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Syntheses of new ionic liquid crystal compounds having a 2, 5-diaryl-1, 3-dioxane structure

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A new pyridinium type thermotropic ionic liquid crystal materials having a 2, 5-diaryl-1, 3-dioxane structure in its central core: N-Alkyl-4-[5-(p-alkoxyphenyl)-1, 3-dioxane-2-yl]-pyridinium bromides (6) were synthesized. As these compounds have three rings in its central core, the effect of core length to the phase transition in the case of ionic liquid crystal was investigated. And compared with the case of non-ionic 1, 3-dioxane compounds.

1. INTRODUCTION

In the last fifteen years, 2, 5-disubstituted 1, 3-dioxanes and 1, 3-oxathianes and 1, 3-dithianes have been reported as a new types of non-ionic liquid crystal materials.[1)-6)] In these studies, 2, 5-diaryl-1, 3-dioxanes as a non-ionic liquid crystal compounds having three rings in their core were also reported.[3)] Though these compounds have short terminal alkyl groups, they could exhibit a nemasic liquid crystal phase. On the contrary compounds having two rings and short terminal alkyl groups could not exhibit any liquid crystal phase.[2)] Therefore, three ring system is more advantageous to exhibit liquid crystal phase than two ring system in these non-ionic materials. As a new pyridinium type ionic liquid crystal materials having two rings in its core, N-ethyl-4-[5-(9-decenyl) -1, 3- dioxan -2- yl]-pyridinium bromide 6' was synthesized. And N-alkyl-4-[5-(p-substitutedphenyl)-1, 3-dioxan-2-yl]pyridinium bromides 6 were also synthesized as a ionic compounds having three rings in their core. In this paper, we wish to report the syntheses and phase transition of these ionic compounds 6 having three

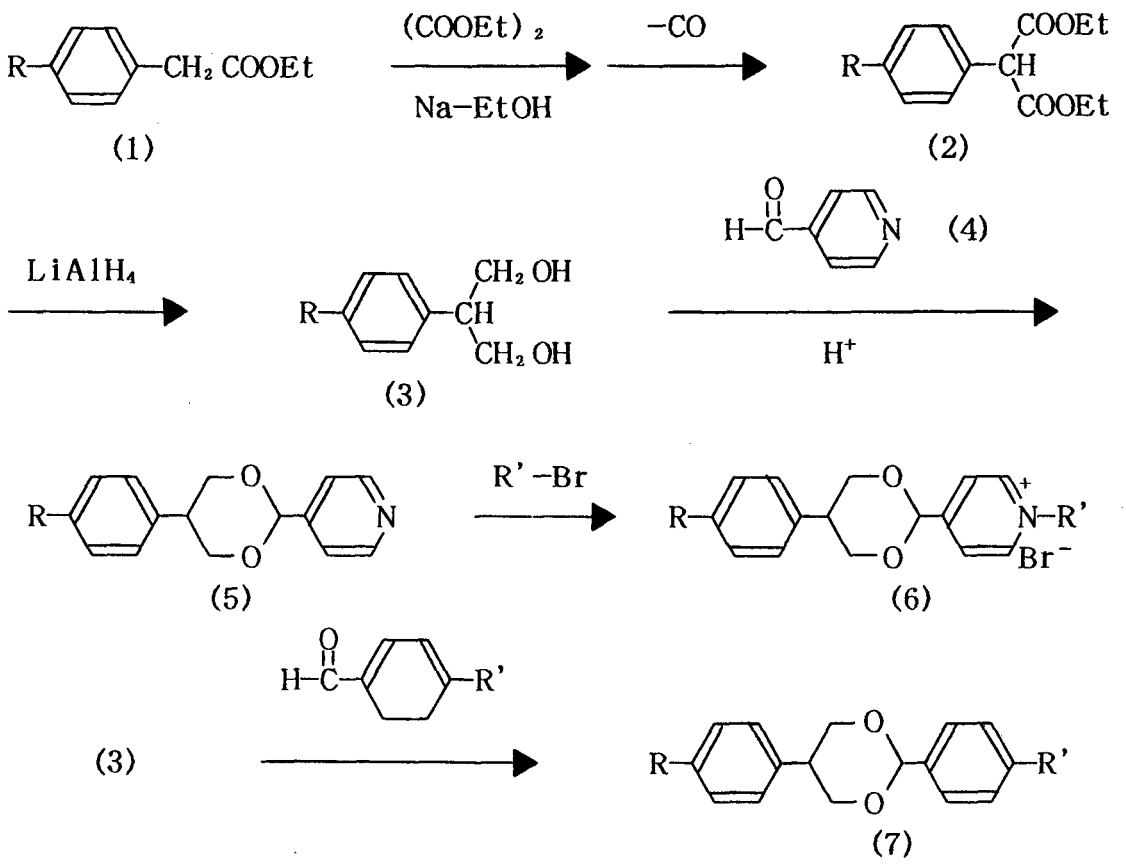


Fig. 1. Synthetic pathway for the compounds 6 and 7

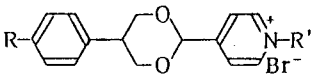
rings in their core.

