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Mesomorphic properties of 2-acyloxy-5-(4-alkoxyphenylazo)tropones, 2-acyloxy-5-(4-alkylphenylazo)tropones, and 2-acyloxy-5-(4-alkoxycarbonylphenylazo)tropones

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Three series of mesomorphic 2-acyloxy-5-phenylazotropones with alkoxy, alkyl, and alkoxycarbonyl groups at C-4 on the phenyl ring were prepared. It was known that the corresponding 5-phenylazotropolone derivatives and their methyl ethers were not mesomorphic. 2-Acetyl-5-(4-hexyloxyphenylazo)tropone, however, shows a monotropic smectic A phase. Even an acetyl group is therefore able to induce a mesophase. The effects of terminal substitution of the tropone ring by groups such as alkoxy, alkoxycarbonyl, and alkyl on the clearing points are discussed.

1. Introduction

Much attention has been paid to liquid crystal materials with an azo linking group because the azobenzene unit is one of the typical cores of liquid crystals [1] and the preparation of new types of liquid crystals with the azobenzene unit is being continued [2]. At the same time, it is known that the azobenzene chromophore is reversibly isomerized through *trans*-*cis*-*trans*-cycles under irradiation. This *trans*-*cis*-isomerization is widely used for light switching devices [3]. We have recently reported that troponoids provide a useful core for liquid crystals because we observed in several examples that troponoids were mesomorphic whereas the corresponding benzenoids were not [4].

In 1983, Kusabayashi and his coworkers reported the behaviour of 5-(4-alkoxyphenylazo) tropolones (**1**), 5-(4-alkylphenylazo)tropolones (**2**) with a polar tropolone ring at the terminal position and their methyl ethers (**3**) [5]. This was the first example of the preparation of mesogens containing the monocyclic tropolone moiety. However, they were not mesomorphic under normal conditions and had only virtual nematic–isotropic transition temperatures. The following reasons why they were not mesomorphic have been proposed: the tropolone derivatives **1** and **2** are in equilibrium with a keto form, which has a freedom to rotate around the single bond to the azo group, so increasing conformational flexibility and decreasing mutual conjugation, while the methyl ethers **3** have decreased dispersion forces and increased molecular width, all these factors contributing to reduce the mesomorphic properties.

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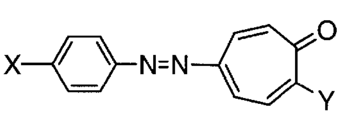
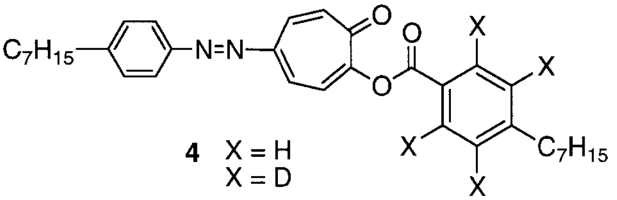
Table 1. Transition temperatures (°C) of compounds **5**. Cr = crystal, SmA and SmC = smectic A and C phase, I = isotropic liquid. The number in parenthesis refers to a monotropic phase transition.

	*R*1	*R*2	Cr		SmC		SmA		I
5a	C_2H_5	C_7H_{15}	•			91.7	•	123.0	•
5b	C_2H_5	C_9H_{19}	•			105.7	•	126.8	•
5c	C_2H_5	$C_{11}H_{23}$	•			105.2	•	129.5	•
5d	C_3H_7	CH_3	•					131.1	•
5e	C_3H_7	C_7H_{15}	•			83.7	•	122.6	•
5f	C_3H_7	C_9H_{19}	•			92.5	•	125.6	•
5g	C_3H_7	$C_{11}H_{23}$	•			84.3	•	125.9	•
5h	C_4H_9	C_7H_{15}	•			88.1	•	134.6	•
5i	C_5H_{11}	C_7H_{15}	•			86.0	•	133.0	•
5j	C_5H_{11}	C_9H_{19}	•			85.2	•	133.9	•
5k	C_5H_{11}	$C_{11}H_{23}$	•			86.1	•	133.9	•
5l	C_6H_{13}	CH_3	•			123.0	(•	93.3)	•
5m	C_6H_{13}	C_7H_{15}	•			89.6	•	136.9	•
5n	C_6H_{13}	C_9H_{19}	•			84.9	•	135.9	•
5o	C_6H_{13}	$C_{11}H_{23}$	•			82.9	•	137.2	•
5p	C_7H_{15}	C_7H_{15}	•	90.6	•	104.0	•	135.4	•
5q	C_8H_{17}	C_7H_{15}	•	89.4	•	112.0	•	136.2	•
5r	C_8H_{17}	C_9H_{19}	•	93.9	•	118.1	•	137.1	•
5s	$C_{11}H_{23}$	C_9H_{19}	•	93.8	•	126.3	•	132.7	•
5t	$C_{11}H_{23}$	$C_{11}H_{23}$	•	94.1	•	126.7	•	132.6	•

