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Preparation of New Liquid Crystals with a Benzoyloxytropone Core

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Compounds having liquid crystal properties with a tropolone core were synthesized: A series of 5-alkoxy-2-benzoyloxytropones showed the mesophase(s), whereas corresponding 5-alkoxy-2-benzyloxytropones did not. A [1,9] sigmatropy seems to play an important role to this mesomorphic behavior.

In 1983, Kusabayashi et al.[1] synthesized a series of liquid crystals having a terminal troponoid core and pointed out that a C-2 alkoxy substituent at the tropolone ring decreased the nematic stability.

Recently, we showed[2] that a migration of acetyl group in 2-acetoxytropones[3] is a concerted [1,9] sigmatropic process. It is therefore interesting to determine whether the 2-acyloxytropones can be a core of the liquid crystals or not, although, a wider tropone ring is probably less favorable than the benzene ring. We herein describe the findings with several 5-alkoxy-2-benzoyloxytropones, whose 2-benzoyloxy groups are also [1,9] sigmatropic systems.[4]

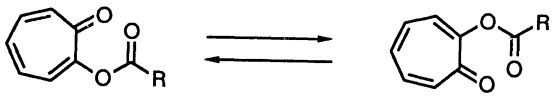
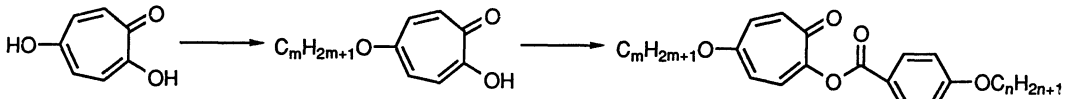


Table 1 shows synthesized derivatives of 5-alkoxy-2-(p-alkoxybenzoyloxy)tropones (**1**). The intermediates 5-alkoxytropolones (**2**), were prepared by monoalkylation of 5-hydroxytropolone (**3**) with alkyl bromide in the presence of NaH in hexamethylphosphoric triamide, and subsequent acylation of **2** with p-substituted benzoyl chlorides afforded **1**. The broadened ^{1}H NMR signals ascribable to the protons on the tropone ring at room temperature in $CDCl_3$ solutions indicated an occurrence of migration of the benzoyl groups.[5]



3 → **2a** (m=11), 88%; **2b** (m=12), 90% → **1**

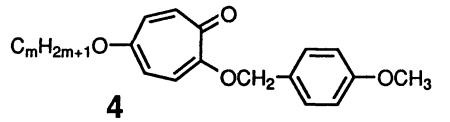
Determinations of the phase transition temperatures and observations of microscopic textures were carried out using a differential scanning calorimeter (DSC) and a polarized microscope equipped with a hot stage. The compound **1a** and **1c** showed a monotropic nematic liquid crystal phase, whereas **1b** and **1e** did enantiotropic smectic liquid crystal phases as shown in Table 1. The DSC curves of **1e** were shown in Fig. 1, in which the run 3 revealed a glass transition around -20 °C.[6]

Table 1. Synthesis of **1** and their transition temperatures and enthalpy changes[a)]

	m	n	Yield/%	Tt (ΔH/kJ mol^{-1})
1a	11	1	81	K 66 °C (53.9) I; I 45 °C (1.7) N; N 44 °C (34.8) K
1b	11	12	78	K 51 °C (54.5) S 85 °C (7.0) I; I 85 °C (6.3) S; S K
1c	12	1	83	K 71 °C (42.3) I; I 50 °C (1.7) N; N 44 °C (34.8) K
1d	12	4	65	K 64 °C (24.3) M* 70 °C (4.7) I; I 70 °C (5.5) M*; M* K
1e	12	12	43	K 64 °C (68.9) S 90 °C (9.8) I; I 90 °C (10.2) S; S K

a) K: Crystalline, I: Isotropic, N: Nematic, S: Smectic, M*: Unspecified mesophase.

On the other hand, 5-alkoxy-2-(p-methoxybenzyloxy)tropone (**4**), where alkoxyl groups were up to C_{12}, showed no mesophase character. An evaluation for this apparent difference in mesophase character will be discussed independently.



4

m=11, K 68 °C (49.3 kJ mol^{-1}) / 63 °C (50.6 kJ mol^{-1}) I

m=12, K 69 °C (51.7 kJ mol^{-1}) / 60 °C (52.8 kJ mol^{-1}) I

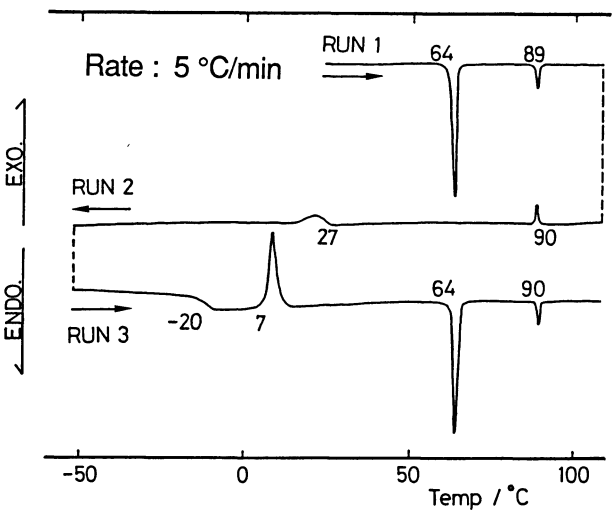


Fig. 1. DSC Curves of **1e**.

Thus, a [1,9] sigmatropy is favored, at least in certain cases, to exhibit the mesophase character, and further investigations with several other related compounds are in progress and will be matters of forthcoming full papers.

References

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