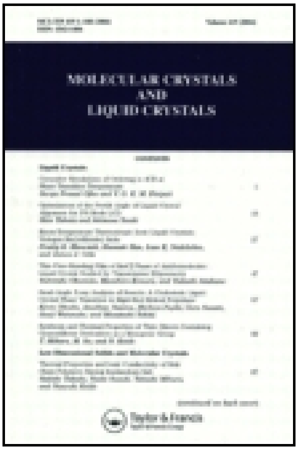

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Synthesis of 1,3-Dioxane Derivatives with Large Negative Dielectric Anisotropies

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Synthesis of 1,3-Dioxane Derivatives with Large Negative Dielectric Anisotropies

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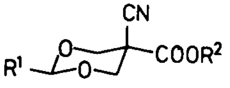
(Received May 9, 1989)

Liquid crystalline *r*-2-*t*-5-disubstituted *c*-5-cyano-1,3-dioxanes have been synthesized. The melting temperature of the new substances are increased in comparison to simpler 2,5-disubstituted 1,3-dioxanes, whereas the clearing temperatures are of the same order of magnitude. These compounds exhibit large negative dielectric anisotropies. Some of the 2-cyclohexyl-substituted derivatives have S_C-phases.

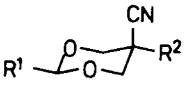
Keywords: liquid crystals, negative dielectric anisotropy, S_C-phases, 5-cyano-1,3-dioxane derivatives, synthesis, selective reduction

1. INTRODUCTION

Recently, Tschierske *et al.* have described the synthesis and the mesomorphic properties of *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates (*1*) which* exhibit only modest negative or even positive Δε-values.[1] This has been explained by the compensation of the dipole moments of the cyano- and the neighbouring carboxylate groups.



1



2

Now we report upon the synthesis and liquid crystalline properties of some *r*-2-*t*-5-disubstituted *c*-5-cyano-1,3-dioxanes (*2*) in which a carbonyl group is not directly attached to the 1,3-dioxane framework. Such substances should exhibit large negative values of the dielectric anisotropy (Δε) due to the strong CN-dipole perpendicular to the long axis of the molecule.

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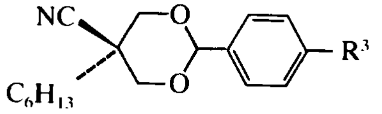
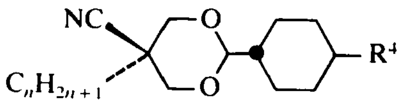
*In the convention used here, *r* indicates the substituent to which stereochemical reference (*c*, *cis*; *t*, *trans*) is made (Ed)

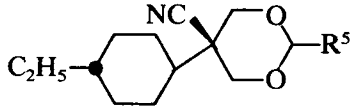
The following classes of substances were synthesized and investigated:



