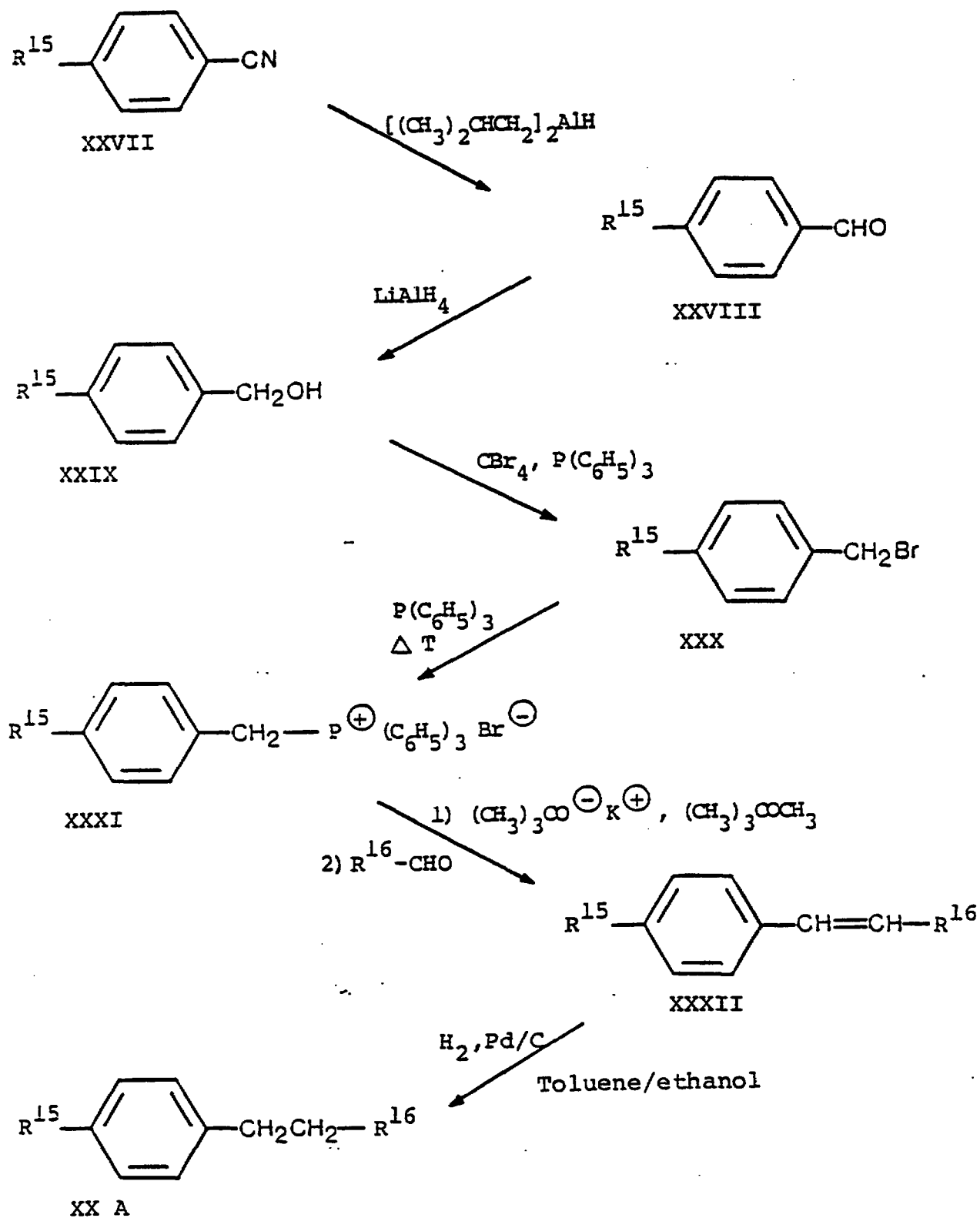
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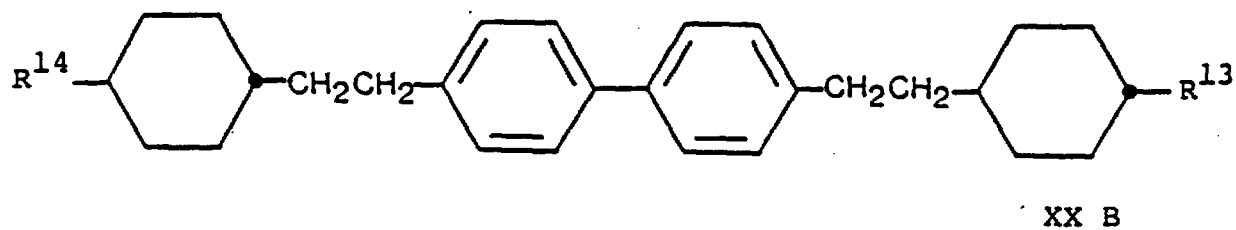
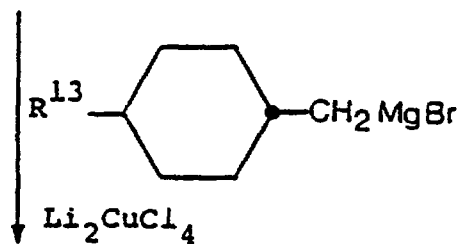
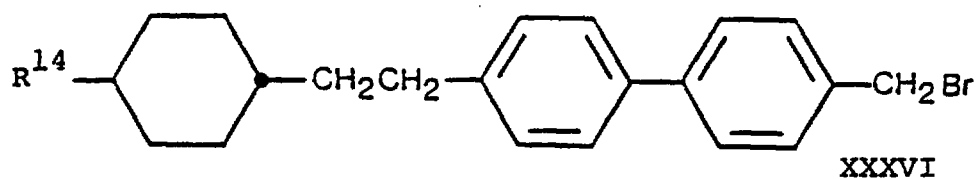
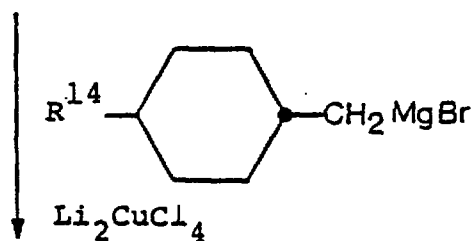
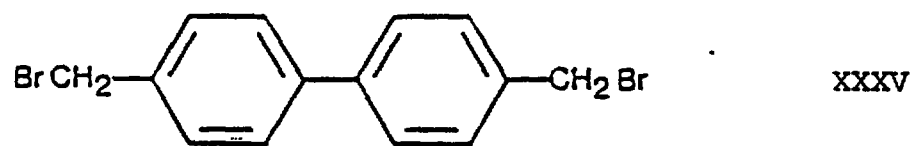
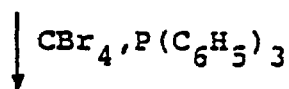
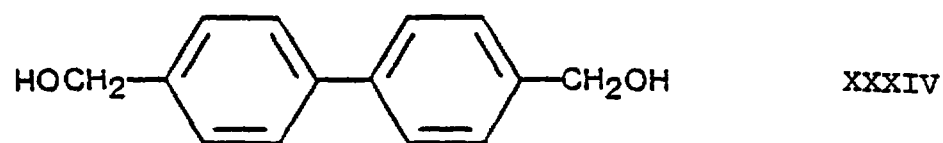
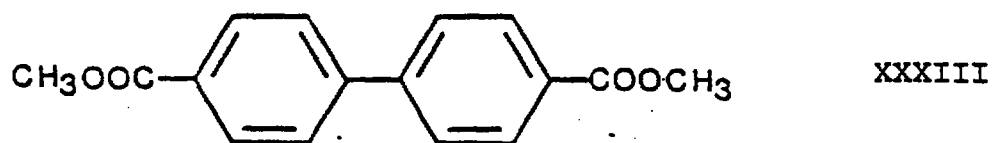
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25

Scheme 1



Scheme 2



The compounds of formula R^{16} -CHO in Scheme 1 can be obtained in a simple manner from known compounds; for example, the trans-4-alkylcyclohexanecarboxaldehydes can be
5 obtained by Rosenmund reduction of the corresponding acid chlorides and the remaining compounds can be obtained by reducing the corresponding cyano compounds.

