CHEMISTRY LETTERS, pp. 1663-1666, 1993.

3-Arylcyclohex-2-en-1-ones and 3,6-Diarylcyclohex-2-en-1-ones. New Liquid Crystalline Compounds

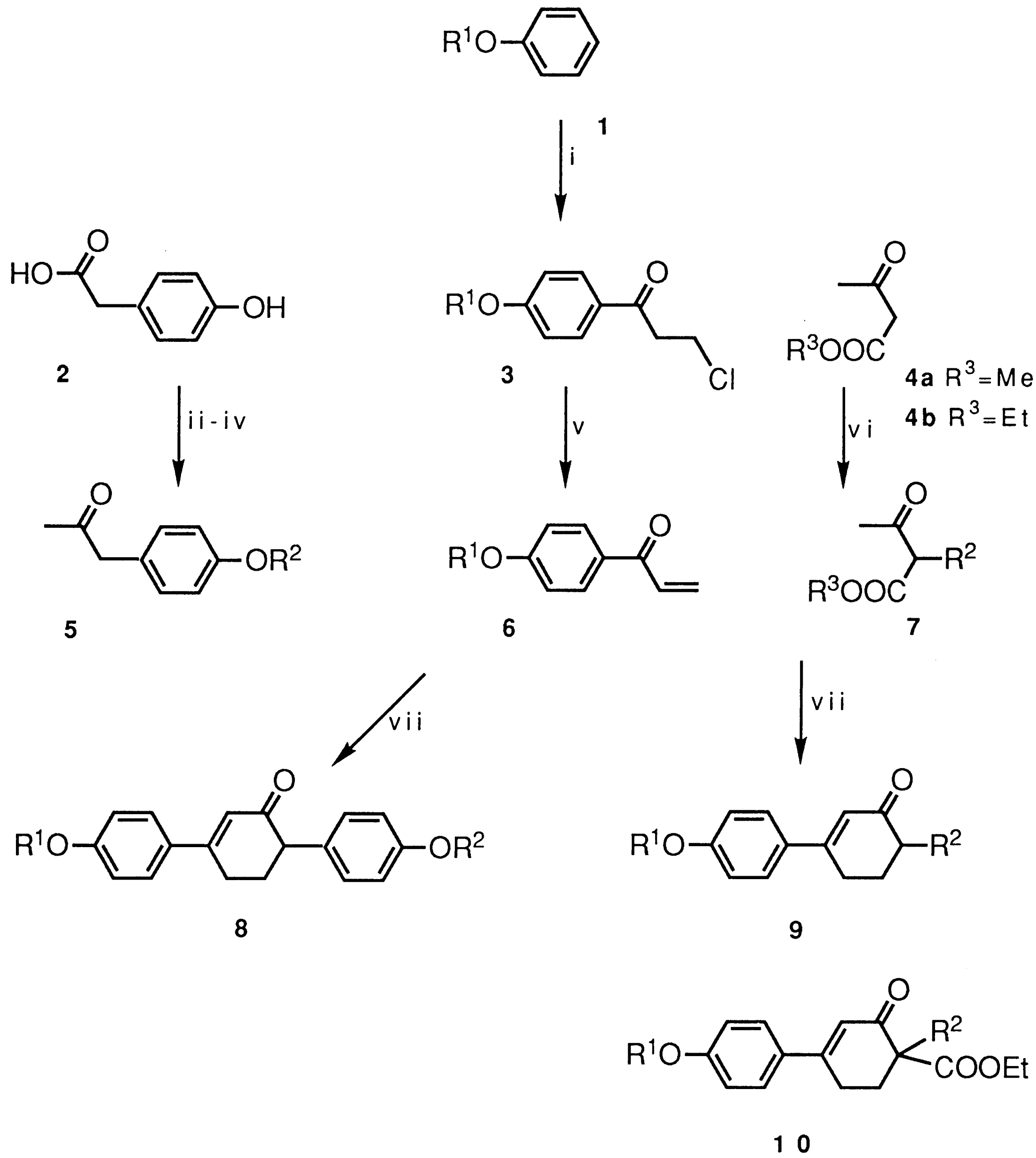
Roger Brettle, David A. Dunmur, Louise D. Farrand, Nigel J. Hindley, and Charles M. Marson*
Department of Chemistry, The University, Sheffield S3 7HF, U.K.

The cyclohex-2-en-1-one unit flanked by one or more aryl rings is shown to provide a new system which can exhibit liquid crystal properties; these new mesogens contain a chiral centre which is both adjacent to a lateral dipolar carbonyl group and is also located in the central core.