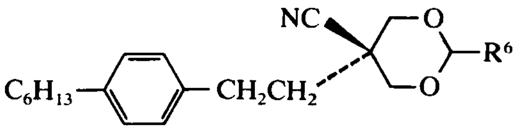
2.1–2.10



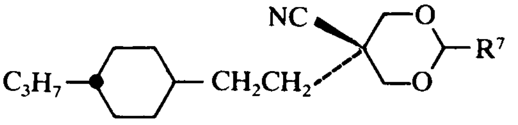
2.11–2.25



2.26–2.27



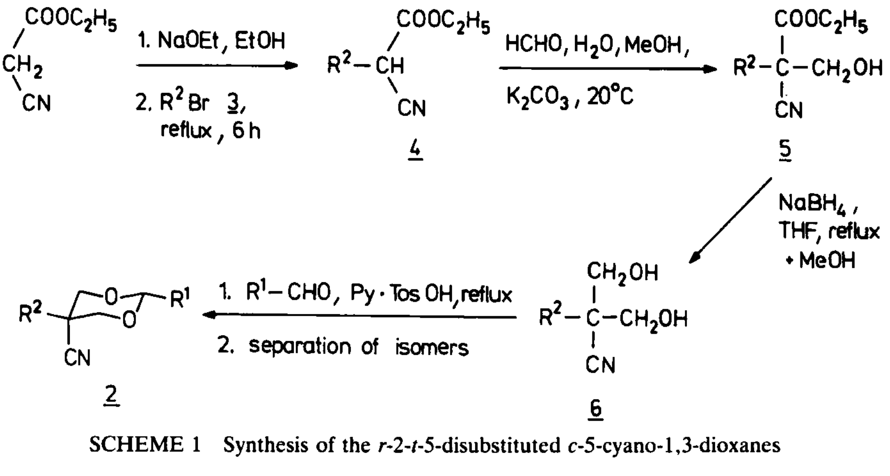
2.28–2.33



2.34–2.39

2. SYNTHESIS

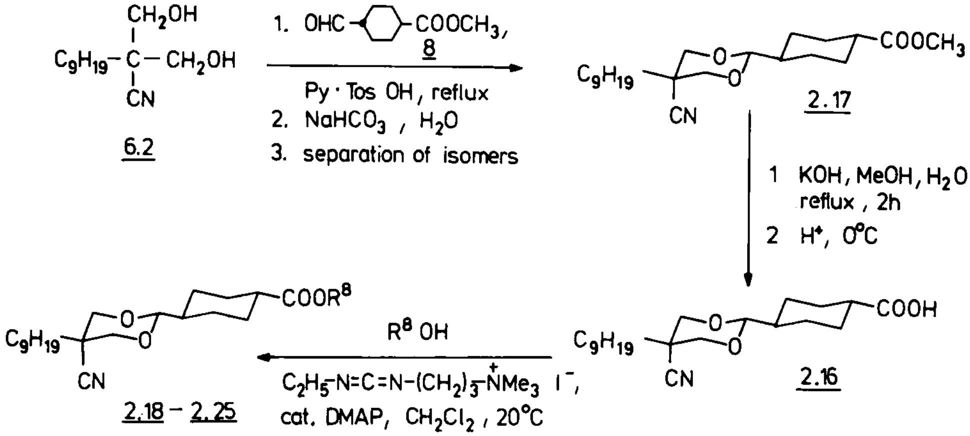
The synthesis of the 2,5-disubstituted *c*-5-cyano-1,3-dioxanes was carried out according to Scheme 1.



SCHEME 1 Synthesis of the *r*-2-*t*-5-disubstituted *c*-5-cyano-1,3-dioxanes

Appropriate alkyl bromides (*3*) were treated with ethyl sodiocyanoacetate to give the 2-substituted ethyl cyanoacetates (*4*) which were converted into the ethyl 2-alkyl-2-hydroxymethylcyanoacetates (*5*) by treatment with aqueous formaldehyde, in the presence of catalytic amounts potassium carbonate, in quantitative yield. Afterwards, the carboxylate group was selectively reduced to a hydroxymethyl group—without affecting the cyano-group—by means of $NaBH_4$ in boiling tetrahydrofuran, while absolute methanol was added simultaneously.[2] The 2-alkyl 2-cyano-propan-1,3-diols (*6*) were purified by crystallization from hexane. The acid-catalyzed acetalization of these 1,3-diols (*6*) with different aldehydes (*7*) gave mixtures of the two diastereomeric 2,5-disubstituted 5-cyano-1,3-dioxanes from which the desired *r*-2-*t*-5-disubstituted *c*-5-cyano-1,3-dioxanes (*2*) were easily separated by repeated recrystallization from appropriate solvents. The synthesis of the aldehydes (*7*) has been described in a recent paper.[3]

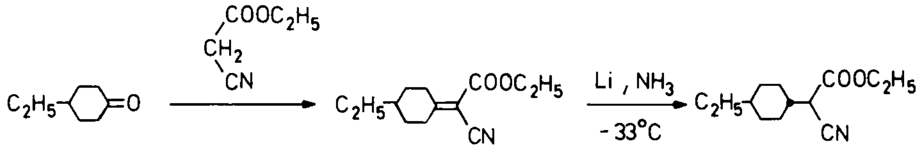
The compounds *2.18* – *2.25* were obtained according to reaction Scheme 2:



SCHEME 2 Synthesis of the *trans*-4-(*c*-5-cyano-*t*-5-nonyl-1,3-dioxane-*r*-2-yl)cyclohexane carboxylates (*2.18* – *2.25*)

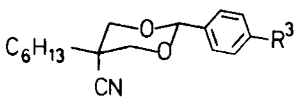
The methyl carboxylate (*2.17*) was first prepared by acetalization of methyl 4-formylcyclohexanecarboxylate (*8*)[3] as described above, and then saponified with potassium hydroxide in boiling moist methanol. The carboxylic acid (*2.16*) was liberated by careful acidification and purified by crystallization from hexane/ethyl acetate. Subsequent esterification with substituted cyclohexanols or phenols gave the desired carboxylates (*2.18* – *2.25*).[4]