By reacting the compound of formula XXXV with Grignard
10 reagents in accordance with Scheme 2 there can be obtained compounds of formula XXXVI or directly compounds of formula XXB in which R^{13} and R^{14} have the same significance. When at least about 2 mol of Grignard reagent are used per mol of the compound of formula XXXV there is generally pre-
15 dominantly formed directly a compound of formula XXB.

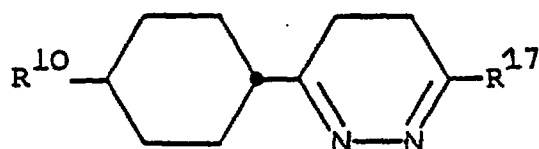
The esters of formula XXI are also novel. They can be obtained according to esterification methods known per se (e.g. in an analogous manner to the preparation of the
20 compounds of formula XXV described below). The starting materials required for the preparation of the esters of formula XXI are known or are analogues of known compounds and can be prepared according to known methods.

25 The compounds of formula XXIV are also novel. They can be prepared in a manner known per se by

(a) for the preparation of the compounds of formula XXIV in which R^9 represents an alkyl, p-alkylphenyl, p-alkoxy-

phenyl or trans-4-alkylcyclohexyl group, subjecting a compound of the general formula

5



XXXVII

10 wherein R^{17} represents an alkyl, p-alkyl-phenyl, p-alkoxyphenyl or trans-4-alkylcyclohexyl group, the alkyl and alkoxy groups in R^{17} are straight-chain groups containing 1 to 10 carbon atoms and R^{10} has the above significance,

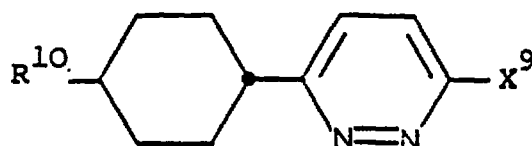
15

or a tautomeric dihydropyridazine to oxidation (e.g. with 2,3-dichloro-5,6-dicyano-p-benzoquinone in dioxan, with sodium nitrite in glacial acetic acid and ethanol, with isopentyl nitrite in glacial acetic acid or preferably by

20 catalytic dehydrogenation with palladium, platinum and the like), or

(b) for the preparation of the compounds of formula XXIV in which R^9 represents an alkoxy group, reacting a compound

25 of the general formula



XXXVIII

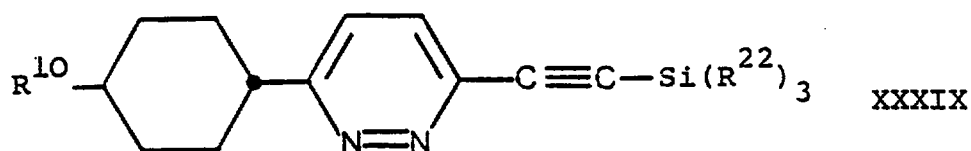
wherein X^9 denotes chlorine or bromine and
 R^{10} has the above significance,

with an alkali metal alcoholate (e.g. sodium methyllate), or

5

(c) for the preparation of the compounds of formula XXIV
 in which R^9 represents the ethynyl group, reacting a com-
 pound of the general formula

10



15

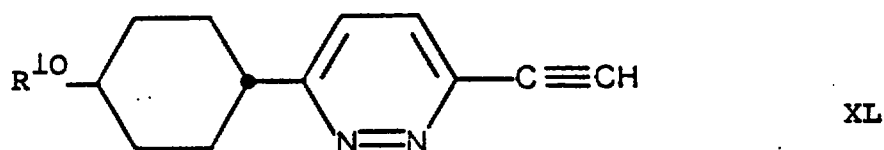
wherein R^{22} denotes an alkyl group containing
 1 to 5 carbon atoms and R^{10} has the above
 significance,

with a base (e.g. potassium hydroxide, sodium hydroxide or
 butyl lithium), or

20

(d) for the preparation of the compounds of formula XXIV
 in which R^9 represents a 1-alkynyl group containing 3 to 10
 carbon atoms, converting a compound of the general formula

25

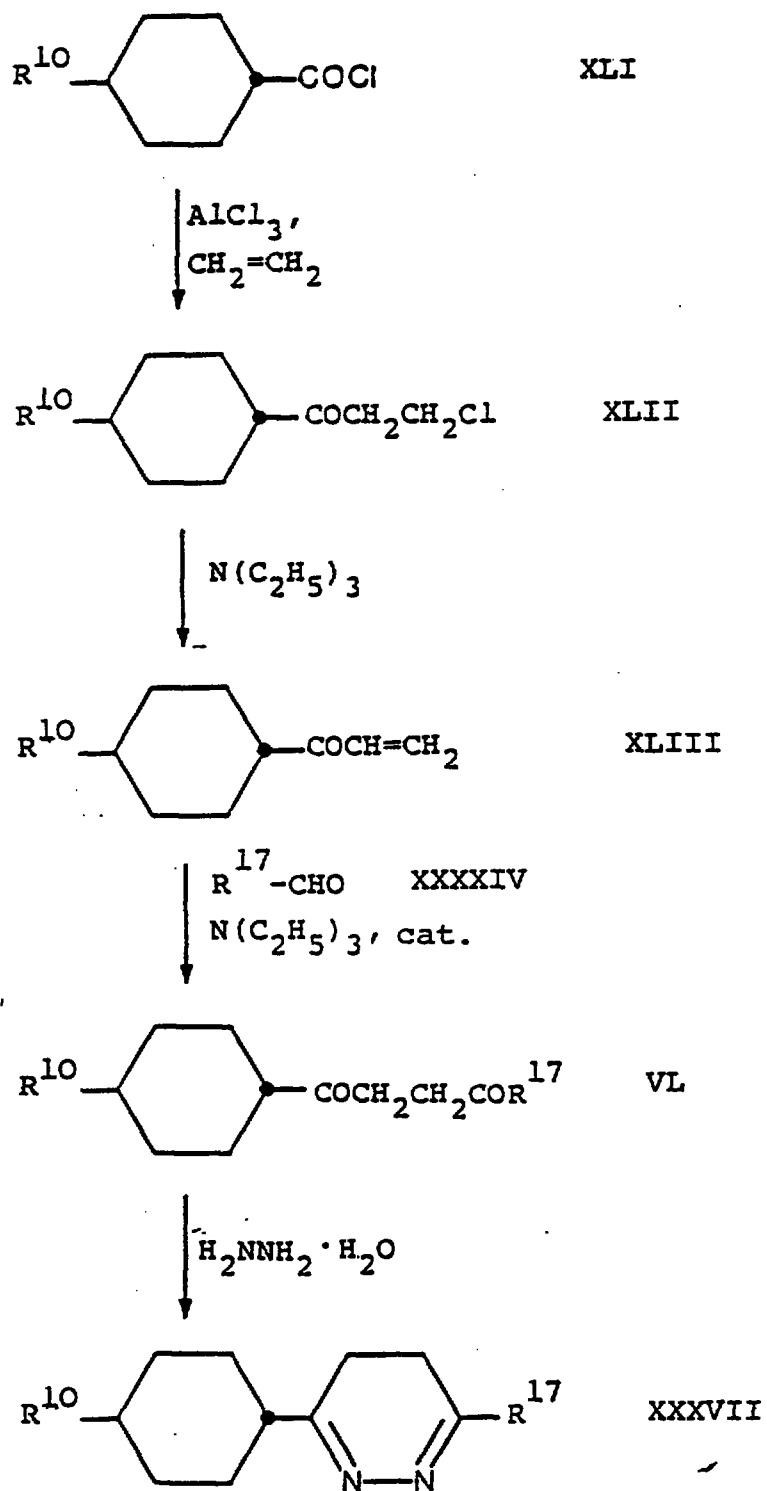


wherein R^{10} has the above significance,
with a base (e.g. butyl lithium, methyl lithium, sodium
amide or lithium diisopropylamide) into the corresponding
5 ethynylide and alkylating the ethynylide with an alkyl
bromide or alkyl iodide.