A linear and unfused assembly of carbocyclic rings is a common feature of liquid crystalline compounds. These rings may be phenyl, cyclohexyl or bicyclooctyl, and it is usually necessary to have at least two rings in the rigid core of the molecule to impart liquid crystal properties. The rings may be directly coupled as in biphenyls, terphenyls, phenylcyclohexanes etc., or separated by one of a number of suitable linking groups,1) of which the ester linkage is widely used. Materials of high dielectric anisotropy are made by attaching strongly dipolar groups to the molecular core, either longitudinally to give materials of positive dielectric anisotropy, or laterally for negative dielectric anisotropy.2) For new electro-optical applications based on ferroelectric smectic liquid crystals a high chirality coupled with a large transverse dipole moment is required.3) Chirality is usually introduced through a chiral centre in an attached alkyl chain and the effectiveness of the chiral centre in promoting macroscopic chiral properties in liquid crystals increases as the chiral centre is brought closer to the molecular core.4) This paper reports new liquid crystalline materials that combine a large transverse dipole with chirality in the the core of the molecule. We have prepared a number of mesogens containing two or three rings and incorporating the cyclohex-2-en-1-one ring, either as a terminal ring, or as a central ring in the core of the molecule.5) These compounds exhibit smectic phases at relatively low temperatures, and the new core structure promises to be widely applicable to the design and synthesis of a wide range of new liquid crystal materials for applications.

We now report syntheses of the first mesogenic 3-arylcyclohex-2-en-1-ones **9**6) and also of the first mesogenic 3,6-diarylcyclohex-2-en-1-ones **8**. These compounds exhibit smectic A phases between 41 °C and 111 °C, and between 120 °and 164 °C respectively, and all compounds showed mesophases. The two alkyl groups R^1 and R^2 may be the same or different, and the chirality of the molecules may be adjusted by additional substitution at the carbon 6 of the cyclohexenone ring, as in **10**. The 3,6-diarylcyclohex-2-en-1-ones **8** were prepared by the convergent route shown in the Scheme. The phenyl ethers **1** were prepared by alkylation of phenol with the appropriate alkyl bromide (R^1Br in refluxing ethanolic KOH). Friedel-Crafts acylation of **1** with 3-chloropropionyl chloride (1 equiv.) and $AlCl_3$ (1.1 equiv.) in pentane (20 °C, 24 hours) afforded the aryl ketones **3**. *p*-Hydroxyphenylacetic acid on treatment with the appropriate alkyl bromides (R^2Br) in ethanolic KOH (reflux, 2 hours) afforded the corresponding alkoxylated esters which were saponified (10 M NaOH, reflux, 2 hours) to give the corresponding carboxylic acids; those were treated with MeLi7) (2 equiv.) in ether (34 °C, 35 min) to give the arylacetones **5**.

The desired diarylcyclohexenones **8** were obtained in a one-pot procedure from **3** and **5.** The chloro ketone **3** (1 equiv.) was treated with *t*-BuOK (1 equiv.) in ethanol to generate the enone **6** *in situ.* To this was added a mixture of the ketone **5** (1 equiv.) and NaOEt (1 equiv.) in ethanol. After heating at reflux for 12 h the mixture was concentrated, extracted with CH_2Cl_2, thereby affording an oil which was dissolved in ethyl acetate-petroleum (1:4) and cooled to give a solid which recrystallised from ethyl acetate to give the diarylcyclohexenones **8**. ^1H and ^{13}C NMR spectra were in accordance with expected signals. Thus, the ^1H NMR spectrum (250 MHz in $CDCl_3$) of cyclohexenone **8c** exhibited an alkenic signal at δ 6.5 (1H, s) and a signal for the cyclohexenone ring methine hydrogen atom at δ 3.55 (1H, dd, *J* 15 and 5 Hz); the ^{13}C NMR spectrum (62.9 MHz in $CDCl_3$) showed lines at δ 199.4 (s, C=0), 51.6 (d, cyclohexenone ring CH).



Scheme.

i) $ClOCCH_2CH_2Cl$, $AlCl_3$ in pentane, 0 to 25 °C, ii) KOH, R^3Br, EtOH, reflux, iii) NaOH aq., reflux, iv) MeLi, Et_2O, v) *t*-BuOK, EtOH, 25 °C, vi) NaOEt, EtOH, RI, reflux, vii) NaOEt, reflux.

All compounds were characterised by microanalysis, mass spectrometry, and ^1H and ^{13}C NMR spectrometry.