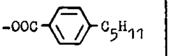
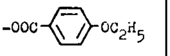
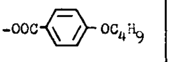
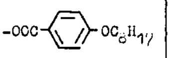
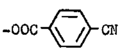
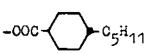
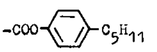
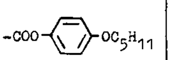
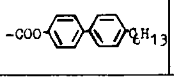
The substituted 2-cyclohexylcyanoacetate (*4.5*) was synthesized by Knoevennagel condensation of 4-ethylcyclohexanone with ethyl cyanoacetate, followed by Birch-reduction of the double bond (Scheme 3).[5]



SCHEME 3 Synthesis of ethyl *trans*-2-(4-ethylcyclohexyl) cyanoacetate (*4.5*)

TABLE I Transition temperatures (°C) for *r*-2-(4-substituted phenyl)-*c*-5-cyano-*t*-5-hexyl-1,3-dioxanes (*2.1* – *2.10*).

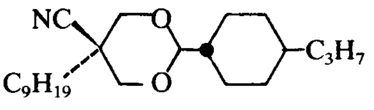


Comp.	R^3	cr	N	is
2.1	$-OC_8H_{17}$	. 106	- -	.
2.2		. 116	(.113,5)	.
2.3		. 139	. 173,5	.
2.4		. 121	. 156	.
2.5		. 118	. 137	.
2.6		. 166	(. 157)	.
2.7		. 133	. 147,5	.
2.8		.129.5	(. 120)	.
2.9		. 155	(. 150)	.
2.10		. 193	. 257	.

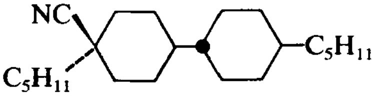
3. RESULTS AND DISCUSSION

The phase transition temperatures of the various *r*-2-*t*-5-disubstituted *c*-5-cyano-1,3-dioxanes synthesized are listed in Tables I–III.

These compounds exhibit enantiotropic nematic, smectic A, and smectic B phases in the case of the three-ring compounds. However, two-ring compounds give—if any—only monotropic smectic phases, due to their rather high melting temperatures. The melting points of the 2,5-disubstituted 5-cyano-1,3-dioxanes are generally elevated in comparison with analogous 1,4-disubstituted cyanocyclohexanes,[6] while the clearing temperatures are comparable:



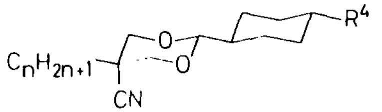
cr 71 (S_A 68) is

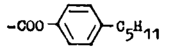
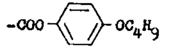
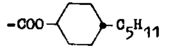
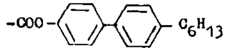
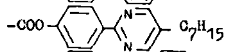
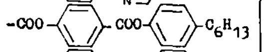
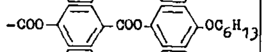
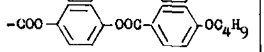


cr 24 (S 24) N 66 is

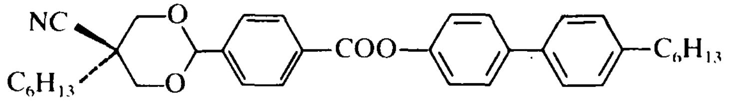
cr = crystal, is = isotropic

TABLE II Transition temperatures (°C) for the *r*-2-(*trans*-4-substituted cyclohexyl)-*c*-5-cyano-*t*-5-alkyl-1,3-dioxanes (*2.11* – *2.25*).

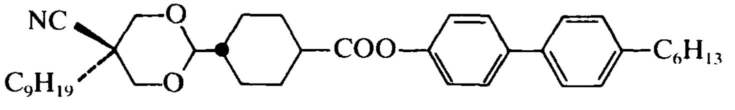


Comp.	n	R^4	cr	S_G	$S_{I/F}$	S_B	S_C	S_A	N	is
2.11	6	$-C_3H_7$	• 79	– –	– –	– –	– –	– –	– –	•
2.12	6	$-C_7H_{15}$	• 79	– –	– –	– –	– –	– –	– –	•
2.13	6	$-COOCH_3$	• 105	– –	– –	– –	– –	– –	– –	•
2.14	9	$-C_3H_7$	• 71	– –	– –	– –	– –	(• 68)	– –	•
2.15	9	$-C_7H_{15}$	• 74.5	– –	– –	– –	– –	• 77	– –	•
2.16	9	$-COOH$	• 225	– –	– –	– –	– –	– –	– –	•
2.17	9	$-COOCH_3$	• 99.5	– –	– –	– –	– –	– –	– –	•
2.18	9		• 118	– –	– –	– –	– –	• 134.5	– –	•
2.19	9		• 92	– –	– –	– –	– –	• 141	• 154	•
2.20	9		• 104	– –	– –	(• 92)	– –	• 126	• 135	•
2.21	9		• 95	• 140	• 150	– –	• 211	– –	• 236	•
2.22	9		• 137	(• 129)	– –	– –	• 166	– –	• 236	•
2.23	9		• 99	– –	– –	– –	– –	• 234	• 246	•
2.24	9		• 102	– –	– –	• 128	• 158	• 232	• 262	•
2.25	9		• 141	(• 129)	– –	– –	• 155	– –	• 277	•