2. RESULTS AND DISCUSSION

N-alkyl-4-[5-(4-alkoxyphenyl)-1,3-dioxan-2-yl]pyridiniumbromide 6 were synthesized via the route shown in Fig. 1.

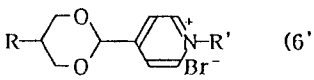
In the syntheses of compounds 2, the progress of reaction can be checked by the evolution of CO gas. It was necessary to keep the reaction temperature at 200~210 °C for about 30~40 min under a reduced pressure (20~25 mmHg). Compounds 5 were purified by column chromatography and repeated recrystallizations. (hexane:ether=2:1) Compounds 6 were purified by column chromatography (solvent:methanol) and reprecipitation (chloroform-ether). By the N-alkylation, ^{1}H-NMR signals for pyridinium

Table 1 Phase transition temperatures for compounds 6, 6' and 7



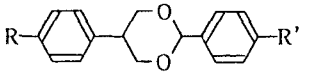
(6)

	R	R'	Phase transition temperatures (°C)
6-1	CH_3	C_2H_5	C 110 I
6-2	CH_3O	C_2H_5	C 185 I
6-3	C_2H_5O	C_2H_5	C 105 I
6-4	CH_3	$C_{10}H_{21}$	C 162 I
6-5	CH_3O	$C_{10}H_{21}$	C 137 I
6-6	$CH_2=CH(CH_2)_8O$	C_2H_5	G -25 SmA 125 I



(6')

	R	R'	Phase transition temperatures (°C)
6'	$CH_2=CH(CH_2)_8$	C_2H_5	C 58 SmA 96 I



(7)

	R	R'	Phase transition temperatures (°C)
7-1	C_2H_5O	C_2H_5	C 135 N 145 I
7-2	C_2H_5O	CH_3	C 136 N 147 I

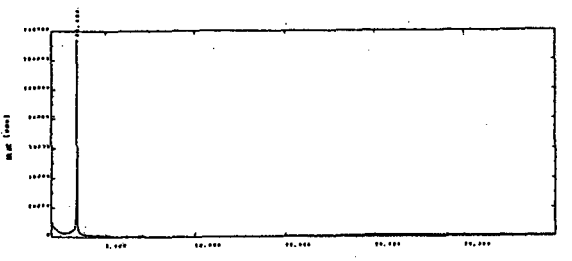
* C: Crystal, N: Nematic, SmA: Smectic A, I: Isotropic

proton and acetal proton (C-2 proton of the 1,3-dioxane ring) were shifted about 0.9 and 0.3 ppm to the lower magnetic field, respectively. The purity of compounds 6 was checked by the ^{1}H-NMR data and elemental analyses.

Measurement of transition temperarures and assignment of the mesophases were carried out by means of a micro-melting point apparatus equipped with polarizers, a differential scanning calorimeter (DSC), and a X-ray system. Phase transition temperatures for compounds 6 are given in Table 1.

Compounds 6-1 and 6-2 having short alkyl or alkoxyl grops did not exhibit any liquid crystal phases. In the non-ionic liquid crystal material, compounds 7 exhibit a nematic phase, and

there are many three rings compounds which exhibit liquid crystal phases in spite of having short alkyl or alkoxyl grops.[3] But this did not hold to ionic compounds. Then compounds 6-3 and 6-4 having a long alkyl chain ($C_{10}H_{21}$) as a N-alkyl group were synthesized. But these compounds also did not exhibit any liquid crystal phases. In the syntheses of pyridinium type compounds having two rings in their core, compound 6' having a 9-decenyl group exhibited a smectic A phase. Therefore, as a three ring ionic compound, compound 6-6 having a 9-decenyl group was synthesized. This compound exhibited a smectic phase over a very wide range including ordinary room temperature. Observation of this texture indicated that the type of liquid crystal phase is smectic A. To confirm this result X-ray diffraction was measured for the phase of compound 6-6. (Fig. 2) This result also support the assignment of the liquid crystal phase as smectic A. The transition temperature of isotropic to mesophase for compound 6-6 is about 30°C higher than that for compound 6'. This seems to originate in the length of core. That is, compound 6-6 having three rings as its core can exhibit smectic A phase to the higher temperature by the stronger molecular interaction amoung their cores.



(2 θ /deg.)

Fig. 2 X-ray diffraction pattern of new ionic liquid crystal compound 6-6

The most remarkable feature of this new ionic liquid crystal compound having three rings in its core is to exhibit liquid crystal phase over a very wide range including ordinary room temperature (G -25 SmA 125 I).

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