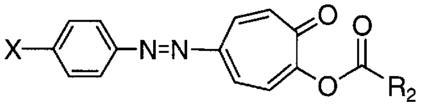


1 X = OR, Y=OH
2 X = C_6H_{13}, Y=OH
3 X = OR, Y=OCH_3
8 X = COOR, Y=OH



4 X = H
X = D

In 1993, Italian researchers prepared the 2-(4-heptylbenzoyloxy)-5-(4-heptylbenzenazo)tropone (**4**) and its partially deuteriated analogue to prove the [1, 9]-sigmatropy [6, 7] by using deuterium NMR spectrometry [8]. In continuation of our work on troponoid liquid crystals [9], we now report the preparation of 2-acyloxy derivatives **5**, **6** and **7** of a phenylazotropolone moiety to establish their thermal properties.



5 X = OR_1
6 X = $COOR_1$
7 X = C_6H_{13}

2. Synthesis

2-Acyloxy-5-(4-alkoxyphenylazo)tropones (**5**), 2-acyloxy-5-(4-alkoxycarbonylphenylazo) tropones (**6**), and 2-acyloxy-5-(4-alkylphenylazo)tropones (**7**) were prepared by acylation of the corresponding tropolone derivatives (**1**, **2**, **8**), which were obtained as reported in [5]. The transition temperatures and the thermal behaviour of the textures were determined using a polarizing optical microscope equipped with a hot stage. Differential scanning calorimetry, as well as measurements using X-ray diffraction were also used to provide further information. The transition temperatures of the compounds **5**, **6**, and **7** are summarized in tables 1–3.

Table 2. Transition temperatures (°C) of compounds **6**.

	*R*1	*R*2	Cr		SmA		I
6a	C_2H_5	C_7H_{15}	•	103.5	•	111.0	•
6b	C_2H_5	C_9H_{19}	•	98.4	•	113.1	•
6c	C_2H_5	$C_{11}H_{23}$	•	95.7	•	115.4	•
6d	C_3H_7	C_7H_{15}	•	97.3	•	115.3	•
6e	C_3H_7	C_9H_{19}	•	83.1	•	116.2	•
6f	C_3H_7	$C_{11}H_{23}$	•	81.5	•	116.3	•
6g	C_4H_9	C_7H_{15}	•	92.1	•	110.0	•
6h	C_4H_9	C_9H_{19}	•	90.8	•	110.7	•
6i	C_4H_9	$C_{11}H_{23}$	•	91.3	•	109.7	•
6j	C_5H_{11}	C_7H_{15}	•	88.2	•	114.1	•
6k	C_6H_{13}	C_7H_{15}	•	92.3	•	111.6	•
6l	C_6H_{13}	C_9H_{19}	•	87.3	•	111.0	•
6m	C_6H_{13}	$C_{11}H_{23}$	•	85.1	•	109.9	•
6n	C_7H_{15}	C_7H_{15}	•	93.9	•	111.9	•
6o	C_8H_{17}	C_7H_{15}	•	95.1	•	111.4	•
6p	C_8H_{17}	C_9H_{19}	•	89.0	•	110.1	•
6q	C_8H_{17}	$C_{11}H_{23}$	•	85.0	•	109.9	•