This is also true for substituted 2-aryl-5-cyano-1,3-dioxanes (compounds *2.1* – *2.10*, *2.27*, *2.29* – *2.33* and *2.37* – *2.39*), but the melting temperatures of the substituted 2-cyclohexyl compounds are often considerably lower. Some of these 2-cyclohexyl derivatives also exhibit S_C-phases:



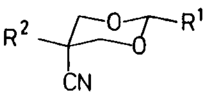
cr 193 N 257 is

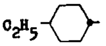
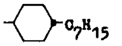
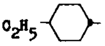
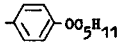
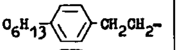
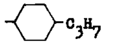
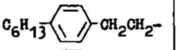
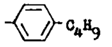
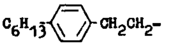
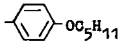
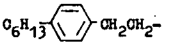
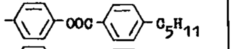
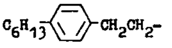
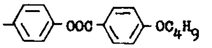
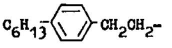
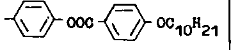
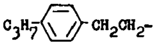
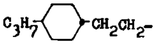
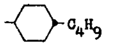
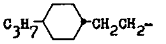
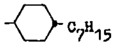
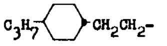
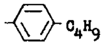
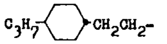
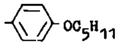
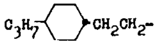
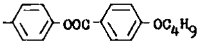


cr 95 S_G 140 $S_{I/F}$ 150 S_C 211 N 236 is

Table IV gives the results for the dielectric measurements. Due to the high melting temperatures and the often metastable liquid crystalline phases, the dielectric meas-

TABLE III Transition temperatures (°C) for differently substituted *c*-5-cyano-1,3-dioxanes (*2.26* – *2.39*).



Comp.	R^2	R^1	cr	S_B	S_A	N	is
2.26			. 120	- -	- -	. 127	.
2.27			. 150	- -	- -	- -	.
2.28			. 133	(. 125)	- -	- -	.
2.29			. 133	- -	- -	- -	.
2.30			. 122	(. 111)	- -	- -	.
2.31			. 185	- -	- -	(. 184.5)	.
2.32			. 176	- -	- -	. 202	.
2.33			. 165	- -	. 172	. 184	.
2.34		$-C_6H_{13}$	. 97	- -	- -	- -	.
2.35			. 145	. 203	- -	- -	.
2.36			. 126	. 195.5	- -	- -	.
2.37			. 122	- -	. 134	- -	.
2.38			. 92-3	- -	- -	. 122	.
2.39			. 153	- -	- -	. 270	.

urements were performed using mixtures. From known data for the mixture Mi 5 ($\epsilon_{\|}$ (1) = 4.69; $\epsilon_{\perp}$ (1) = 4.92) consisting of four different phenyl benzoates,[7] and the measured dielectric constants parallel and perpendicular to the magnetic field ($\epsilon_{\|(\perp)}$ (1.2)), the dielectric constants of the added compounds (2) could be calculated (knowing x = mole fraction) according to:

$$\epsilon_{\|(\perp)}(1.2) = \epsilon_{\|(\perp)}(1) \cdot x_1 + \epsilon_{\|(\perp)}(2) \cdot x_2 \qquad (1)$$

$$\Delta\epsilon\,(1.2) = \Delta\epsilon\,(1) \cdot x_1 + \Delta\epsilon(2) \cdot x_2 \qquad (2)$$

Additionally to the usually used equation (2), we also considered equation (1) in order to obtain information about the change in the components of ϵ. The error in the experimentally determined value of $\Delta\epsilon(2)$ increases with decreasing x_2 and is at x_2 = 0.02 of the order of magnitude ± 1. Generally, the validity of the additivity proposed by equations (1) and (2) is controversial, but for comparative purposes the data are useful.[8]

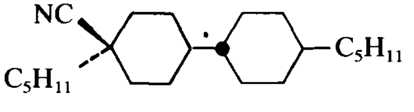
TABLE IV Dielectric constants of representative 2,5-disubstituted *c*-5-cyano-1,3-dioxanes measured using mixtures.