The desired 3-arylcyclohexenones **9** were obtained in a one-pot procedure from **3** and **7.** The chloro ketone **3** (1 equiv.) was treated with *t*-BuOK (1 equiv.) in ethanol. To this was added a mixture of the keto ester **7** (1 equiv.) and NaOEt (1 equiv.) in ethanol. After heating at reflux for 2 h the mixture was concentrated, extracted with CH_2Cl_2, thereby affording an oil which was dissolved in ethyl acetate-petroleum (1:4). On cooling, crystals of the 3-arylcyclohexenone **9** were obtained. ^1H and ^{13}C NMR spectra were in accordance with expected signals. Thus, the ^1H NMR spectrum (250 MHz in $CDCl_3$) of cyclohexenone **9a** exhibited an alkenic signal at δ 6.35 (1H, s); the ^{13}C NMR spectrum (62.9 MHz in $CDCl_3$) showed lines at δ 202.1 (s, C=0), 45.7 (d, cyclohexenone ring CH).

3-Arylcyclohex-2-en-1-ones have not previously been prepared by the [3C+3C] condensations herein reported.[8)] This convergent condensation also has the advantage that the unwanted activating alkoxycarbonyl group is cleaved during the one-pot procedure. However in the preparation of **9b**, minor quantities (*ca.* 8%) of the keto ester **10b** were isolated. Interestingly, no mesogenic properties were observed for **10b**.

Enone	R^1	R^2	Transition Temp °C (Optical Microscopy)	T°C (onset)	ΔHkJ mol^{-1}	ΔSJK^{-1} mol^{-1}
9a	C_4H_9O	C_3H_7	$K_1 \xrightarrow{60°} K_2 \xrightarrow{68°} S_A \xrightarrow{97°} I$	53.6	7.6	23.2
				64.6	10.3	31.0
				89.5	7.5	20.7
9b	C_4H_9O	C_5H_{11}	$K \xrightarrow{41°} S_A \xrightarrow{111°} I$	42.8	20.3	64.3
				106.3	7.9	20.8
9c	$C_6H_{13}O$	C_3H_5	$K \xrightarrow{48.9°} S_A \xrightarrow{63°} I$	47.5	17.6	54.9
				59.5	5.2	15.6
9d	$C_6H_{13}O$	C_3H_7	$K \xrightarrow{45°} S_A \xrightarrow{96°} I$	46.4	14.6	45.7
				89.9	6.9	19.0
9e	$C_6H_{13}O$	C_5H_{11}	$K \xrightarrow{52.4°} S_A \xrightarrow{109°} I$	51.1	15.7	48.4
				102.2	8.1	21.6
8a	C_6H_{13}	C_4H_9	$K \xrightarrow{127°} S_A \xrightarrow{164°} I$	126.8	21.6	55.5
				159.9	12.1	25.6
8b	C_6H_{13}	C_6H_{13}	$K \xrightarrow{120°} S_A \xrightarrow{160°} I$	114.8	16.4	42.2
				148.4	6.4	15.1
8c	C_4H_9	C_6H_{13}	$K \xrightarrow{126°} S_A \xrightarrow{150°} I$	101.5	8.2	21.9
				133.5	5.2	12.7

The transition temperatures of the mesogenic cyclohexenones **8** and **9** are listed in Table 1. Phase types were identified by the optical textures, and phase transitions and temperatures were confirmed by differential scanning calorimetry (DSC). All of the homologues prepared so far exhibit smectic A phases, which can be attributed to the presence of a localized dipole in the core of the molecule. It is likely that appropriate modification of the groups attached to the arylcyclohex-2-en-1-one core will result in the formation of liquid crystal phases of other symmetries. A chiral separation of the enantiomers of **9d** was carried out using 0.7% propan-2-ol in petroleum as the mobile phase on a Pirkle chiral column impregnated with D-phenylglycine. Each enantiomer exhibited a strong twisting power when mixed in low concentrations with a proprietary nematic mixture, I-eutectic (Merck UK Ltd). Mixtures of the separated enantiomer (5%, 7% and 12% by weight) in a non-chiral commercial smectic C mixture produced a chiral smectic C phase, which could be ferro-electrically switched.9) The mixtures had spontaneous polarizations of the order of 10nCcm^{-2}, and we are carrying out further measurements on these materials to establish their suitability for ferroelectric liquid crystal devices.

Financial support from Hitachi Limited (Hitachi Research Laboratory and Electron Tube Division) is gratefully acknowledged, and we also thank Mr C Murray and Dr J A S Kang (University of Sheffield) for carrying out the ferroelectric measurements, and Mr. I. Statton for chiral chromatographic separations. Valuable discussions with Professor K Toriyama are also gratefully acknowledged.

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(Received June 21, 1993)