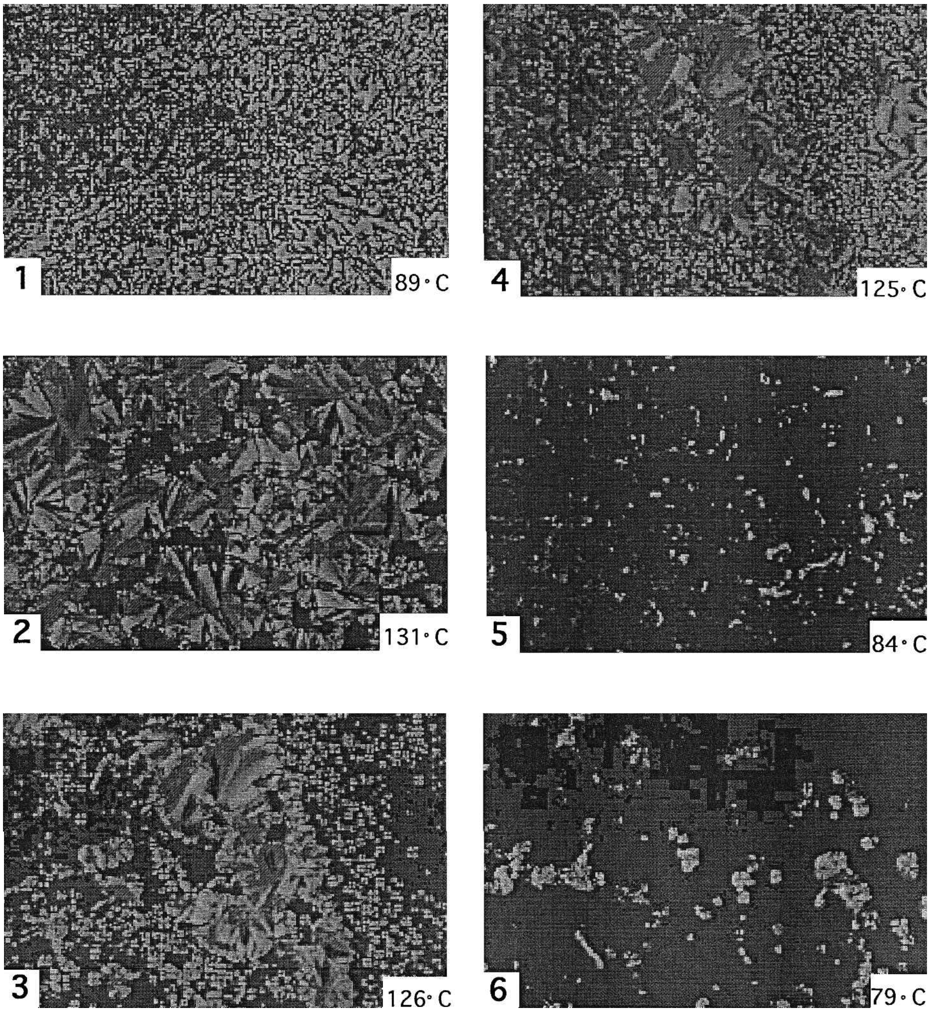


Figure 1. Photographs of textures of the perpendicularly oriented compound **5t** as obtained on heating and cooling processes.

Table 3. Transition temperatures (°C) of compounds **7**.

	*R*2	Cr		SmA		I
7a	C_7H_{15}	•	87.4	•	103.1	•
7b	C_9H_{19}	•	76.9	•	103.9	•
7c	$C_{11}H_{23}$	•	75.6	•	103.5	•

3. Mesomorphic properties

Compounds **5** with shorter chains showed focal-conic fan textures which were assigned to smectic A (SmA) phases with the enthalpy changes between the SmA phase and the isotropic liquid state were 3.9–11.0 kJ mol^{-1}. Compounds **5** with longer side chains gave SmA and smectic C (SmC) phases on heating. Figures 1 and 2 show the textures of perpendicularly and horizontally oriented samples of compound **5t**, respectively.† Photograph 1 in figure 1, which was taken at 89°C on heating the supercooled phase showed the schlieren texture of the SmC phase. By heating from the SmC phase, photograph 2 taken at 131°C shows the focal-conic fan texture of the SmA phase. Photographs 3–6 were taken during a cooling process. Photograph 3 shows the focal-conic fan and homeotropic textures of SmA above 126°C and photograph 4 the fan and schlieren textures of the SmC phase at 125°C. The homeotropic texture of a smectic B (SmB) phase is shown in photograph 5 at 84°C and homeotropic and focal-conic fan textures of the SmB phase are in photograph 6 at 79°C. On the other hand, photographs of the horizontally oriented samples were measured on a cooling process. Photograph 1 in figure 2 shows the focal-conic fans at 125°C, while broken fans of the SmC phase are clearly observed in photograph 2 at 94°C. In photograph 3, fans with transition bars are observed at 83°C and mosaic/fan textures at 74°C in photographs 4 and 5. These microscopic observations indicate that the phase sequence of **5t** is as follows:

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†Homeotropic alignment was obtained spontaneously in a non-treated sandwich cell whereas focal-conic fan and mosaic textures were obtained in a rubbed sandwich cell.