Compound	x_2	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
2.1	0.030	8.3	16.9	- 8.6
2.9	0.030	9.3	13.6	- 4.3
2.10	0.030	9.2	13.1	- 3.9
2.11	0.063	9.9	16.6	- 6.7
2.12	0.070	9.9	17.5	- 7.6
2.15	0.070	9.4	17.1	- 7.7
2.19	0.07	9.3	16.5	- 7.2
2.20	0.07	7.9	16.8	- 8.9
2.24	0.056	5.3	9.3	- 4.0
2.26	0.03	6.6	15.2	- 8.6
2.28	0.03	11.2	21.2	-10.0
2.31	0.032	5.3	9.3	- 4.0
2.33	0.024	7.3	12.6	- 5.3
2.36	0.03	13.6	18.2	- 4.6

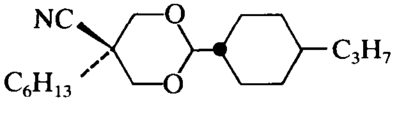
Dielectric constants at $T_{N/is}-T$ = 30 K measured at the molar fraction x_2 of the respective compounds

Generally speaking, there is the expected tendency that $\epsilon_{\perp}$ increases much more than $\epsilon_{\parallel}$ with respect to the values of the base mixture. $\Delta\epsilon$ also decreases if the benzene rings in the compounds (*2*) are replaced by cyclohexane rings, because of the decreased mesomeric interaction in direction of the molecular long axis. $\Delta\epsilon$ is increased by elongation of the molecule due to the bigger molar volume.

The observed dielectric anisotropies are between -3.9 and -10.0 and they are of the same order of magnitude as those observed for axial cyano-substituted cyclohexanes[6] measured in the same way, but the values of the axial cyano-substituted 1,3-dioxanes are slightly larger:

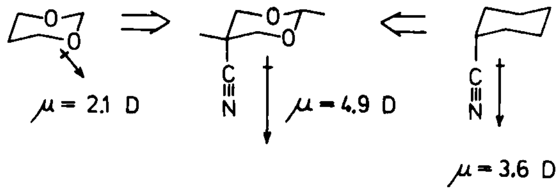


$\Delta\epsilon = -8$



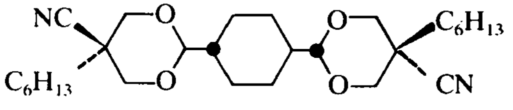
$\Delta\epsilon = -8.6$

The dielectric constants are in good agreement with our suggestion that the dipole moment of the 1,3-dioxane ring (μ = 2.1 D)[9] should also contribute to the total dipole moment of the molecule. Simple vector addition gives a value of μ = 4.9 D for the axial cyano-substituted 1,3-dioxane ring,[9] which explains the observed dielectric anisotropies.



In Table V, the mesomorphic properties of some of the compounds (*2*) are compared with those of related 1,3-dioxane derivatives. The expected depression of the clearing temperatures due to the lateral substitution was not always found. There are two examples (compounds *2.35* and *2.37*) with enhanced mesophase stability for the cyano-substituted derivatives. These are examples of the very rare situation in which a lateral substituent causes a stabilization of the mesophase. As in the case[1] of *r*-2-alkyl-*c*-5-cyano-1,3-dioxane-*t*-5-carboxylates (1), this behaviour can be explained by an enhancement of the attractive intermolecular forces due to the strongly polar and highly polarizable cyano-group, which gives rise to an increased packing density compared with the related unsubstituted compounds.

The melting points of the 1,3-dioxane derivatives are always significantly enhanced by the introduction of an axial 5-cyano-group. This is especially true for compounds with additional CN-groups, like compound (*2.40*).



m.p. 245°C

2.40

4. EXPERIMENTAL

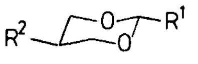
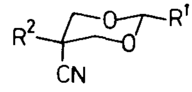
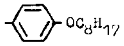
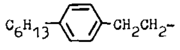
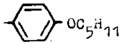
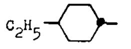
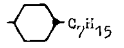
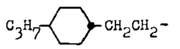
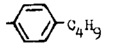
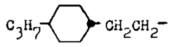
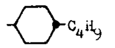
General remarks

The transition temperatures were determined by hot-stage polarizing microscopy and have not been corrected. The single component nature of the materials was checked by thin layer chromatography using hexane/ethyl acetate mixtures as eluents. Combustion analysis results were satisfactory and the structures of the compounds were checked by analysis of their ^{1}H-NMR, ^{13}C-NMR, IR and mass spectra. ^{1}H-NMR spectra were recorded using a Bruker WP 200 spectrometer (200.13 MHz) or a Varian HA 100-15 (100 MHz). ^{13}C-NMR spectra were recorded on the Bruker WP 200 spectrometer (50.327 MHz). Representative examples of these spectra are given below.