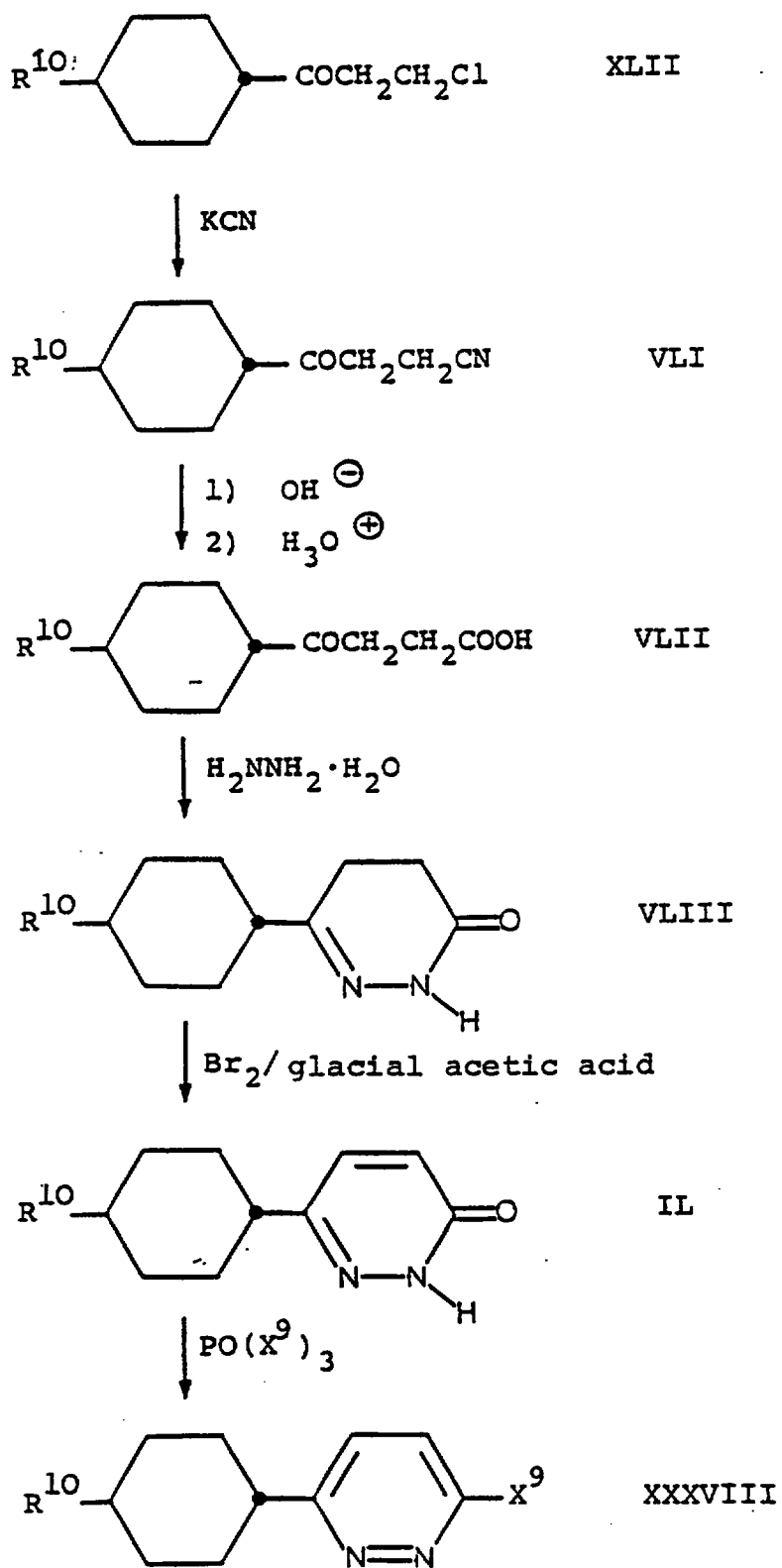
The compounds of formula XXXVII can rearrange to
tautomeric compounds by migration of the double bonds in
10 the dihydropyridazine ring. Such rearrangements can be
brought about, for example, by the presence of a trace of
acid or base. Since the tautomeric dihydropyridazines can,
however, also be oxidized under the above conditions to
compounds of formula XXIV, not only a compound of formula
15 XXXVII but also a tautomeric dihydropyridazine or a mixture
of such compounds can be reacted in accordance with
variant (a).

The starting materials of formulae XXXVII and XXXVIII
20 are novel. They can be prepared as illustrated in the
following Reaction Schemes 3-6 in which R^{10} , R^{17} and X^9 have
the above significances and R^{18} represents a straight-chain
alkyl or alkoxy group containing 1 to 10 carbon atoms.

