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Synthesis and properties of some laterally substituted liquid crystals

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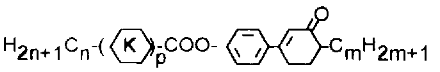
This paper presents a number of laterally substituted liquid crystalline compounds which have been synthesized by systematically varying both the position and the type of the lateral substituent. The influences of such structural changes on the physico-chemical properties of new compounds are discussed and compared with those of the corresponding laterally unsubstituted analogues.

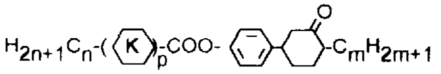
1. Introduction

We recently reported our results and liquid crystalline properties of some strong polar laterally substituted liquid crystals [1–4]. The purpose of that work was to produce liquid crystals (LCs) of positive dielectric anisotropy ($+\Delta\varepsilon$) which are required as the components of liquid crystalline materials for twisted nematic (TN) and super twisted nematic (STN) display applications. The lateral (F, Cl, Br, CH_3) substituents were chosen because of their ability to reduce smectic tendencies and vary other LC properties.

Since a single liquid crystal shows at best one or two distinguished properties [1–4], mixtures consisting of up to twenty or more strong polar ($\Delta\varepsilon \gg 0$) and weakly polar components have to be developed for a given display application.

In an attempt to synthesize weakly polar liquid crystals of low smectic tendencies and, at the same time, having a high clearing point (T_{NI}) (i.e., with a wide temperature range), some new series of laterally substituted liquid crystalline compounds (**I**–**VI**) have been synthesized:


I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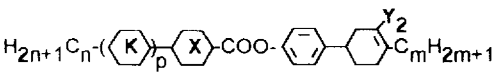
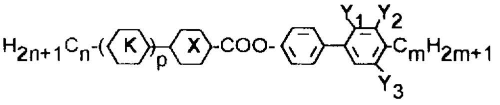
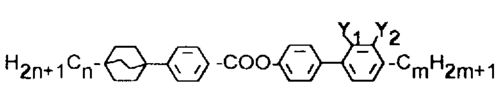
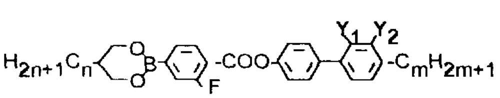

III


IV


V


VI

n, $m = 3$–7; *K*, $X = 1,4$-phenylene group or *trans*-1,4-cyclohexylene group; $p = 0$ or 1; Y_1, Y_2, Y_3, = H, CH_3, C_2H_5, Cl, OCH_3.

2. Synthesis and discussion

The mesomorphic esters (**I**–**VI**) were prepared by the interaction of chlorides of 4-alkylbenzoic acid, *trans*-4-alkylcyclohexanecarboxylic acid, 4-alkylbiphenyl-4-carboxylic acid, 4-(*trans*-4-alkylcyclohexyl)benzoic acid, 4-(1-alkylbicyclo[2,2,2]octyl-4)benzoic acid, 4-(5-alkyl-1,3,2-dioxaborinanyl-2)-2-fluorobenzoic acid

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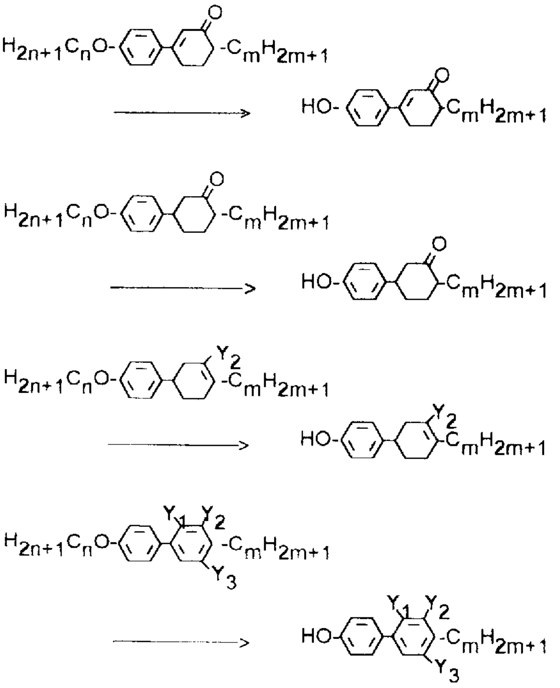
[1] with 4-(6-alkylcyclohex-2-enonoyl-3)phenol (**VII**), 4-(6-alkylcyclohexanonoyl-3)phenol (**VIII**), 4-(1-alkyl-2-Y_2-cyclohex-1-enyl-4)phenol (**IX**), 4-hydroxy-2-Y_1-3-Y_2-5-Y_3-4-alkylbiphenyls (**X**).