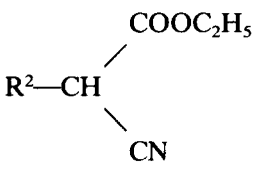
Ethyl 2-substituted cyanoacetates (*4.1* – *4.4*)

Sodium (11.5 g, 0.5 g·atom) was dissolved in absolute ethanol (200 ml). To this solution ethyl cyanoacetate (113 g, 1.0 mole) and KI (1 g) were added. The mixture was stirred at reflux temperature while the corresponding alkyl bromide (0.5 mole) was slowly added. After this, the mixture was heated for 2 h. The cooled reaction mixture was poured into water (500 ml) and the product was isolated by extraction

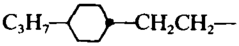
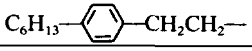
TABLE V Comparison of the mesomorphic properties of related 2,5-disubstituted 1,3-dioxanes[10,11] and c-5-cyano-1,3 dioxanes (transition temperatures are given in °C).

											
R^2	R^1	ref.	cr	S	N	is	comp.	cr	S	N	is
C_6H_{13}-		[10]	· 46	· 52.5	· 58	·	2.1	· 106	– –	– –	·
		[10]	·	· 137	– –	·	2.30	· 122	(· 111)	– –	·
		[10]	·	· 194	– –	·	2.26	· 120	– –	· 127	·
		[11]	· < 20	· 131	– –	·	2.37	· 122	· 134	– –	·
		[11]	· < 20	· 182	– –	·	2.35	· 145	· 203	– –	·

into ether. The combined organic layers were washed with water (100 ml), dried (Na_2SO_4), and the solvent was removed. The residue was fractionated under reduced pressure to give the ethyl 2-substituted cyanoacetates:



$$R^2{-}CH(COOC_2H_5)(CN)$$

Comp.	R^2	b.p. (°C/mm Hg)	yield (%)
4.1	C_6H_{13}—	93 – 97/0.2	68
4.2	C_9H_{19}—	150/0.3	83
4.3		155/0.1	87
4.4		165/0.05	69

4.1: IR (CCl_4, cm^{-1}): 1030, 1190, 1255, 1375, 1470, 1755 (C=O), 2250 (CN), 2850, 2920
^{1}H-NMR (100 MHz, $CDCl_3$, ppm): 4.20 (q, J = 7.0 Hz, 2H, —OCH_2—), 3.46 (t, J = 7.0 Hz, 1H, H—2), 2.0 – 0.7 (m, 16H, —CH_2—, —CH_3)

4.4: ^{1}H-NMR (100 MHz, $CDCl_3$, ppm): 7.04 (s, 4H, CH-ar), 4.15 (q, J = 7.0 Hz, 2H, —OCH_2—), 3.40 (t, J = 7.0 Hz, 1H, H—2), 2.78 (t, J = 7.0 Hz, 2H, ar—CH_2—), 2.53 (t, J = 7.0 Hz, 2H, ar—CH_2—), 2.3 – 0.7 (m, 15H, —CH_2—, —CH_3)

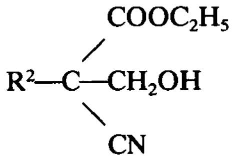
Ethyl trans-2-(4-ethylcyclohexyl)cyanoacetate (*4.5*)

A mixture of ethyl 4-ethylcyclohexylidene cyanoacetate[12] (5 g, 0.023 mole), butanol (1.7 g, 0.023 mole) and dry ether (60 ml) was added to a solution of lithium (0.35

g, 0.05 g·atom) in liquid NH_3 (400 ml) at −33°C. After 2 h, NH_4Cl (30 g) was added and the ammonia was allowed to evaporate over night. The residue was dissolved in ether and dilute hydrochloric acid; the organic phase was separated and worked up as described above, to give ethyl 2-(4-ethylcyclohexyl)cyanoacetate (*4.5*), 2.5 g, 50%, b.p. 119 − 122°C/0.07 kPa.
IR (neat, cm^{-1}): 1750 (C═O), 2270, 2850, 2900

