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Synthesis of 2-(Alkanoyloxy)-5-alkoxytropones. Novel Monocyclic Rod-Type Liquid Crystals

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Compounds that form liquid crystals have rod-like structures consisting of a rigid core with flexible terminal substituents.[1] The core moiety usually consists of at least two six-membered aromatic rings with or without bridging groups.

As liquid crystal core material, tropones have the potential of yielding novel liquid crystal forming derivatives with unique properties which stem from the fact that acyl substituents of 2-(acyloxy)-2,4,6-cycloheptatrien-1-ones (2-(acyloxy)tropones) are known to migrate (acylotropy) between the two oxygen atoms at C-1 and C-2.[2] The mechanism of an acetotropic rearrangement (i.e., acetyl group migration) has been shown to involve a concerted [1,9] sigmatropic rearrangement.[3] The sigmatropic behavior was inferred from substituent and solvent effects[4] as well as from high-pressure kinetic analysis.[5]

Liquid crystalline compounds capable of exhibiting this [1,9] sigmatropy may be expected to possess unique and novel properties. In a previous paper, we reported the preparation of new liquid crystals with a 2-(benzoyloxy)tropone core.[6] The present paper describes the synthesis of several potential liquid crystalline, rod-like compounds with a 2-(acyloxy)tropone core and offers evidence that these novel compounds exhibit liquid crystalline behavior.

On the basis of pK_a difference between the two hydroxy groups of 5-hydroxytropolone (**1**) (pK_{a_1} = 6.5; pK_{a_2} = 10.1),[7] 2-(acyloxy)-5-alkoxytropones (**2**) were prepared as follows; **1** (2 g) was treated with NaH (792 mg) in hexamethylphosphoric triamide (50 mL) at 0 °C for 30 min (Scheme I). Various alkyl bromides were added to the resultant greenish solution at 0 °C, and the mixture was kept at room temperature for 24 h. The resulting 5-alkoxytropolones (**3**), obtained in 56–90% yields,[8] were reacted with the desired acyl chloride in pyridine to give **2** in 20–88% yields.[8] Phase-transition temperatures and their enthalpies and entropies were determined by differential scanning calorimetry (DSC). The DSC curves did not change after several scannings. The appearance of the mesomorphic phases was determined with a polarizing microscope equipped with a hot stage. The results are summarized in Table I.

Except for **2g** and **2k**, the 2-(acyloxy)-5-alkoxytropones (**2**) exhibited the formation of monotropic meso phases. The S_A phase separated from the isotropic liquid in the form of bâtonnets (elongated rods). As an example of the behavior of the compounds, typical microscopic photographs and DSC thermograms of **2e** are shown in Figures 1 and 2. The DSC-determined enthalpies of the S_A–I transition (9.7–17 kJ·mol^{-1}), except for **2j**, are not unlike those of other systems having an S_A–I transition (2.9–12.6 kJ·mol^{-1}).[6,9-11] The transition entropies (31.1–52.5 J·mol^{-1}·K^{-1}) are almost twice as large as those of 5-alkoxy-2-((4-alkoxybenzoyl)oxy)tropones (13–28 J·mol^{-1}·K^{-1}),[12] of 4-propionyl-4′-(*n*-alkanoyloxy)azobenzenes (19.0–22.0 J·mol^{-1}·K^{-1}),[10] and of 4,4′-dialkoxy-α,α'-dimethylbenzalazines (15.3–28.3 J·mol^{-1}·K^{-1}).[11] On the other hand, the 2,5-dialkoxytropones (**4a**, mp 63 °C; **4b**, mp 63 °C; **4c**, mp 64–66 °C) were nonmesogenic.