The phenols (**VII–X**) were obtained by the dealkylation of the corresponding alkoxy derivatives [5, 6] with aluminum bromide or chloride and boron tribromide or by boiling of them in a mixture of acetic and hydroiodic or hydrobromic acids, or by heating with pyridine hydrochloride



VII

VIII

IX

X

It was found that the phenols (**VII–X**) are formed with the highest yield (70–80 per cent) during refluxing of the corresponding alkoxy derivatives in the mixture of acetic and hydroiodic acids or heating with pyridine hydrochloride. It should be noted that the interaction of 4-(4-alkoxyphenyl)-1-alkylcyclohex-1-ene with aluminium chloride at 40–50°C leads to the mixture of the phenols (**IX**) with products of the reduction of the double bond, 4-(4-hydroxyphenyl)-1-alkylcyclohexanes (**XI**). The latter compounds are obtained with a yield of 50 per cent. Increasing the reaction temperature and time causes a decrease in the yield of the phenols (**IX**, **XI**) and leads to the isomerisation of the *trans*-1,4-cyclohexylene and 1,4-cyclohexenylene fragments.

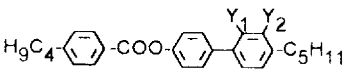
Since the optimization of the methods for obtaining phenols (**IX**) was of obvious interest, other possible ways of the dealkylation of the starting compounds were considered. It was found that the treatment of 4-(4-alkoxyphenyl)-1-alkylcyclohex-1-enes with an equivalent quantity of boron tribromide lead to the connection of the Lewis acid to the double bond and then, after the decomposition of the reaction mixture, to 4-(4-alkoxyphenyl)-1-alkyl-1-bromocyclohexanes (**XIII**). An analogous reaction with two or more equivalents of boron tribromide allowed us to synthesize the products of the dealkylation bromocyclohexanes (**XIII**)–4-(4-hydroxyphenyl)-1-alkyl-1-bromocyclohexanes (**XIV**),which are easily converted into the unsaturated phenols (**IX**) during the reaction with alkaline hydroxide or alkaline metal alcoholates.

We found that it was not possible to synthesize the hydroxybiphenyls (**X**, Y_1, $Y_2 = CH_3$, C_2H_5) by the dealkylation of the corresponding alkoxybiphenyls using aluminum chloride or bromide. In this case, the products of the double dealkylation, 4-hydroxy-2-Y_1,3-Y_2-biphenyls (**XV**) are formed and the disturbance of the coplanarity of the 1,4-phenylene groups after the incorporation of methyl group in the second position of the 1,4-phenylene group does not influence on the yield of the products of double dealkylation. However, it should be noted that the dealkylation of the alkyl fragment in the forth position of the 1,4-phenylene group does not take place if a chlorine atom is in *ortho* position to this tail.

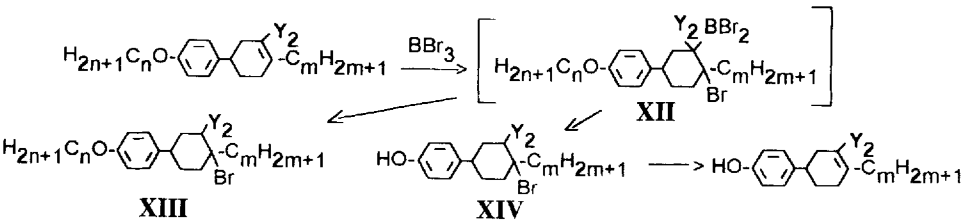
The proton NMR spectra (δ/ppm) analysis of *trans*-4-(4-hydroxyphenyl)-1-alkylcyclohexanes (**XI**) showed that a multiplet at 5·40 belonging to the protons located at the double bond of the 1,4-cyclohexenylene group was absent. The signals of the *trans*-1,4-cyclohexylene and bromocyclohexane fragments of compounds (**XI**, **XIII**) are observed in the NMR spectra at 1·30–2·56. It was found that the triplet or the quartet signals at 2·53 and 3·98 of the methylene protons of the alkyl and alkoxy groups are not observed in the proton NMR spectra of the compounds (**XV**).