2-substituted 2-cyanopropan-1,3-diols (6)

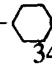
A mixture of the corresponding ethyl 2-substituted cyanoacetate (*4*) (0.1 mole), 40% aqueous formaldehyde (12 ml), K_2CO_3 (0.2 g), and methanol (70 ml) was stirred at room temperature for 2 h. The mixture was diluted with water (200 ml) and shaken several times with ether. The extracts were dried over Na_2SO_4 and the solvent was removed at room temperature. The residue (compound *5*) was dissolved in THF (200 ml) and $NaBH_4$ (11.4 g, 0.3 mole) was added. At reflux temperature, methanol (100 ml) was added slowly while stirring during 2 h. Afterwards hydrochloric acid (150 ml, 15% solution) was added, the solvents were evaporated, and the residue was dissolved in water (100 ml). This solution was extracted 5 times with ether (total 250 ml). The combined ether solutions were washed with KOH (200 ml 10% solution), water (50 ml), and brine (100 ml) and dried (Na_2SO_4). The solvent was then removed and crystallization from hexane/ethyl acetate gave the pure diols (*6*).

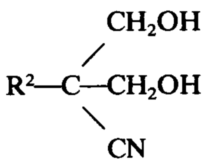


$$R^2{-}C(COOC_2H_5)(CN){-}CH_2OH$$

(*5*)

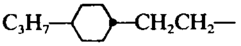
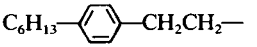
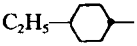
5.1 (R^2 = C_6H_{13}): IR (CCl_4, cm^{-1}): 1070, 1230, 1370, 1465, 1745 (C═O), 2235 (CN), 2850, 2920, 3450 (OH)
^1H-NMR (100 MHz, $CDCl_3$, ppm): 4.23 (q, J = 7 Hz, 2H, —OCH_2—), 4.0 − 3.6 (m, 3H, —CH_2O*H*), 1.9 − 0.7 (m, 16H, —CH_2—, —CH_3)

5.5 (R^2 = C_2H_5——): IR (CCl_4, cm^{-1}): 1750 (C═O), 2220 (CN), 3830, 3900, 3480 (OH)
^1H-NMR (100 MHz, $CDCl_3$, ppm): 4.22 (q, J = 7 Hz, 2H, —OCH_2—), 3.90 (broad, 2H, C*H*$_2$OH), 3.19 (broad, 1H, —OH), 2.0 − 0.7 (m, 18H, ═CH—, —CH_2—, —CH_3)



$$R^2{-}C(CH_2OH)(CN){-}CH_2OH$$

(*6*)

Comp.	R^2	m.p. (°C)	yield (%)
6.1	C_6H_{13}—	68	75
6.2	C_9H_{19}—	66	68
6.3		cr 118 (S 112) is	60
6.4		liquid	52
6.5		103	37

6.1: IR ($CHCl_3$, cm^{-1}): 1050, 1205, 1465, 2230 (CN), 2850, 2910, 3430 (OH), 3570 (OH)
^{1}H-NMR (100 MHz, $CDCl_3$, ppm): 4.00 (broad, 2H, —OH), 3.69 (AB-q, 4H, —C*H*$_2$OH), 1.6 – 1.0 (m, 10H, —CH_2—), 0.83 (t, 3H, —CH_3)

6.3: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 3.85 (dd, ^2J = 10.5 Hz, ^3J = 6.8 Hz, 2H, —C*H*$_a$H$_b$OH), 3.71 (dd, ^2J = 11.7 Hz, ^3J = 6.8 Hz, 2H, —CH$_a$*H*$_b$OH), 3.09 (t, J = 6.8 Hz, 2H, —OH), 1.72 (m, 4H, Hequ), 1.61 – 0.71 (m, 17H, =CH—, —CH_2—, —CH_3)

6.4: ^{1}H-NMR (100 MHz, $CDCl_3$, ppm): 7.01 (s, 4H, H-ar), 3.75 (d, J = 6 Hz, 2H, —C*H*$_a$H$_b$OH), 3.68 (d, J = 6 Hz, 2H, —CH$_a$*H*$_b$OH), 3.07 (broad, 2H, —OH), 2.81 – 2.38 (m, 4H, ar—CH_2—), 2.0 – 0.7 (m, 13H, —CH_2—, —CH_3)

Acetalization

In a flask fitted with a water separator, the appropriate diol (*6*) (10 mmole), the appropriate aldehyde (*7*) (10 mmole), and toluene-4-sulphonic acid (100 mg) in benzene (100 ml) were heated under reflux for 0.5 h. The cooled reaction mixture was washed with 5% aqueous $NaHCO_3$ and dried (Na_2SO_4). After removing the solvent, the residue was crystallized from methanol until constant transition temperatures were obtained.