The solid-state ^{13}C CPMAS (cross polarization magic angle spinning) NMR of 5-(dodecyloxy)-2-((4-(dodecyloxy)benzoyl)oxy)tropones (**5**) suggested that it formed an enantiotropic S_C phase from 64 to 90 °C.[6] At 50 °C, the spectrum was unchanged from that at 25 °C. At 75 °C, approximately the midpoint of the temperature range of the S_C phase, the intensities of the signals of seven-membered-ring carbons were diminished, indicating their

Scheme I

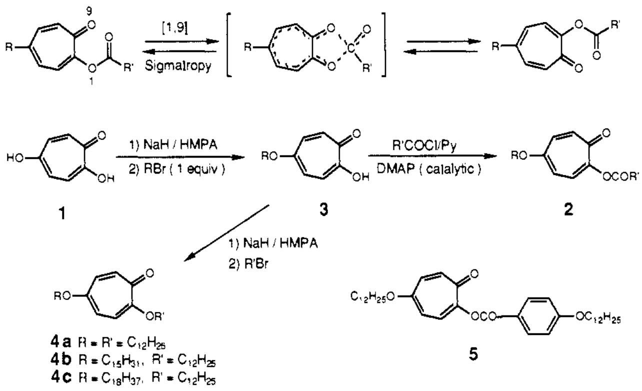

Table I. Transition Temperatures, Enthalpies, and Entropies of Transition for **2**[a]

	R	R′	S_A–I	mp	recrystn temp
2a	$C_{12}H_{25}$	C_9H_{19}	[46]	48	36
			ΔH = 11.7,	55.1; ΔS = 36.5	
2b[b]	$C_{12}H_{25}$	$C_{11}H_{23}$	[45]	58	41
2c[b]	$C_{12}H_{25}$	$C_{13}H_{27}$	[51]	63	48
2d	$C_{15}H_{31}$	C_7H_{15}	[39]	41	*c*
			ΔH = 9.7,	56.9; ΔS = 31.1	
2e	$C_{15}H_{31}$	C_9H_{19}	[47]	48	24
			ΔH = 12.6,	64.4; ΔS = 39.5	
2f	$C_{15}H_{31}$	$C_{11}H_{23}$	[52]	60	47
			ΔH = 10.9,	73.9; ΔS = 33.6[d]	
2g	$C_{15}H_{31}$	$C_{13}H_{27}$		67	60
2h	$C_{18}H_{37}$	C_7H_{15}	[39]	49	32
			ΔH = 10.1,	64.2; ΔS = 32.3	
2i	$C_{18}H_{37}$	C_9H_{19}	[46]	53	29
			ΔH = 14.9,	71.1; ΔS = 46.6	
2j	$C_{18}H_{37}$	$C_{11}H_{23}$	[52]	60	44
			ΔH = 17.0,	62.2; ΔS = 52.5	
2k	$C_{18}H_{37}$	$C_{13}H_{27}$		72	61

[a] All thermodynamic values determined by differential scanning calorimetry (DSC). Values in brackets, monotropic phase transitions; ΔH, enthalpy of transition, kJ·mol^{-1}; ΔS, entropy of S_A–I transition, J·mol^{-1}·K^{-1}; mp, melting point of crystals to isotropic liquid, °C; recrystn temp, recrystallization temperature, °C. [b] Enthalpies for **2b** and **2c** could not be detected by DSC (5 °C·min^{-1}). [c] Recrystallization peak could not be observed until −30 °C. [d] This figure was smaller than that of **2e** due to the small temperature difference between the transition and the recrystallization temperatures.