The phase transition temperatures of some cyclohexenones and cyclohaxenones (**I**, **II**) are collated in table 1. The dependence of the transition temperatures of some reference liquid crystals and new esters series (**III–VI**) on the type and position of lateral substituents can be defined by comparing the corresponding values presented in tables 2 and 3.

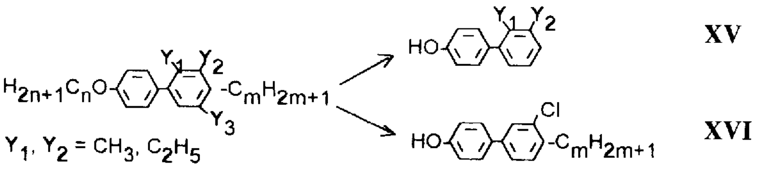
As can be seen from table 3, the introduction of a lateral methyl substituent into the rigid core of the 4-alkylbiphenyl esters of 4-alkylbenzoic acids sufficiently reduces the melting points, smectic and nematic thermostabilities (**IV**, **a**, **b**, **q**). The influence of the position of methyl substituent on the clearing points (T_{NI}) and nematic ranges (ΔT) of the laterally substituted 4-pentylbiphenyl esters of 4-butylbenzoic acid can be expressed by the following orders of increasing T_{NI} and ΔT:



T_{NI} and ΔT: $Y_1 = CH_3$, $Y_2 = H < Y_1 = H$, $Y_2 = CH_3 < Y_1 = H$, $Y_2 = H$.

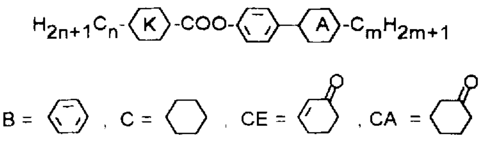


Scheme 1.



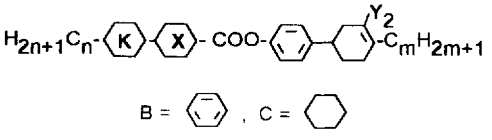
Scheme 2.

Table 1. Yields and transition temperatures of esters (**I**, **II**).



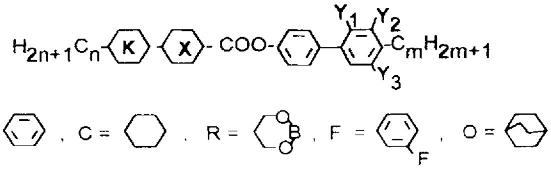
Compound	*n*	*K*	*A*	*m*	Yield/ per cent	Transition temperatures/°C Cr		S		N		I	Reference
Ia	7	–	CE	3	57	●				●	110	●	
Ib	3	B	CE	3	53	●	88	●	142	●	176	●	
Ic	3	B	CE	5	68	●	91	●			171	●	
Id	4	B	CE	5	60	●	118	●			194	●	
Ie	4	C	CE	5	59	●	106	●			184	●	
IIa	3	B	CA	5	49	●	84	●			136	●	
IIb	4	B	C	5	–	●	67	●	149	●	154	●	[7]

Table 2. Yields and transition temperatures of esters (**III**).



Compound	*n*	*K*	*X*	Y_2	*m*	Yield/per cent	Transition temperatures/°C Cr		S		N		I
IIIa	4	–	C	H	5	36	●	81	●	113	●	122	●
IIIb	4	–	C	CH_3	3	47	●	23			●	91	●
IIIc	4	–	C	CH_3	5	34	●	28			●	108	●
IIId	5	B	B	CH_3	5	40	●	78	●	163	●	228	●
IIIe	5	B	B	C_2H_5	5	33	●	77	●	162	●	214	●
IIIf	5	C	B	C_2H_5	5	45	●	83	●	126	●	197	●

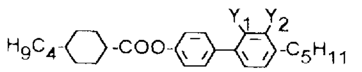
Table 3. Yields and transition temperatures of esters (**IV**, **V**, **VI**).