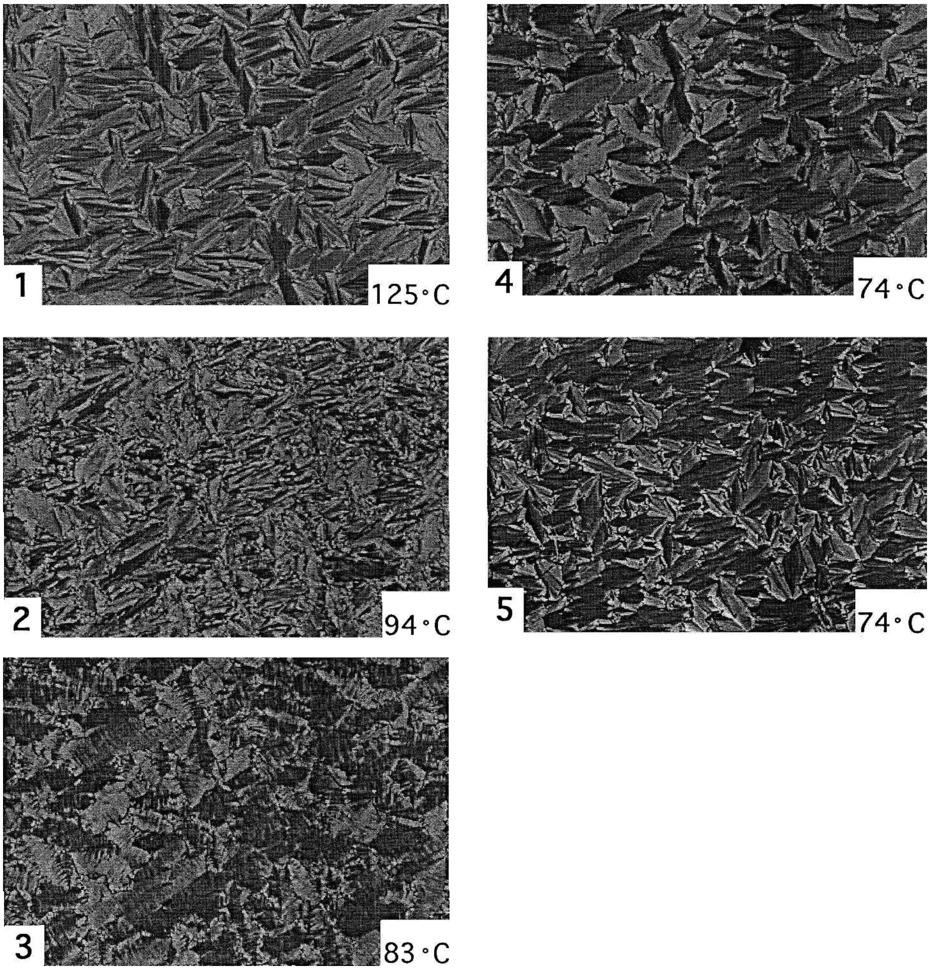
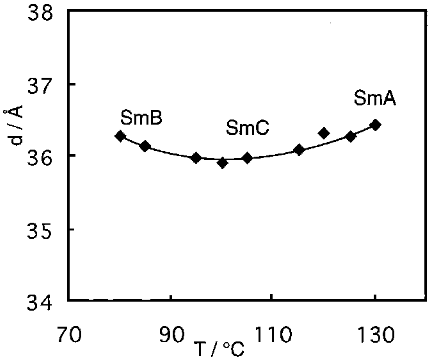


Figure 2. Photographs of textures of the horizontally oriented compound **5t** as obtained on cooling from the isotropic liquid.



T / °C	d / Å
130	36.4
125	36.3
120	36.3
115	36.1
105	36.0
100	35.9
95	36.0
85	36.1
80	36.3

Figure 3. Layer spacings of the perpendicularly oriented compound **5t** as obtained on cooling from the isotropic liquid: I · 132 · SmA · 126.5 · SmC · 87.1 · SmB · 71.1 · Cr (°C).