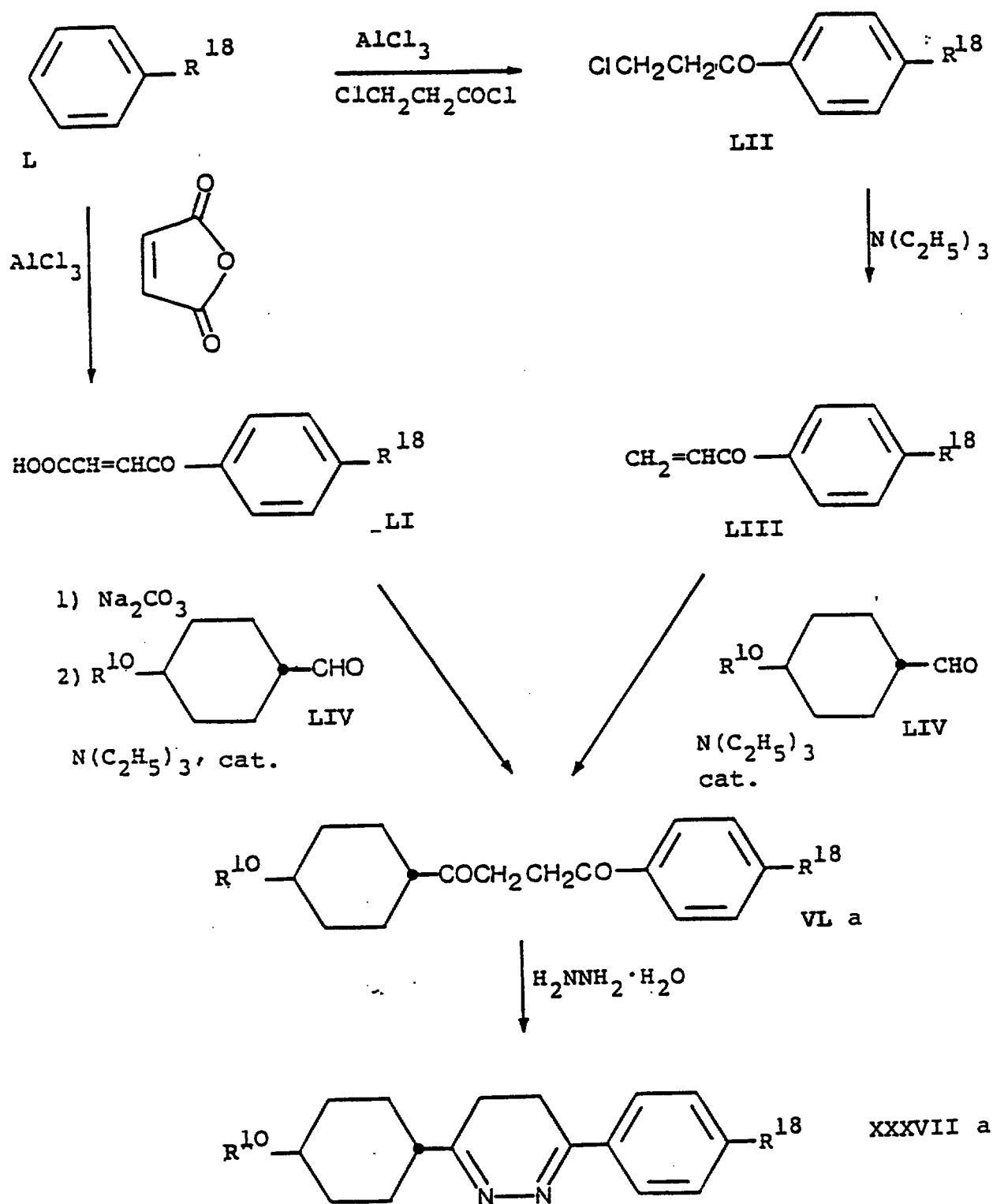
Scheme 3



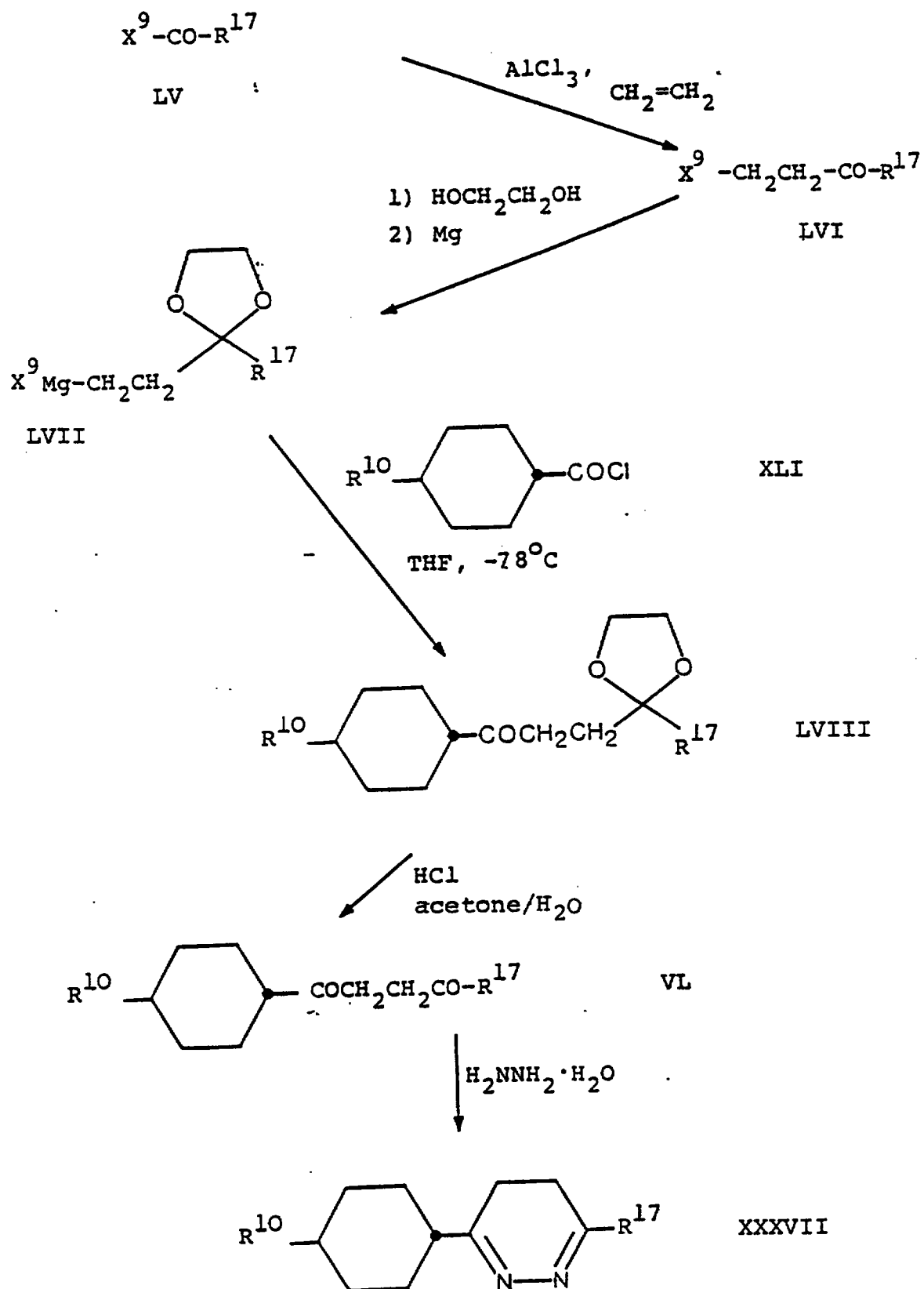
Scheme 4



Scheme 5



Scheme 6



The starting materials of formulae XLI, XXXXIV, L, LIV and LV are known or are analogues of known compounds and can be prepared in a known manner. For example, the
5 aldehydes of formula LIV can be prepared by Rosenmund reduction of the acid chlorides of formula XLI.

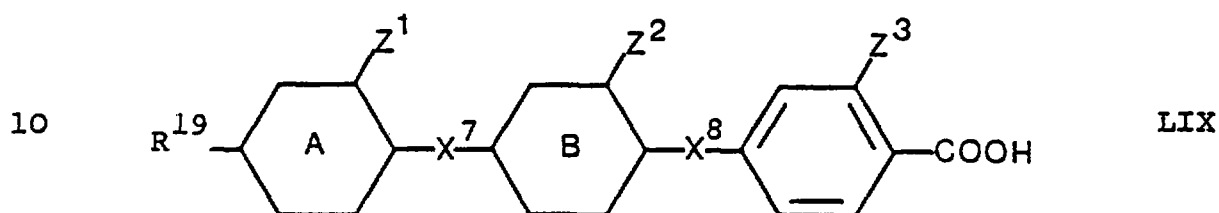
The addition of an aldehyde to a compound of formula XLIII, LI or LIII can be carried out according to the method
10 of Stetter (Chem. Ber. 114 (1981) 581) in the presence of a 1,3-thiazolium salt catalyst. 3-Benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride is the preferred catalyst for the addition of an aldehyde of formula LIV or of an
aldehyde of formula XXXXIV in which R¹⁷ signifies alkyl or
15 trans-4-alkylcyclohexyl and 3,4-dimethyl-5-(2-hydroxyethyl)-1,3-thiazolium iodide is the preferred catalyst for the addition of an aldehyde of formula XXXXIV in which R¹⁷ signifies p-alkylphenyl or p-alkoxyphenyl.

20 The coupling of a compound of formula LVII with a compound of formula XLI can be carried out according to the method of T. Sato et al., Bull. Chem. Soc. Japan 54 (1981) 505.

25 The compounds of formula XXXIX are also novel. They can be obtained in a manner known per se by reacting a compound of formula XXXVIII with an ethynyl-trialkylsilane in the presence of triethylamine, bis-(triphenylphosphine)-

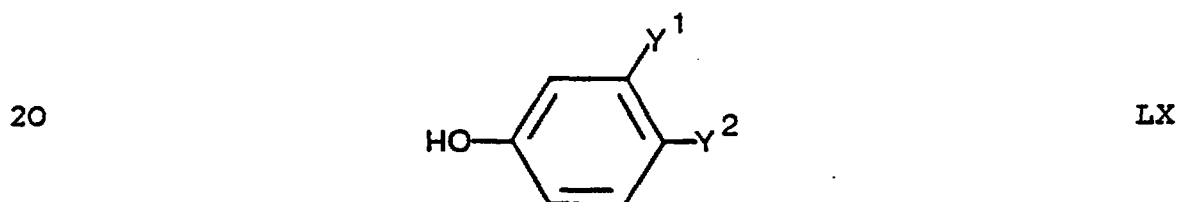
-palladium (II) dichloride and copper (I) iodide.