Compound	*n*	*K*	*X*	Y_1	Y_2	Y_3	*m*	Δε†	Yield/ per cent	Transition temperatures/°C							Reference
										Cr		S		N		I	
IVa	4	—	B	—	CH_3	—	5	—	43	●	46			●	106	●	
IVb	4	—	B	CH_3	—	—	5	—	42	●	25			●	69	●	
IVc	4	—	C	—	—	—	5	—	36	●	123	●	136	●	184	●	
IVd	4	—	C	—	CH_3	—	0	—	41	●	65			●	76	●	
IVe	4	—	C	—	CH_3	—	3	0·23	49	●	69			●	116	●	
IVf	4	—	C	—	CH_3	CH_3	3	—	62	●				●	79	●	
IVg	4	—	C	—	CH_3	—	4	—	50	●	61			●	121	●	
IVh	4	—	C	—	CH_3	—	5	—	52	●	44			●	128	●	
IVi	4	—	C	CH_3	—	—	5	—	42	●	68			●	82	●	
IVj	4	—	C	—	C_2H_5		5	—	38	●	47			●	67	●	
IVk	4	—	C	—	CH_3	C_8H_{17}	0	—	34	●				●	49	●	
IVl	6	—	C	—	CH_3	—	5	—	47	●	54	●	84	●	123	●	
IVm	5	C	B	—	CH_3	—	5	—	56	●	91	●	170	●	220	●	
IVn	5	C	B	CH_3	—	—	5	—	60	●	85	●	96	●	205	●	
IVo	4	—	C	—	Cl	—	5	—	57	●	54	●	110	●	129	●	[5]
IVp	4	—	C	—	OCH_3	—	5	—	61	●	48	●	74	●	94	●	
IVq	4	—	C	—	—	—	5	—		●	88	●	98	●	171	●	[8]
Va	4	R	F	—	CH_3	—	5	4·01	52	●	73			●	184	●	
Vb	5	R	F	—	CH_3	—	5	—	52	●	73			●	184	●	
Vc	5	R	F	CH_3	—	—	5	—	51	●	68			●	166	●	
Vd	5	R	F	—	C_2H_5	—	5	—	54	●	52	●	66	●	138	●	
VI	4	O	B	—	CH_3	—	5	—	47	●	104	●	140	●	249	●	

† $T = T_{NI} - 50°C$.

The influence of the position of the methyl substituent on the clearing points and nematic ranges of the corresponding laterally substituted 4-pentylbiphenyl esters of *trans*-4-butylcyclohexanecarboxylic acid and laterally unsubstituted analogue can be expressed by the following orders of increasing T_{NI} and ΔT (see table 3):

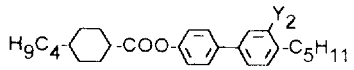


$$T_{NI}: Y_1=CH_3,\ Y_2=H < Y_1=H,\ Y_2=CH_3 < Y_1=H,\ Y_2=H,$$
$$\Delta T: Y_1=CH_3,\ Y_2=H < Y_1=H,\ Y_2=H,\ Y_2=CH_3.$$

The results reveal that the orders of increasing the nematic ranges of the liquid crystals studied in this work can be affected by the introduction of different groups in their rigid cores. The same effects have been found for other liquid crystalline derivatives [9–11].

The introduction of the second lateral alkyl substituent (CH_3 or C_8H_{17}) into the rigid core of the 3-methyl-4-alkylbiphenyl esters of *trans*-4-alkylcyclohexanecarboxylic acid leads to the disappearance of the mesophase for the 3,5-dimethyl-4-alkylbiphenyl and 3-methyl-5-octyl-4-alkylbiphenyl esters of *trans*-4-alkylcyclohexanecarboxylic acid (**IV f**, **k**). The same effects have been found for other three-ring liquid crystalline derivatives [3].