Cr · 94.1 · SmC · 126.7 · SmA · 132.6 · I · 132 · SmA · 125.5 · SmC · 87.1 · SmB · 71.1 · Cr (°C). The SmB phase is therefore monotropic.

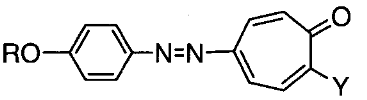
Next, X-ray diffraction (XRD) patterns were measured to determine the layer spacings of perpendicularly oriented **5t** as shown in figure 3. The layer spacings decrease when the mesomorphic state changes from SmA to SmC. The molecular length was calculated to be 40.7 Å by the MM2 method. Since the layer spacing (*d*) of the SmA phase was found to be 36.4 Å at 130°C, the terminal chains must be deformed and cores randomly tilted to be on average orthogonal to the layer planes. When the temperature was lowered, the layer spacings decreased slightly to 36 Å at 105°C. Although the decrease in *d*-value is small, it is consistent with the appearance of the SmC phase. Furthermore, when the temperatures were lowered further, the *d*-value increased slightly to 36.3 Å at 80°C. This indicated that the molecules became perpendicular to the layer plane with formation of the SmB phase. Thus the phase sequence SmA–SmC–SmB is supported by XRD. Compounds **6** and **7** showed focal-conic fan textures. The XRD study of **6k** showed that the layer spacing is 30.4 Å, which is slightly shorter than the calculated molecular length (31.8 Å) by the MM2 method. Similarly the layer spacing of **7c** is 34.4 Å, which is also slightly shorter than the molecular length (34.9 Å).

4. Discussion

It has been reported [5] that the reasons why compounds **1** and the methyl ethers **3** are not mesomorphic, are the lack of the planarity of the core part due to free rotation around the single bonds to the azo group of the keto form of **1**, and the increased molecular width. Table 4 gives a comparison of the transition temperatures of tropolone derivatives **1b** and **1e**, the methyl ethers **3a** and **3b**, and the acetates **5d** and **5l**. When the melting point of a tropolone derivative is compared with that of its methyl ether, they are not much different. Acetates **5d** and **5l** have the lowest melting points however and acetate **5l** with a hexyloxy group had a monotropic SmA phase. These results supported the view that the acetyl group at the C-2 position did not expand the molecular width like the methyl ether, because it stayed within the molecular width due to [1, 9]-sigmatropy. This is a parallel conclusion to that which we have already reached for other sigmatropic derivatives [6]. Additionally, the keto form contribution in the tropolone derivatives (**1**) is not present in the tropolone acetates.

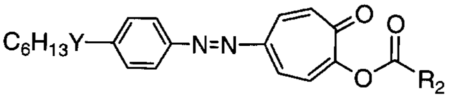
The effects of the terminal substituents are summarized in table 5, where the length of the substituent on the phenyl ring is restricted to C_6H_{13}–Y (Y = O, OOC, none). As when considering the effect of the side chain in the phenyl ring on the mesomorphic properties, the compounds **5** have the highest clearing points. The compounds with the highest melting points are the compounds **6**, whereas the compounds **7** have the lowest clearing points. Table 5 summarizes the transition temperatures of **5**, **6**, and **7**. The order of thermal stability as defined by the clearing points is **5** with an alkoxy group > **6** with an alkoxycarbonyl group > **7** with an alkyl group. The order is explained as follows: the alkoxy groups of **5** donate electrons to induce a large dipole moment along the molecular long axis, enhancing the thermal stability. In the case of the electron-withdrawing alkoxycarbonyl groups of **6**, the total dipole moment of the molecule would be reduced, so decreasing the thermal stability. Table 6 summarizes the transition temperatures when the number of atoms contributing to the lengths of the substituents on the phenyl ring is identical. The results are similar to those in table 5.

Table 4. Comparison of transition temperatures (°C) of compounds **1**, **3** and **5**.



R	Y = OH	Y = OCH$_3$	Y = OCOCH$_3$
C_3H_7	**1b**: Cr · 177.2 · I	**3a**: Cr · 161.2 · I	**5d**: Cr · 131.1 · I
C_6H_{13}	**1e**: Cr · 151.2 · I	**3b**: Cr · 152.2 · I	**5l**: Cr · 123.0 (SmA · 93.3) · I

Table 5. Comparison of transition temperatures (°C) of compounds **5**, **6** and **7**.

