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Monocyclic Rod-Type Liquid Crystals, 2-(2-Alkenoyloxy)-5-alkoxytropones

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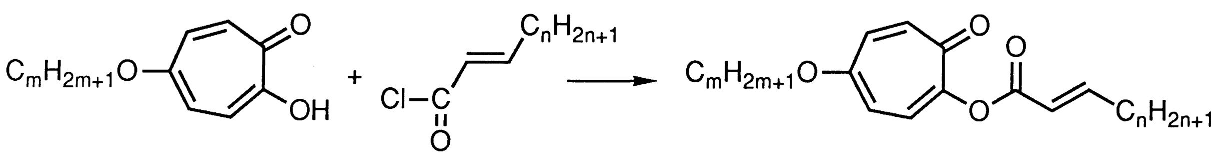
In 2-(2-alkenoyloxy)-5-alkoxytropones, showing a monotropic smectic A phase, the introduction of a double bond lowers the melting and clearing points as well as the recrystallization temperatures.

The core part of rod-type thermotropic liquid crystals usually has at least two six-membered rings.[1] A few monosaccharides[2,3] and aromatic acid derivatives[4] form a stable dimer through hydrogen bonding to show mesophase formation. Recently, however, we reported that the monocyclic troponoids, 2-alkanoyloxy-5-alkoxytropones, were monotropically mesogenic and that the characteristic molecular rearrangement, the [1,9] sigmatropy, played an important role to exhibit the mesophase.[5,6] In this paper, we report the preparation of monocyclic rod-type liquid crystals with 2-(2-alkenoyloxy)-5-alkoxytropone structure, which was expected to extend the linearity of the molecule by introducing the double bond.

2-(2-Alkenoyloxy)-5-alkoxytropones (**1**) were prepared in 39-74% yields from 5-alkoxytropolones (**2**) and alkenoyl chlorides (**3**). Alkenoic acids were obtained by the Horner-Emmons reaction (K_2CO_3/H_2O, 25 °C, 79-92% yields) of aldehydes and ethyl diethylphosphonoacetate and followed by the hydrolysis (KOH/EtOH-H_2O, 78-95% yields) of ethyl alkenoates.



2 **3** **1**

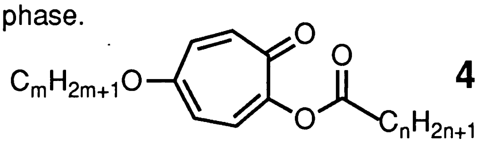
Phase transition temperatures were determined by a differential scanning calorimeter (DSC). The mesomorphic phases were identified to be a smectic A phase (S_A) on the basis of the microscopic texture.

The phase transition behaviors are summarized in Table 1. The melting and clearing points as well as the recrystallization temperatures of **1** are lower than those of the corresponding 2-alkanoyloxy-5-alkoxytropones (**4**) with the same side chain length.[5,6] Although the thermal stability of **1** decreased, the temperature range showing the liquid crystalline property increased. In the cases of **1f** and **1i**, they showed a S_A phase, whereas the corresponding **4f** and **4i** were nonmesogenic. The double bond seems to extend the linearity and planarity of the molecule to order the molecules. Related studies on monocyclic rod-type liquid crystals are in progress.

Table 1. Phase transition temperatures and enthalpy changes of **1** and **4**[a)]

Entry	m	n	Transition temp / °C (ΔH / kJ·mol^{-1})	Entry	m	n	Transition temp / °C (ΔH / kJ·mol^{-1})
1a	12	7	K → Iso 36; Iso → S_A 28; S_A → K -4	**4a**	12	9	K → Iso 48(55.1); Iso → S_A 46(11.7); S_A → K 36(21.2)
1b	12	9	K → Iso 47(50.3); Iso → S_A 42(11.8); S_A → K 22(36.8)	**4b**	12	11	K → Iso 58; Iso → S_A 45; S_A → K 41
1c	12	11	K → Iso 67; Iso → S_A 48; S_A → K 36	**4c**	12	13	K → Iso 63; Iso → S_A 51; S_A → K 48
1d	15	7	K → Iso 48(54.6); Iso → S_A 42(12.8); S_A → K -11(16.1)	**4d**	15	9	K → Iso 48(64.4); Iso → S_A 47(12.6); S_A → K 24(28.1)
1e	15	9	K → Iso 54(72.8); Iso → S_A 49(14.6); S_A → K 35(54.5)	**4e**	15	11	K → Iso 60(73.9); Iso → S_A 52(10.9); S_A → K 47
1f	15	11	K → Iso 61(74.0); Iso → S_A 53; S_A → K 51	**4f**	15	13	K → Iso 67(83.7); Iso → K 60(57.7)
1g	18	7	K → Iso 56(67.7); Iso → S_A 43(13.1); S_A → K 5(29.7)	**4g**	18	9	K → Iso 53(71.1); Iso → S_A 46(14.9); S_A → K 29(20.3)
1h	18	9	K → Iso 62(83.0); Iso → S_A 51(17.1); S_A → K 35(59.9)	**4h**	18	11	K → Iso 60(62.2); Iso → S_A 52(17.0); S_A → K 44(36.5)
1i	18	11	K → Iso 69(88.9); Iso → S_A 56; S_A → K 55	**4i**	18	13	K → Iso 72; Iso → K 61

a) K: crystals, Iso: isotropic liquid, S_A: smectic A phase.



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