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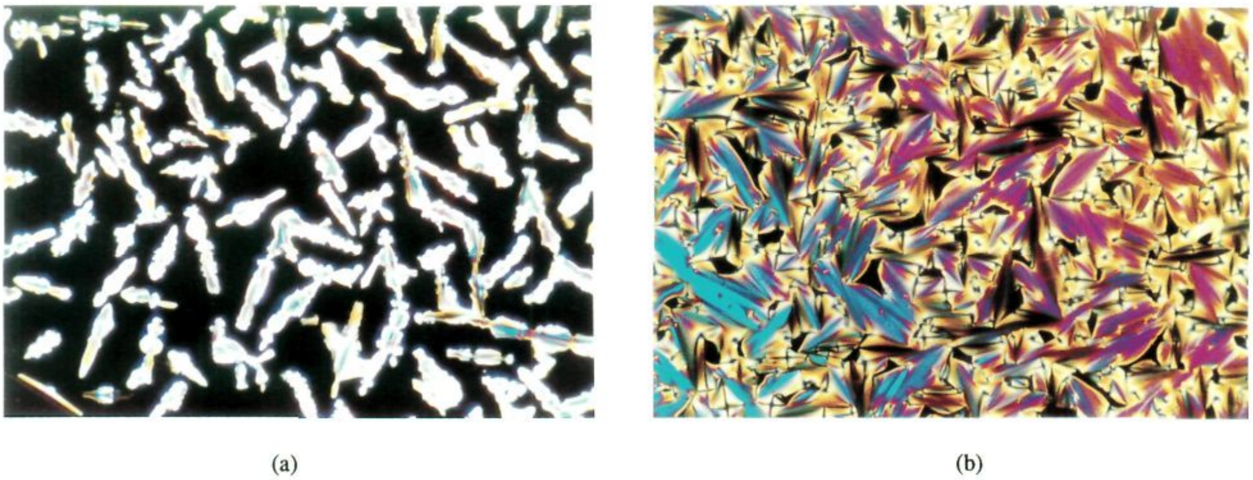
(a) (b)

Figure 1. Optical textures observed with **2e**: (a) bâtonnets and (b) fan-shape textures.

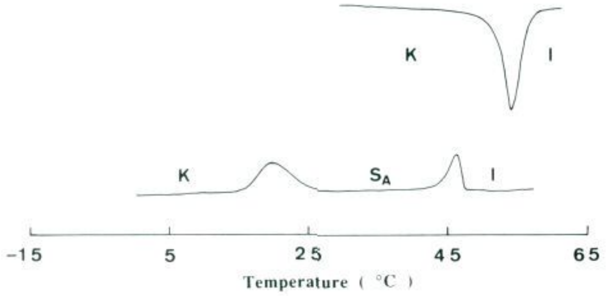

Figure 2. DSC thermograms of **2e** (K = crystals, S_A = smectic A phase, I = isotropic liquid). The upper thermogram shows the heating process, whereas the lower one shows the cooling process.

increased mobility. All other signals remained sharp. This behavior suggests that the [1,9] sigmatropy was occurring at 75 °C, i.e., in the meso phase, and that the rod-like monocyclic tropone derivatives became liquid crystalline via this dynamic molecular rearrangement.

The length of the terminal alkyl chains had appreciable effects on meso-phase formation;[3] the longer the alkyl chain, the higher the melting point and the larger the entropy change of the S_A–I transition (see Table I). When R = $C_{18}H_{37}$, the melting point changed from 49 (R′ = C_7H_{15}) to 60 °C (R′ = $C_{11}H_{23}$) while the entropy changed from 32.3 to 52.5 J·mol^{-1}·K^{-1}. On the other hand, when R′ = C_9H_{19}, the melting point changed from 48 (R = $C_{12}H_{25}$) to 53 °C (R = $C_{18}H_{37}$) while the entropy changed from 36.5 to 46.6 J·mol^{-1}·K^{-1}, showing that the chain length of the migrating portion (R′) plays a much more important role than that of R.

The evidence presented herein supports the suggestion that the 2-(acyloxy)-5-alkoxytropones are able to form time-averaged liquid crystal structures with a linear rod-type geometry via [1,9] acylotropy. In all cases, they exhibited a large induced dipole moment along the longer molecular axis. Further studies on these novel compounds are underway.

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Registry No. 2a, 129787-48-0; **2b**, 129787-49-1; **2c**, 129787-50-4; **2d**, 129787-51-5; **2e**, 129787-52-6; **2f**, 129787-53-7; **2g**, 129787-54-8; **2h**, 129787-55-9; **2i**, 129787-56-0; **2j**, 129787-57-1; **2k**, 129787-58-2; **4a**, 129787-59-3; **4b**, 129787-60-6; **4c**, 129787-61-7.