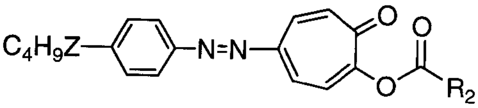


	Y	R^2	M.p.	Clearing point
5m	O	C_7H_{15}	89.6	136.9
6k	OOC		92.3	111.6
7a	none		87.4	103.1
5n	O	C_9H_{19}	84.9	135.9
6l	OOC		87.3	111.0
7b	none		76.9	103.9
5o	O	$C_{11}H_{23}$	82.9	137.2
6m	OOC		85.1	109.9
7c	none		75.6	103.5

5. Conclusion

We have prepared three types of 2-acyloxy derivatives of 5-(4-alkoxyphenylazo)-, 5-(4-alkylphenylazo)-, and 5-(4-alkoxycarbonylphenylazo)-tropones to compare their mesomorphic properties. Electron-donating alkoxy groups enhance the thermal stability because they assist polarization of the tropone carbonyl group. On the other hand, electron-withdrawing alkoxycarbonyl groups reduce the thermal stability. Even an acetyl group is effective in inducing mesomorphic properties, although the molecular lengths of the acetate and the methyl ether are similar. As observed here, troponoid azo derivatives

Table 6. Comparison of transition temperatures (°C) of compounds **5**, **6** and **7**.



	Z	R^2	M.p.	Clearing point
5i	CH_2O	C_7H_{15}	86.0	133.0
6g	OOC		92.1	110.0
7a	C_2H_4		87.4	103.1
5j	CH_2O	C_9H_{19}	85.2	133.9
6h	OOC		90.8	110.7
7b	C_2H_4		76.9	103.9
5k	CH_2O	$C_{11}H_{23}$	86.1	133.9
6i	OOC		91.3	109.7
7c	C_2H_4		75.6	103.5

showed only smectic phases whereas the corresponding benzene derivatives usually have nematic phases [10]. This parallels conclusions from other troponoid derivatives, where the carbonyl group of the troponoids functioned as a lateral polar substituent to increase the thermal stability of layer structures [11].

6. Experimental

The elemental analyses were performed at the elemental analysis laboratory of Kyushu University. NMR spectra were measured using a JEOL Lambda 400 spectrometer and solutions in $CDCl_3$; the chemical shifts are expressed in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were recorded with a JASCO IR-A102 spectrometer using KBr disks for crystalline compounds. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate and hexane. The transition temperatures and the mesomorphic phases were observed by a polarizing optical microscopy (Olympus BHSP BH-2 microscope equipped with a Linkam TH-600RMS hot stage). Enthalpy changes were measured using a differential scanning calorimeter (Seiko DSC 200). The XRD measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K_α radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage. One example of elemental analysis data is given for one homologue of each compound type. The elemental analyses of all other compounds were in acceptable agreement with the calculated values.

6.1. *Preparation of 5-(4-ethoxyphenylazo)tropolone*

A diazotized solution of 4-ethoxyaniline (253 mg, 1.84 mmol), prepared in 2M HCl (2.2 cm^3) and water (1 cm^3) with 98.5% sodium nitrite (106 mg, 1.51 mmol) at 0 to 2°C, was added dropwise to a cooled pyridine solution (1 cm^3) of tropolone (204 mg, 1.67 mmol). After stirring for 1 h in an ice bath, the reaction was stopped by addition of water. The mixture was extracted by shaking with $CHCl_3$. The organic layer was washed with sat. NaCl solution and dried with Na_2SO_4. The solvent was removed under vacuum to leave a residue which was recrystallized from ethanol to give 5-(4-ethoxyphenylazo)tropolone, **1a** ($R = C_2H_5$), 247 mg, m.p. 188.7°C, 50%. ^{1}H NMR δ 1.47 (3H, t, $J = 7.0$ Hz), 4.13 (2H, q, $J = 7.0$ Hz), 7.01 (2H, dm, $J = 9.2$ Hz), 7.48 (2H, dd, $J = 10.6$, 1.1 Hz), 7.90 (2H, dm, $J = 9.2$ Hz), and 8.17 (2H, dd, $J = 10.6$, 1.1 Hz). Calc for $C_{15}H_{14}N_2O_4$: C 66.66, H 5.22, N 10.36; found: C 66.58, H 5.20, N 10.40%. **1b** ($R = C_3H_7$) [4], 63%. **1c** ($R = C_5H_{11}$), m.p. 164.8–168.9°C, 64%. **1d** ($R = C_6H_{13}$), 72%, [4]. **1e** ($R = C_7H_{15}$), m.p. 174.6°C, 60%. **1f** ($R = C_{11}H_{23}$), m.p. 153.6–156.2°C, 65%.