Increasing the size of the lateral substituent ($CH_3 \rightarrow C_2H_5$, or $CH_3 \rightarrow OCH_3$, or $CH_3 \rightarrow Cl$) in 3-methyl-4-pentylbiphenyl ester of *trans*-4-butylcyclohexanecarboxylic acid (**IV h**) sufficiently lowers the clearing point and introduces the smectic phase in the second case (**IV j**, **p**), while in the last case, the replacement of the CH_3 group by a chlorine atom does not alter the clearing point, but introduces the smectic phase (**IV o**). The same effects have been found for other liquid crystalline compounds [3, 12]. The influence of the type of lateral substituent on the clearing points and nematic ranges for the 4-pentyl-3-substituted biphenyl esters of *trans*-4-butylcyclohexanecarboxylic acid can be expressed by the following orders of increasing T_{NI} and ΔT:



$$T_{NI} \rightarrow Y_2: C_2H_5 < OCH_3 < CH_3 \approx Cl < H,$$
$$\Delta T \rightarrow Y_2: C_2H_5 \approx OCH_3 \approx Cl < H < CH_3.$$

The introduction of the additional 1,4-phenylene group into the molecular structure of the 2-methyl-4-alkylbiphenyl and 3-methyl-4-alkylbiphenyl esters of *trans*-4-alkylcyclohexanecarboxylic acid causes the appearance of the smectic phase and sufficiently increases the nematic thermostability of the 2-methyl-4-alkylbiphenyl and 3-methyl-4-alkylbiphenyl esters of 4-(*trans*-4-alkylcyclohexyl)benzoic acid (**IV m**, **n**; see table 3). Interestingly, as in the case of the three-ring esters, laterally 3-methyl substituted four-ring esters (**IV m**) exhibit higher clearing points compared to those of the corresponding 2-methyl substituted four-ring esters (**IV n**).

The same effect can be seen for four-ring 3-methyl-4-alkylbiphenyl and 2-methyl-4-alkylbiphenyl esters of 4-(5-alkyl-1,3,2-dioxaborinanyl-2-)benzoic acid (**V b**, **c**; see table 3). As in the case of three-ring esters, increasing the size of the lateral substituent ($CH_3 \rightarrow C_2H_5$) leads to a decrease in the clearing point (**V d**). The substitution of the *trans*-1,4-cyclohexylene group by the 1,4-bicyclo[2,2,2]octylene group in the 3-methyl-4-alkylbiphenyl esters of 4-(*trans*-4-alkylcyclohexyl)-benzoic acid leads to increasing nematic thermostability of the 3-methyl-4-alkylbiphenyl esters of 4-(4-alkyl-[2,2,2]bicyclooctanyl-1)benzoic acid (**VI**). The same effects have been found for other weakly polar liquid crystalline derivatives [10, 12]. The data on the phase transition temperatures collated in tables 2 and 3 show that the compounds incorporating the 1,4-cyclohexenylene fragment exhibit lower values of melting and clearing points, lower smectic thermostability compared to the corresponding esters incorporating the 1,4-phenylene group (**IIIa** and **Ivc**, **IIIb** and **IVe**, **IIIc** and **IVh**; see tables 2, 3). The same effects including the additional decrease of the clearing point caused by increasing the size of the lateral substituent are found for the corresponding 3-methyl substituted three-ring and four-ring esters (see tables 2 and 3).

As supported by the data presented in tables 2, 3 and [13], the lateral 3-methyl substitution of the different groups incorporated into the rigid core of the three-ring weakly polar esters has a considerable effect on their mesomorphic properties which can be expressed by the following orders of increasing the clearing points and nematic ranges depending on the type of the fragment *A*;

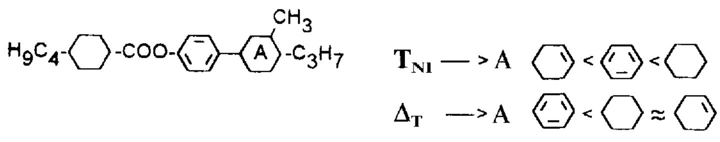


Table 4. Electrooptic parameters of the liquid crystalline mixtures†.

Compounds in mixture	Treshold voltage/V	Saturation voltage/V	ΔU/V
IIb	1·52	2·51	0·189
IIIa	1·48	2·19	0·202
IVc	1·50	2·09	0·174
IVh	1·49	2·06	0·190
IVo	1·41	1·96	0·188

†The mixtures were composed of 58 per cent 4-pentyl-4-cyanobiphenyl, 32 per cent 4-cyano-4-biphenyl ester of *trans*-4-propylcyclohex-2-encarboxylic acid and 10 per cent of the compounds indicated in the first column of the table.