2.11: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 4.19 (d, J = 11.7 Hz, 2H, H—4, 6equ), 4.17 (d, J = 4.7 Hz, 1H, H—2), 3.42 (d, J = 11.6 Hz, 2H, H—4, 6ax), 1.9 – 0.7 (m, 30H, =CH—, —CH_2—, —CH_3)

2.14: ^{13}C-NMR (50 MHz, $CDCl_3$, ppm): 121.4 (CN), 105.8 (C—2), 72.7 (2C, C—4, 6), 42.0, 39.6, 37.9 (C—5), 37.2, 32.4 (2C), 31.7, 31.6, 29.5, 29.3, 29.1 (2C), 26.9 (2C), 23.7, 22.5, 19.9, 14.2, 14.0

2.17: ^{13}C-NMR (50 MHz, $CDCl_3$, ppm): 176.1 (C=O), 121.3 (CN), 105.2 (C—2), 72.7 (2C, C—4, 6), 51.3, 43.1, 41.2, 37.9, 31.7 (2C), 29.6, 29.3, 29.1 (2C), 28.2 (2C), 25.9 (2C), 23.8, 22.5, 14.0

2.7: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 7.50 (d, J = 8.6 Hz, 2H, H—ar) 7.05 (d, J = 8.6 Hz, 2H, H—ar), 5.40 (s, 1H, H—2), 4.35 (d, J = 11.7 Hz, 2H, H—4, 6equ), 3.67 (d, J = 11.7 Hz, 2H, H—4, 6ax), 2.44 (m, 1H, =C*H*—COO—), 2.2 – 0.8 (m, 33H, =CH—, —CH_2—, —CH_3)

t-5-Nonyl-c-5-cyano-1,3-dioxane-r-2-yl-cyclohexane carboxylic acid (*2.16*)

A mixture of the ester (*2.17*) (7.6 g, 0.02 mole) and potassium hydroxide (11.2 g, 0.2 mole) in water (10 ml) and methanol (200 ml) was boiled for 20 min. The solvents were removed and the residue was dissolved in water (200 ml), neutralized with 25% sulfuric acid and extracted 3 times with ethyl acetate. After washing with brine, drying (Na_2SO_4), and removing the solvent the residue was crystallized from hexane/ethyl acetate to give the carboxylic acid (*2.16*), 6.8 g, 93%, m.p. 225°C.

Esterification

To a solution of (*2.16*) (0.73 g, 1 mmole), the appropriate phenol or cyclohexanol (1 mmole), and 4-dimethylaminopyridine (10 mg) in dry dichloromethane (10 ml) was added 1-(3-dimethyl-aminopropyl)-3-ethylcarbodiimide methiodide (0.4 g, 1.2 mmole). The mixture was stirred overnight at room temperature. After dilution with CH_2Cl_2 (50 ml), the organic layer was washed twice with water (10 ml) and brine (50 ml). Drying (Na_2SO_4), and evaporation of the solvent gave the crude esters, which were purified by crystallization from methanol.

2.16: IR ($CHCl_3$, cm^{-1}): 1710 (C=O), 2240 (CN), 2850, 2930, 2600 − 3600 (OH) ^{1}H-NMR (100 MHz, $CDCl_3$, ppm): 9.2 (broad, 1H, COOH), 4.20 (d, J = 4.7 Hz, H—2), 4.16 (d, J = 11.7 Hz, 2H, H—4, 6equ), 3.42 (d, J = 11.7 Hz, 2H, H—4, 6ax), 2.2 − 0.7 (m, 23H, =CH—, —CH$_2$—, —CH$_3$)

2.22: ^{1}H-NMR (200 MHz, $CDCl_3$, ppm): 8.58 (s, 2H, pyrimidine), 8.41 (d, 2H, CH-ar), 7.15 (d, 2H, CH-ar), 4.25 (d, J = 4.7 Hz, 1H, H—2), 4.21 (d, J = 11.6 Hz, 2H, H—4, 6equ), 3.44 (d, J = 11.6 Hz, 2H, H—4, 6ax), 2.59 (t, J = 7.6 Hz, 2H, ar-CH$_2$—), 2.48 (m, 1H, =CH—COO—), 2.2 − 1.1 (m, 37H, =CH—, —CH$_2$—,), 0.86 (t, 6H, —CH$_3$)

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