6.2. *Preparation of 2-acyloxy-5-(4-alkoxyphenylazo)-tropolones*

A THF solution (3 cm^3) of 5-(4-ethoxyphenylazo)-tropolone (50 mg, 0.19 mmol) was stirred in the presence of sodium hydride (60%, 9 mg, 0.2 mmol) at room temperature for 0.5 h under an N_2 stream. Octanoyl chloride (0.04 cm^3, 0.2 mmol) was added dropwise to the THF solution and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and shaken with ethyl acetate. The organic layer was washed with saturated NaCl solution and dried with Na_2SO_4. After the solvent was evaporated in vacuum, the residue was chromatographed on a silica gel column eluting with a mixed solvent of hexane and ethyl acetate (50:6) and the product was recrystallized from hexane to give **5a**, 150 mg, 70%. ^{1}H NMR δ 0.89 (3H, t, $J = 6.8$ Hz), 1.23–1.41 (8H, m), 1.47 (3H, t, $J = 7.0$ Hz), 1.79 (2H, m), 2.65 (2H, t, $J = 7.3$ Hz), 4.14 (2H, q, $J = 7.0$ Hz), 7.01 (2H, dm, $J = 9.2$ Hz), 7.36 (2H, d, $J = 12.1$ Hz), 7.91 (2H, dm, $J = 9.2$ Hz), and 7.91 (2H, d, $J = 12.1$ Hz). IR (KBr) ν: 2926, 2854, 1764, 1628, 1590, 1501, 1472, 1409, 1391, 1324, 1260, 1209, 1165, 1133, 1096, 1060, and 841 cm^{-1}. Calc for $C_{23}H_{28}N_2O_4$: C 69.97, H 7.12, N 7.07; found: C 69.75, H 7.12, N 6.98%. **5b**: 81%. **5c**: 70%. **5d**: 57%. **5e**: 74%. **5f**: 56%. **5g**: 63%. **5h**: 70%. **5i**: 19%. **5j**: 88%. **5k**: 57%. **5l**: 78%. **5m**: 68%. **5n**: 68%. **5o**: 68%. **5p**: 93%. **5q**: 85%. **5r**: 65%. **5s**: 44%. **5t**: 87%.

6.3. *Preparation of 5-(4-ethoxycarbonylphenylazo)-tropolone*

As described in the above procedure for 5-(4-ethoxyphenylazo)tropolone, ethyl 4-aminobenzoate gave 5-(4-ethoxycarbonylphenylazo) tropolone **8a** ($R = C_2H_5$), m.p. 204.7°C, 66%. ^{1}H NMR δ 1.43 (3H, t, $J = 7.3$ Hz), 4.43 (2H, q, $J = 7.3$ Hz), 7.50 (2H, d, $J = 11.7$ Hz), 7.94 (2H, d, $J = 8.8$ Hz), 8.21 (2H, d, $J = 8.8$ Hz), and 8.26 (2H, d, $J = 11.7$ Hz). Calc for $C_{16}H_{14}N_2O_4$: C 64.42, H 4.73, N 9.39; found: C 64.40, H 4.77, N 9.46%. **8b** ($R = C_3H_7$): m.p. 199.0°C, 57%. **8c** ($R = C_4H_9$): m.p. 175.5–178.0°C, 59%. **8d** ($R = C_5H_{11}$): m.p. 169.2–171.9°C, 58%. **8e** ($R = C_6H_{13}$): m.p. 174.9–176.1°C, 37%. **8f** ($R = C_7H_{15}$): m.p. 168.7°C, 39 . **8g** ($R = C_8H_{17}$): m.p. 164.4°C, 46%.