The compounds of formula XXV are also novel. They
5 can be prepared in a manner known per se by esterifying
the acid chloride of a compound of the general formula



wherein R^{19} , A, B, X^7 , X^8 , Z^1 , Z^2 and Z^3
15 have the significances given in formula
XXV,

with a phenol of the general formula



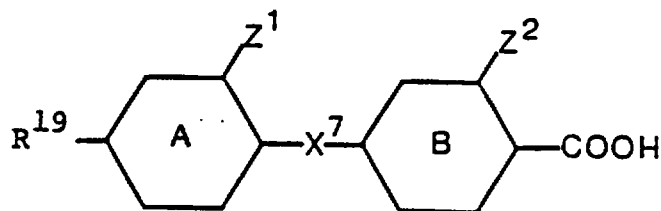
wherein Y^1 and Y^2 have the significance
given in formula XXV,

25 and, if desired, reacting a compound of formula XXV obtained
in which Z^1 , Z^2 or Z^3 signifies bromine with copper (I)
cyanide, sodium cyanide or potassium cyanide.

The compounds of formula LX in which Y^2 signifies 2,2-dicyanovinyl can be prepared, for example, by converting 3- Y^1 -anisole into 4-methoxy-2- Y^1 -benzaldehyde by a Vilsmeier reaction with dimethylformamide in the presence of phosphorus oxychloride, then hydrolyzing the methoxy group (e.g. by heating under reflux with pyridinium chloride and subsequent fractional distillation) and finally converting the 4-hydroxy-2- Y^1 -benzaldehyde obtained into the compound of formula IV in which Y^2 signifies 2,2-dicyanovinyl by a Knoevenagel condensation with malononitrile (e.g. in the presence of catalytic amounts of glacial acetic acid and sodium acetate in boiling toluene). The remaining compounds of formula LX are known or are analogues of known compounds.

The compounds of formula LIX are also known or are analogues of known compounds and can be prepared according to known methods.

The compounds of formula LIX in which X^8 denotes the ester group $-COO-$ can be prepared, for example, by esterifying a compound of the general formula



LXI

wherein X^7 , R^{19} , A, B, Z^1 and Z^2 have
the significances given in formula XXV,
with 4-hydroxy-2- Z^3 -benzaldehyde in methylene chloride in
the presence of dicyclohexylcarbodiimide and 4-(dimethyl-
amino)pyridine and converting the resulting aldehyde into
the corresponding acid of formula LIX by Jones' oxidation
with chromic acid and sulphuric acid.

In the preparation of the acids of formula LIX in
which X^7 signifies $-CH_2CH_2-$, $p-C_6H_4-CH_2CH_2-$ or
 $-CH_2CH_2-p-C_6H_4-$ and X^8 signifies a single covalent bond and
of the acids of formula LXI in which X^7 signifies $-CH_2CH_2-$,
 $p-C_6H_4-CH_2CH_2-$ or $-CH_2-CH_2-p-C_6H_4-$, the linkage of rings A
and B is conveniently carried out by a Fouquet-Schlosser
reaction or by a Wittig reaction. For example, 4-(bromo-
methyl)-2- Z^2 -benzonitrile, 4'-(bromomethyl)-4-biphenyl-
carbonitrile or trans-4-(tosyloxymethyl)cyclohexanecarbo-
nitrile can be reacted with (4- R^{19} -2- Z^1 -phenyl)methyl-
magnesium bromide or (trans-4- R^{19} -cyclohexyl)methyl-
magnesium bromide in the presence of dilithium tetrachloro-
cuprate and the nitrile obtained can be hydrolyzed to the
desired acid. Further, for example, 4- R^{19} -2- Z^1 -benzaldehyde
or trans-4- R^{19} -cyclohexanecarboxaldehyde can be reacted
with (4-methoxycarbonyl-3- Z^2 -phenyl)methyl-triphenylphos-
phonium bromide (Z^1 and Z^2 signifying hydrogen, fluorine,
cyano or methyl) in the presence of a base (e.g. sodium
methyllate), then the double bond can be catalytically

hydrogenated and finally the ester group can be saponified.

5 The starting materials required for these reactions are known or can be prepared according to methods known per se. For example, 4-alkoxy-2-Z¹-acetophenone can be converted by haloform degradation into 4-alkoxy-2-Z¹-benzoic acid and this can be converted into 4-alkoxy-1-(bromo-

10 methyl)-2-Z¹-benzene by reduction with lithium aluminium hydride and bromination (e.g. with tetrabromomethane and triphenylphosphine). From methyl 2,4-dimethylbenzoate there can be obtained, for example, by reaction with N-

15 -bromosuccinimide and subsequent isomer separation methyl 4-(bromomethyl)-2-methylbenzoate which can be converted into methyl 4-formyl-2-methylbenzoate in an analogous manner to Org. Synth. Coll. V, 825; the methyl 4-alkyl-

-2-methylbenzoate obtained after reaction with alkyl-

-triphenylphosphonium bromide and base and subsequent

20 catalytic hydrogenation of the double bond can be saponified with sodium hydroxide to the acid or reduced with lithium aluminium hydride to the alcohol which finally can be converted with hydrogen bromide into 4-alkyl-1-(bromo-

methyl)-2-methylbenzene or with manganese dioxide into the

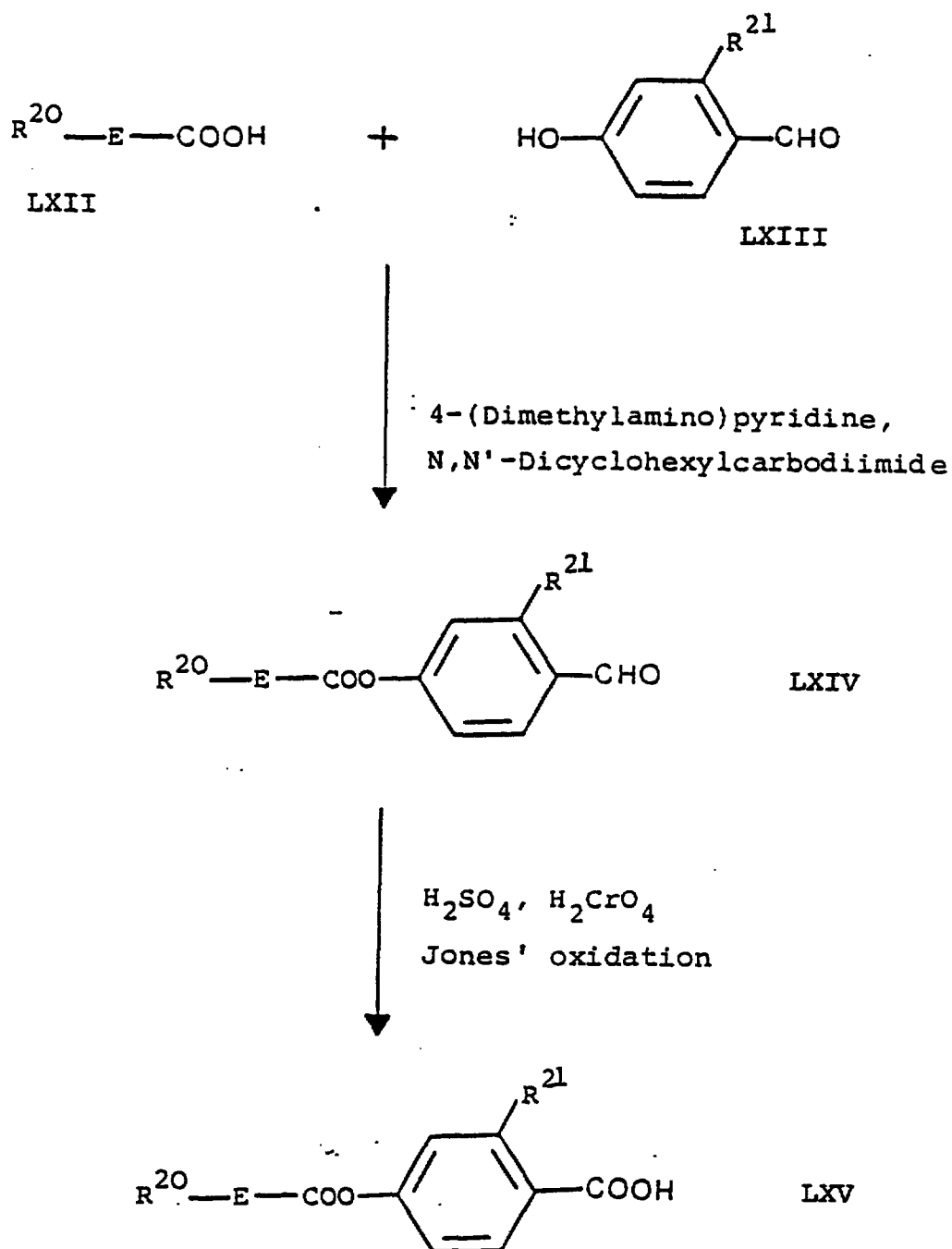
25 4-alkyl-2-methylbenzaldehyde. 1-Alkyl-3-fluorobenzene can be converted, for example, into 4-alkyl-2-fluorobenzoic acid by reaction with butyl lithium and carbon dioxide and subsequent hydrolysis and 1-alkyl-3-chlorobenzene or 1-