The presented results on the mesomorphic properties of laterally substituted esters and the results received for other liquid crystalline derivatives [1–6, 9–13] reveal that the lateral alkyl, alkoxy or halogeno substitution sufficiently reduces the smectic tendency and nematic thermostability. These can be explained in terms of weakening intermolecular interactions due to the broadening of the molecules.

The dielectric anisotropy measured for the compound (**IV e**) has the usual small value observed for many other three-ring dialkyl substituted liquid crystalline derivatives [10, 12]. However the introduction of the very polar 1,3,2-dioxaborinane fragment into molecular rigid core increases its total dipole moment and, according to the theory of Maier and Meier, the dielectric anisotropy of the compound (**Va**; see table 3) [14].

As can be seen from table 4, new laterally substituted esters can be used as components of liquid crystalline materials, which are characterized by low threshold and saturation voltages of the twist-effect and steep voltage-contrast characteristics.

3. Conclusions

The new three and four-ring laterally-substituted esters exhibit low smectic tendencies and moderate clearing points. These make them potentially useful as the promising components for wide temperature range liquid crystalline materials for display applications.

4. Experimental

The proton NMR spectra of 10 per cent solutions in carbon tetrachloride with hexamethyldisiloxane as the internal standard were recorded using a TESLA BS-467. The transition temperatures were determined using a thermometer or a Perkin–Elmer DSC-2 differencial scanning calorimeter. The measurements of the electrooptic parameters of the mixtures were performed at 20°C in twisted nematic cells with a 10 µm spacer, a thin polyimide layer was used to obtain homogeneous oriented samples.

4.1. *4-Hydroxy-3-methyl-4-pentylbiphenyl (X)*

A mixture of 0·05 mol of 4-ethoxy-3-methyl-4-pentylbiphenyl and 15 ml of hydroiodic acid in 150 ml of acetic acid was heated at reflux for 8 h and poured into 200 ml of water. The organic layer was diluted with 100 ml of diethyl ether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from a mixture of toluene and hexane (1:4) and used in subsequent reactions. Yield 72 per cent.

The remaining phenols (**VII**–**X**) were obtained in a similar way.

4.2. *4-Hydroxy-2′-methylbiphenyl (XV)*

A mixture of 0·01 mol of 4-ethoxy-3′-methyl-4′-pentylbiphenyl and 0·025 mol of anhydrous aluminium chloride in 60 ml of benzene was heated at reflux for 5 h and poured into 100 ml of a 10 per cent hydrochloric acid solution. The organic layer was diluted with 100 ml of diethyl ether, washed with water and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from a mixture of toluene and hexane (1:1) and was used in subsequent reactions. Yield 51 per cent, m.p. 83°C.

The remaining phenols (**XV**) were obtained in a similar way.

4.3. *4-(4-Ethoxyphenyl)-1-pentyl-1-bromocyclohexane (XIII)*

Boron tribromide (0·01 mol) was added to solution of 0·01 mol of 4-(4-ethoxyphenyl)-1-pentylcyclohex-1-ene in 40 ml of anhydrous methyle chloride at −70°C. The mixture was stirred for 3 h at room temperature and poured into 100 ml of a 20 per cent sodium hydroxide solution. The organic layer was diluted with 100 ml of diethyl ether, washed with a 10 per cent hydrochloric acid solution, water, and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from isopropyl alcohol. Yield 37 per cent, m.p. 57°C.

4.4. *4-Pentyl-3-chloro-4′-biphenyl ester of* trans*-4-butylcyclohexanecarboxylic acid (IV)*

A mixture of 0·01 mol of 4-pentyl-3-chloro-4′-hydroxybiphenyl, 0·015 mol of *trans*-4-butylcyclohexane carboxylic acid chloride and 0·02 mol of pyridine in 100 ml of anhydrous diethyl ether was stirred for 6 h, washed with 10 per cent hydrochloric acid solution, water, and dried with anhydrous sodium sulphate. The residue obtained after the solvent had been removed was crystallized from isopropyl alcohol. Yield 54 per cent, m.p. 53°C.

The remaining esters (**I**–**VI**) were obtained in a similar way.

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