6.4. *Preparation of 2-acyloxy-5-(4-ethoxycarbonylphenylazo)tropones*

A THF solution (6 cm^3) of 5-(4-ethoxycarbonylphenylazo)tropolone (**8a**, 50 mg, 0.17 mmol) was stirred in the presence of sodium hydride (60%, 8 mg, 0.2 mmol) at room temperature for 0.5 h under an N_2 stream. Octanoyl chloride (0.04 cm^3, 0.2 mmol) was added dropwise to the THF solution and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and shaken with ethyl acetate. The organic layer was washed with saturated NaCl solution and dried with Na_2SO_4. After the solvent was evaporated in vacuum, the residue was chromatographed with a mixed solution of hexane and ethyl acetate (10 : 1) on a silica-gel column and the product was recrystallized from hexane to give **6a** (38 mg, 53%). ^{1}H NMR δ 0.90 (3H, t, $J = 6.6$ Hz), 1.43 (3H, t, $J = 7.0$ Hz), 1.26–1.54 (8H, m), 1.80 (2H, m) 2.66 (2H, t, $J = 7.7$ Hz), 4.43 (2H, q, $J = 7.0$ Hz), 7.39 (2H, d, $J = 11.7$ Hz), 7.96 (2H, dd, $J = 7.0$, 2.0 Hz), 7.96 (2H, m), and 8.21 (2H, dd, $J = 7.0$, 2.0 Hz). Calc for $C_{24}H_{28}N_2O_5$: C 67.91, H 6.65, N 6.60; found: C 68.06, H 6.66, N 6.61%. **6b**: 65%. **6c**: 59%. **6d**: 75%. **6e**: 69%. **6f**: 75%. **6g**: 65%. **6h**: 73%. **6i**: 87%. **6j**: 50%. **6k**: 100%. **6l**: 95%. **6m**: 78%. **6n**: 56%. **6o**: 88%. **6p**: 96%. **6q**: 90%.

6.5. *Preparation of 5-(4-hexylphenylazo)tropolone*

As described in the above procedure for 5-(4-ethoxyphenylazo)tropolone, 4-hexylaniline gave 5-(4-hexylphenylazo)tropolone (**2**, 59%, m.p. 162.8°C). ^{1}H NMR δ 0.89 (3H, t, $J = 7.0$ Hz), 1.27–1.39 (6H, m), 1.66 (2H, quint, $J = 7.7$ Hz), 2.69 (2H, t, $J = 7.7$ Hz), 7.33 (2H, d, $J = 8.4$ Hz), 7.48 (2H, dd, $J = 10.6$, 1.5 Hz), 7.83 (2H, d, $J = 8.4$ Hz), and 8.21 (2H, dd, $J = 10.6$, 1.5 Hz). Calc for $C_{19}H_{22}N_2O_2$: C 73.52, H 7.14, N 9.03; found: C 73.53, H 7.11, N 9.09%.

6.6. *Preparation of 2-acyloxy-5-(4-hexylphenylazo)-tropones*

A THF solution (3 cm^3) of 5-(4-hexylphenylazo)-tropolone (**2**, 50 mg, 0.16 mmol) was stirred in the presence of sodium hydride (60%, 8 mg, 0.2 mmol) at room temperature for 10 min under an N_2 stream. Octanoyl chloride (0.04 cm^3, 0.2 mmol) was added dropwise to the THF solution and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and shaken with ethyl acetate. The organic layer was washed with saturated NaCl solution and dried with Na_2SO_4. After the solvent was evaporated in vacuum, the residue was chromatographed with a mixed solution of hexane and ethyl acetate (20 : 1) on a silica-gel column and the product was recrystallized from hexane to give **7a** (37 mg, 53%). ^{1}H NMR δ 0.89 (3H, t, $J = 7.1$ Hz), 0.90 (3H, t, $J = 7.0$ Hz), 1.27–1.38 (12H, m), 1.44 (2H, m), 1.66 (2H, quint, $J = 7.7$ Hz), 1.79 (2H, quint, $J = 7.7$ Hz), 2.65 (2H, t, $J = 7.7$ Hz), 2.70 (2H, t, $J = 7.7$ Hz), 7.34 (2H, d, $J = 8.4$ Hz), 7.37 (2H, d, $J = 11.7$ Hz), 7.84 (2H, dm, $J = 8.4$ Hz), and 7.92 (2H, br). IR (KBr) ν: 2954, 2924, 2854, 1777, 1636, 1602, 1602, 1467, 1433, 1408, 1379, 1211, 1173, 1124, 1096, 905, 862, and 840 cm^{-1}. Calc for $C_{27}H_{36}N_2O_3$: C 74.28, H 8.31, N 6.42; found: C 74.19, H 8.28, N 6.39%. **7b**: 56%. **7c**: 63%.

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