-alkyl-3-bromobenzene can be converted into 4-alkyl-2-

-(chloro or bromo)benzoic acid by Friedel-Crafts acylation with acetyl chloride in the presence of aluminium tri-chloride and subsequent oxidation with sodium hypobromite; 5 the acids obtained can then be converted with lithium aluminium hydride into the alcohols and these can be converted into the bromides with hydrogen bromide or into the aldehydes with manganese dioxide. Further, for example, 4-methyl-2-Z¹-benzoic acid can be reacted in sequence with 10 thionyl chloride, ammonia and benzenesulphonyl chloride and the 4-methyl-2-Z¹-benzonitrile obtained can be converted into 4-(bromomethyl)-2-Z¹-benzonitrile with N-bromosuccinimide.

15 The compounds of formula XXVI are in part also novel compounds. They can be prepared by esterification in an analogous manner to the compounds of formula XXV. The acids required for the preparation of the compounds of formula XXVI can be obtained as illustrated in Reaction 20 Scheme 7 in which R²⁰, R²¹ and E have the significances given in formula XXVI above:

Scheme 7



The compounds of formulae LXII and LXIII are known or can be prepared according to methods known per se.

5

The following mixtures are examples of preferred mixtures provided by the invention. η signifies the viscosity (bulk viscosity), f_c signifies the cross-over frequency, $\Delta\epsilon_l$ signifies the low frequency ("static") dielectric anisotropy and $\Delta\epsilon_h$ signifies the high frequency dielectric anisotropy measured at 22°C. Mixtures 1-6 have negative dielectric anisotropy and mixtures 7 and 8 are suitable for the two-frequency addressing.

Mixture 1

- 20 11.8 wt.% of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,
- 16.6 " trans-4-butylcyclohexanecarboxylic acid p-pentyloxyphenyl ester,
- 10.7 " trans-4-pentylcyclohexanecarboxylic acid p-
- 25 -methoxyphenyl ester,
- 12.8 " trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,

- 7.3 wt.% of 4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-benzene,
- 3.5 " 3-propyl-6-(trans-4-ethylcyclohexyl)pyridazine,
- 5 8.3 " 3-propyl-6-(trans-4-pentylcyclohexyl)pyridazine,
- 5.3 " 3-propyl-6-(trans-4-heptylcyclohexyl)pyridazine,
- 10.7 " 3-pentyl-6-(trans-4-pentylcyclohexyl)pyridazine,
- 8.7 " 4'-(trans-4-pentylcyclohexyl)-4-[2-(trans-4-butylcyclohexyl)ethyl]biphenyl,
- 10 4.3 " 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-ethyl]-4-propylbenzene;
- m.p. -12°C, cl.p. 60°C, nematic; $\eta = 40$ cp, $\Delta\epsilon_1 = -5.07$.

Mixture 2

- 15 5.6 wt.% of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,
- 5.1 " trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
- 20 9.8 " trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
- 12.7 " 4-ethoxy-1-[2-(trans-4-propylcyclohexyl)-ethyl]-benzene,
- 14.6 " 4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-benzene,
- 25 10.3 " 1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene,
- 3.4 " 3-propyl-6-(trans-4-ethylcyclohexyl)pyridazine,

- 8.2 wt.% of 3-propyl-6-(trans-4-pentylcyclohexyl)pyridazine,
 5.2 " 3-propyl-6-(trans-4-heptylcyclohexyl)pyridazine,
 10.5 " 3-pentyl-6-(trans-4-pentylcyclohexyl)pyridazine,
 5 10.3 " 4'-(trans-4-pentylcyclohexyl)-4-[2-(trans-4-
 -butylcyclohexyl)ethyl]biphenyl,
 4.3 " 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
 ethyl]-4-propylbenzene;

m.p. < 0°C, cl.p. 57.8°C, nematic; $\eta = 31.9$ cp, $\Delta\epsilon_1 = -4.69$.

10

Mixture 3

- 16.5 wt.% of trans-4-butylcyclohexanecarboxylic acid p-
 -ethoxyphenyl ester,
 15 23.3 " trans-4-butylcyclohexanecarboxylic acid p-
 -pentyloxyphenyl ester,
 15.0 " trans-4-pentylcyclohexanecarboxylic acid p-
 -methoxyphenyl ester,
 18.0 " trans-4-pentylcyclohexanecarboxylic acid p-
 -propyloxyphenyl ester,
 20 10.2 " 4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-
 benzene,
 7.0 " 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
 ethyl]-4-propylbenzene,
 25 10.0 " 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
 ethyl]-4-butylbenzene;

m.p. < 0°C, cl.p. 49°C, nematic; $\eta = 45$ cp, $\Delta\epsilon_1 = -4.01$.

Mixture 4

5	10.9	wt.% of trans-4-butylcyclohexanecarboxylic acid p-
		-ethoxyphenyl ester,
	15.4	" trans-4-butylcyclohexanecarboxylic acid p-
		-pentyloxyphenyl ester,
	9.9	" trans-4-pentylcyclohexanecarboxylic acid p-
		-methoxyphenyl ester,
10	11.9	" trans-4-pentylcyclohexanecarboxylic acid p-
		-propyloxyphenyl ester,
	6.7	" 4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)-
		ethyl]benzene,
	9.6	" 1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-
15		-4-pentylcyclohexyl)benzene,
	7.7	" 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-
		-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,
	3.9	" 4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-
		-4-pentylcyclohexyl)biphenyl,
20	9.6	" 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
		ethyl]-4-propylbenzene,
	14.4	" 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
		ethyl]-4-butylbenzene;

m.p. <0°C, cl.p. 61.5°C, nematic; $\eta = 67.9$ cp, $\Delta\epsilon_1 = -5.22$.

25

Mixture 5

12.3 wt.% of trans-4-butylcyclohexanecarboxylic acid p-
-ethoxyphenyl ester,

	17.4	wt. %	of. trans-4-butylcyclohexanecarboxylic acid p-
			-pentyloxyphenyl ester,
	11.2	"	trans-4-pentylcyclohexanecarboxylic acid p-
5			-methoxyphenyl ester,
	13.5	"	trans-4-pentylcyclohexanecarboxylic acid p-
			-propyloxyphenyl ester,
	7.6	"	4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)-
			ethyl]benzene,
10	10.0	"	1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-
			-4-pentylcyclohexyl)benzene,
	8.0	"	4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-
			-4-pentylcyclohexyl)-1,1'-ethylenedibenzene,
	8.0	"	2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
15			ethyl]-4-propylbenzene,
	12.0	"	2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
			ethyl]-4-butylbenzene;

m.p. <0°C, cl.p. 65.4°C, nematic; $\eta = 47$ cp, $\Delta\epsilon_1 = -3.71$.

20 Mixture 6

	11.58	wt. %	of trans-4-butylcyclohexanecarboxylic acid p-
			-ethoxyphenyl ester,
	16.31	"	trans-4-butylcyclohexanecarboxylic acid p-
25			-pentyloxyphenyl ester,
	10.47	"	trans-4-pentylcyclohexanecarboxylic acid p-
			-methoxyphenyl ester,
	12.64	"	trans-4-pentylcyclohexanecarboxylic acid p-
			-propyloxyphenyl ester,

	7.12	wt. %	of 4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)-ethyl]benzene,
5	10.26	"	4-[2-(trans-4-butylcyclohexyl)ethyl]-4'-(trans-4-pentylcyclohexyl)biphenyl,
	3.38	"	3-propyl-6-(trans-4-ethylcyclohexyl)pyridazine,
	8.21	"	3-propyl-6-(trans-4-pentylcyclohexyl)pyridazine,
10	10.51	"	3-pentyl-6-(trans-4-pentylcyclohexyl)pyridazine,
	5.25	"	3-propyl-6-(trans-4-heptylcyclohexyl)pyridazine,
	4.27	"	2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-ethyl]-4-propylbenzene;
15	m.p. < -10°C, cl.p. 61.5°C, nematic; $\eta = 42.8$ cp, $\Delta\epsilon_1 = -5.05$.		

Mixture 7

20	12.9	wt. %	of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,
	18.3	"	trans-4-butylcyclohexanecarboxylic acid p-pentyloxyphenyl ester,
	11.7	"	trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
25	14.1	"	trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
	8.0	"	4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-benzene,

		9.0 wt. % of 4'-(trans-4-pentylcyclohexyl)-4-biphenyl-carboxylic acid 3-chloro-4-[(3-chloro-4-nitrophenoxy)carbonyl]phenyl ester,
5	9.0 "	4'-(trans-4-heptylcyclohexyl)-4-biphenyl-carboxylic acid 3-chloro-4-[(3-chloro-4-nitrophenoxy)carbonyl]phenyl ester,
	7.0 "	2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-ethyl]-4-propylbenzene,
10	10.0 "	2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-ethyl]-4-butylbenzene;
m.p. <0°C, cl.p. 76.6°C, nematic; $f_c = 440$ Hz, $\Delta\epsilon_1 = +5.2$, $\Delta\epsilon_h = -5.0$.		
15	<u>Mixture 8</u>	
	6.8 wt. % of trans-4-butylcyclohexanecarboxylic acid p-ethoxyphenyl ester,	
	9.7 "	trans-4-butylcyclohexanecarboxylic acid p-pentyloxyphenyl ester,
20	6.3 "	trans-4-pentylcyclohexanecarboxylic acid p-methoxyphenyl ester,
	11.2 "	trans-4-pentylcyclohexanecarboxylic acid p-propyloxyphenyl ester,
25	16.4 "	4-ethoxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-benzene,
	11.1 "	1-[2-(trans-4-butylcyclohexyl)ethyl]-4-(trans-4-pentylcyclohexyl)benzene,
	4.5 "	4'-hexyl-4-biphenylcarboxylic acid 3-chloro-4-

-[(3-chloro-4-cyanophenoxy) carbonyl] phenyl
ester,

4.5 wt.% of 4'-heptyl-4-biphenylcarboxylic acid 3-chloro-
5 -4-[(3-chloro-4-cyanophenoxy) carbonyl] phenyl
ester,

4.5 " 4'-hexyl-4-biphenylcarboxylic acid 3-chloro-
-4-[(3-chloro-4-nitrophenoxy) carbonyl] phenyl
ester,

10 4.5 " 4'-heptyl-4-biphenylcarboxylic acid 3-chloro-4-
-[(3-chloro-4-nitrophenoxy) carbonyl] phenyl
ester,

8.2 " 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
ethyl]-4-propylbenzene,

15 12.3 " 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)-
ethyl]-4-butylbenzene;

m.p. <0°C, cl.p. 65.5°C, nematic; $f_c = 3.6$ kHz, $\Delta\epsilon_1 = +6.11$,
 $\Delta\epsilon_h = -5.40$.

20

25

The following Examples illustrate the manufacture of the compounds of the above formula I:

5

Example 1

A solution (50 ml) of 19.5 g of 4-butyloxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-1,4-cyclohexadiene in tetrahydrofuran was placed in a round flask under nitrogen gasification and treated while stirring with a solution of 50 mg of 2,3-dichloromaleic anhydride and 4.1 g of dicyanoacetylene in 50 ml of tetrahydrofuran. The mixture was stirred at room temperature for 24 hours and then evaporated in vacuo. The resulting dark brown oil (30.7 g) was chromatographed on silica gel using methylene chloride and methylene chloride/1% acetone as the eluent. There were thus obtained 15.7 g of dark brown oil which was heated continuously up to 125°C within 1 hour. The residue (15.2 g) was chromatographed on silica gel using toluene as the eluent. There could thus be isolated 11.7 g of a brown solid residue which was dissolved in diethyl ether, treated with active carbon and filtered. After repeated recrystallization (from diethyl ether/hexane, acetone/isopropanol and isopropanol) and chromatographic working-up of the mother liquors, there were finally obtained 5.4 g of pure 4-butyloxy-2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)ethyl]benzene; m.p. 145.1°C.

The 4-butyloxy-1-[2-(trans-4-pentylcyclohexyl)-ethyl]-1,4-cyclohexadiene used as the starting material was prepared as follows:

5

1306 ml of liquid ammonia were placed in a sulphonation flask and then a solution of 38.4 g of 4-butyloxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]benzene in 1.1 l of diethyl ether was added dropwise within 40 minutes while
10 cooling. 23.3 g of lithium wire were subsequently added within 35 minutes and the mixture was stirred for 2 hours. 420 ml of ethanol were then added dropwise to the mixture within 70 minutes and the ammonia was allowed to evaporate overnight under nitrogen. The mixture was cooled
15 to 10°C and 1.5 l of water were then added dropwise within 35 minutes in such a manner that the temperature did not rise above 10°C. The mixture was extracted three times with 0.5 l of diethyl ether each time. The organic phases were washed twice with 0.5 l of water each time, dried over
20 potassium carbonate, filtered and concentrated, there being obtained 39.0 g of 4-butyloxy-1-[2-(trans-4-pentylcyclohexyl)ethyl]-1,4-cyclohexadiene as a colourless crystallizing oil.

25

Example 2

7.4 g of 1,2-dicyano-3-[2-(trans-4-pentylcyclohexyl)-ethyl]-6-propyl-1,4-cyclohexadiene were dissolved in 100 ml

of dioxan in a round flask in an oil-bath (120°C), the solution was treated with 4.76 g of 2,3-dichloro-5,6-dicyano-p-benzoquinone and the mixture was boiled under reflux for 2.5 hours. The mixture was subsequently cooled to room temperature and the resulting precipitate was filtered off under suction and rinsed with dioxan and diethyl ether. The filtrate was concentrated in vacuo. The brown solid residue (9.9 g) was chromatographed on silica gel using toluene/hexane (volume ratio 1:1) and toluene as the eluent. The isolated crude product (7.0 g) was recrystallized several times (from hexane and isopropanol), there being finally obtained 2.3 g of pure 2,3-dicyano-1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-propylbenzene; m.p. 83.6°C.

The 1,2-dicyano-3-[2-(trans-4-pentylcyclohexyl)ethyl]-6-propyl-1,4-cyclohexadiene used as the starting material was prepared as follows:

20

(a) 20.4 g of trans-4-pentylcyclohexanecarboxaldehyde were dissolved in 500 ml of benzene in a round flask under nitrogen and treated with 49.5 g of the phosphorane $(C_6H_5)_3P=CHCOOC_2H_5$ [Helv. Chim. Acta 40, 1242 (1957)]. The mixture was heated to boiling, boiled at reflux for 6 hours under nitrogen and left to stand overnight. After concentration in vacuo, there were obtained 73.2 g of yellowish semi-solid residue. Chromatography of the residue on silica

gel using toluene/hexane (volume ratio 1:1) and toluene finally gave 27.7 g of ethyl β -(trans-4-pentylcyclohexyl)-acrylate as an almost colourless oil; b.p. 104-116°C/
5 0.07 mmHg.

(b) 41.6 g of ethyl β -(trans-4-pentylcyclohexyl)acrylate were dissolved in 368 ml of ethanol, treated with 7.4 g of palladium/carbon (5%) and hydrogenated at room temperature
10 and under normal pressure until the hydrogen uptake came to a standstill (hydrogen uptake 0.167 mol). The mixture was gassed with nitrogen and filtered (rinsing with ethanol and methylene chloride). Concentration of the filtrate in vacuo gave 38.4 g of ethyl β -(trans-4-pentylcyclohexyl)-
15 propionate as a colourless oil which was distilled in a high vacuum; b.p. 113-121°C/0.05-0.06 mmHg.

(c) 250 ml of absolute diethyl ether were placed in a sulphonation flask under nitrogen gasification and treated
20 cautiously with 3.9 g of lithium aluminium hydride. A solution of 46.9 g of ethyl β -(trans-4-pentylcyclohexyl)-propionate in 200 ml of absolute diethyl ether was added dropwise thereto within 50 minutes. A further 250 ml of absolute diethyl ether were then added thereto and the
25 mixture was stirred overnight. Subsequently, there were added dropwise to the mixture within 10 minutes 21 ml of water and then 210 ml of 10% sulphuric acid. The aqueous phase was separated and extracted twice with diethyl ether.

The combined organic phases were washed once with water and once with saturated sodium chloride solution, dried over sodium sulphate and evaporated. There were obtained 39.2 g of 3-(trans-4-pentylcyclohexyl)-1-propanol as a colourless oil.

(d) 70.2 g of pyridinium chlorochromate were suspended in 506 ml of methylene chloride in a sulphonation flask under nitrogen gasification and then treated while stirring well within 5 minutes through a dropping funnel with a solution of 39.2 g of 3-(trans-4-pentylcyclohexyl)-1-propanol in 60 ml of methylene chloride. The dropping funnel was rinsed with 20 ml of methylene chloride and then the mixture was stirred at room temperature and under nitrogen gasification for 2.5 hours. Thereafter, 225 ml of absolute diethyl ether were added and the mixture was stirred at room temperature for a further 15 minutes. The supernatant solution was decanted off from the viscous black precipitate and the sulphonation flask was rinsed four times with 110 ml of absolute diethyl ether each time. The combined organic phases were chromatographed using diethyl ether as the eluent. The greenish oil (34.1 g) obtained after evaporation in vacuo was distilled in a high vacuum under nitrogen, there being obtained 28.1 g of 3-(trans-4-pentylcyclohexyl)propionaldehyde as a colourless crystallizing oil (b.p. 90-99°C/0.08-0.1 mmHg).

(e) 58.2 g of trans-2-hexenyl-triphenylphosphonium bromide were suspended in 219 ml of absolute diethyl ether in a sulphonation flask under nitrogen gasification, cooled to 1°C and treated dropwise within 25 minutes at 1-4°C through a dropping funnel with 89.4 ml of a 1.6M solution of butyl lithium in hexane and with 41 ml of absolute diethyl ether. The dropping funnel was rinsed with 17 ml of absolute diethyl ether and the mixture was stirred at 0°C for 30 minutes. A solution of 28.1 g of 3-(trans-4-pentylcyclohexyl)propionaldehyde in 68.5 ml of absolute diethyl ether was subsequently added dropwise within 30 minutes at 3-4°C through the dropping funnel and the dropping funnel was then rinsed with 17 ml of absolute diethyl ether. The suspension obtained was stirred at 0°C for a further 2 hours and at room temperature for 1 hour, then rinsed into a round flask with diethyl ether and concentrated in vacuo. The residue was rinsed with 410 ml of methanol/water (volume ratio 6:4) into a separating funnel and extracted three times with hexane. The hexane phases were washed once with 410 ml of methanol/water (volume ratio 6:4) and twice with 250 ml of water each time, dried over sodium sulphate and evaporated. Chromatography of the resulting brownish oil (38.5 g) on silica gel using hexane as the eluent finally gave 32.7 g of 1-(trans-4-pentylcyclohexyl)-3,5-trans-nona- diene (cis/trans ratio for the double bond in the 3,4- -position 46:52.4) as a colourless oil.

(f) 9.5 g of 1-(trans-4-pentylcyclohexyl)-3,5-trans-nonadiene were dissolved in 62 ml of tetrahydrofuran in a round flask and treated with 14 mg of hydroquinone. A solution of 3.2 g of dicyanoacetylene in 18 ml of tetrahydrofuran was subsequently added by means of a pipette and the pipette was rinsed twice with 9 ml of tetrahydrofuran each time. The mixture was stirred at room temperature for 2.5 hours and then overnight at 40-45°C (bath temperature) under nitrogen. The dark brown solution was thereafter concentrated in vacuo. The resulting dark brown oil (10.9 g) was chromatographed on silica gel using hexane, hexane/toluene (volume ratio 1:1) and toluene, there being obtained 4.2 g of unreacted 3-cis, 5-trans-diene as a colourless oil and 7.4 g of 1,2-dicyano-3-[2-(trans-4-pentylcyclohexyl)ethyl]-6-propyl-1,4-cyclohexadiene as a slightly yellowish oil.

The trans-2-hexenyl-triphenylphosphonium bromide used above in paragraph (e) was prepared as follows:

(g) Dry carbon dioxide was introduced into a solution of 84.3 g of trans-2-hexen-1-ol in 253 ml of petroleum ether in a sulphonation flask, the solution was then cooled to -15°C and treated dropwise at this temperature within 1 hour with a solution of 155.8 g of phosphorus tribromide in 253 ml of petroleum ether. The mixture was stirred, the temperature being held at -15°C for a further 2 hours and then being

allowed to rise to 0°C within 5 hours and to room temperature overnight. The mixture was subsequently poured on to 1 l of ice/water. The aqueous phase was separated and
5 extracted three times with 250 ml of petroleum ether each time. The combined organic phases were washed in sequence with 250 ml of saturated sodium chloride solution, 250 ml of saturated sodium hydrogen carbonate solution and 250 ml of saturated sodium chloride solution, dried over sodium
10 sulphate, filtered and concentrated. As the residue there were obtained 134.6 g of 1-bromo-2-hexene in the form of a yellowish oil.

(h) 200 g of triphenylphosphine were dissolved in 1 l of
15 benzene in an Erlenmeyer flask and treated with 134.6 g of 1-bromo-2-hexene. The product began to crystallize after a few minutes. The mixture was left to stand at room temperature for a further 2 days. The precipitate was subsequently filtered off under suction, washed with benzene
20 and petroleum ether and dried in vacuo over potassium hydroxide. The resulting crude product (292.6 g) was recrystallized from ethanol, boiled up with diethyl ether, filtered off under suction, dried in vacuo over potassium hydroxide, then pulverized and again dried in a high vacuum
25 over phosphorus pentoxide. There were thus obtained 209.9 g of trans-2-hexenyl-triphenylphosphonium bromide as a colourless powder; m.p. 146°C. Working-up of the mother liquors gave a further 74.7 g of product.

- 60 -

The following compounds were manufactured in an analogous manner:

- 5 2,3-Dicyano-4-propyl-4'-pentylbiphenyl; m.p. 61.4°C;
 2',3'-dicyano-4-pentyl-4"-propyl-p-terphenyl;
 m.p. 134.9°C;

The following compounds can be manufactured in an analogous manner:

- 2,3-Dicyano-1-[2-(trans-4-pentylcyclohexyl)ethyl]-4-
 -butylbenzene; m.p. 71.8°C;
 2,3-dicyano-1-[2-(trans-4-propylcyclohexyl)ethyl]-4-
15 -hexylbenzene; m.p. 67.6°C;
 2,3-dicyano-1-[2-(p-pentylphenyl)ethyl]-4-propyl-
 benzene; m.p. 75.7°C.

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Claims

No English translation of the claims is provided herewith since the Letters Patent already contain an English version of the claims.