Synthesis of New Liquid Crystalline Compounds based on 1,4-Diarylbuta-1,3-dienes

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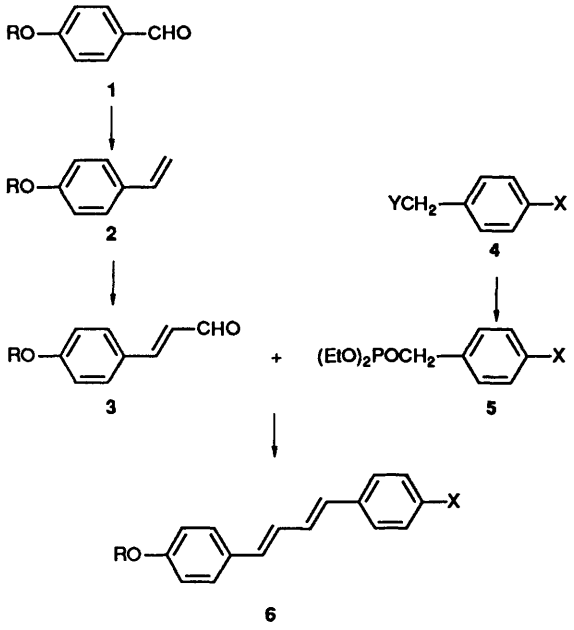
A group of (*E,E*)-1,4-diarylbuta-1,3-dienes, substituted in the *para*-position of one aryl ring by an alkoxy-group and in the *para*-position of the other aryl group by a cyano- or halogeno-group have been synthesised. The compounds are mesogenic and their physical properties make them suitable for liquid crystal display devices when mixed with known liquid crystal materials.

We report the full details of the synthesis of a group of (*E,E*)-1,4-diarylbuta-1,3-dienes **6** for use in liquid crystal display devices. The compounds exhibit low viscosity in mixtures, a wide liquid crystal temperature range, and large anisotropies of refractive index and dielectric constant. When used in mixtures with known liquid crystalline materials, liquid crystal materials can be obtained which have low viscosities (and hence fast switching times) in liquid crystal display devices.[1] A preliminary account of this work has been published[2] and the work is covered by a patent.[1]

Results and Discussion

The dienes were prepared by the convergent route shown in Scheme 1. The 4-alkoxybenzaldehydes[3] **1** were prepared from 4-



when X = CN. R = $Me(CH_2)_nCH_2$; *n* = 2. 4. 5. 6. 7 and 8
when X = F. Cl. Br or $OCH_2(CH_2)_4Me$. R = $Me(CH_2)_4CH_2$
Y = OH, Cl

Scheme 1

hydroxybenzaldehyde and the appropriate 1-bromoalkane in ethanolic potassium hydroxide,[3c] except for **1** (*n* = 4), where the alkylation was effected in cyclohexanone in the presence of potassium carbonate.[3b] 4-(Nonyloxy)- and 4-(decyloxy)-benzaldehydes **1** (*n* = 7 and 8) were found to be very readily oxidised in air, and so were used in the next stage immediately after chromatographic purification of the crude materials.

The cinnamaldehydes **3** (*n* = 6 and 8) have been prepared previously by the alkylation of 4-hydroxycinnamaldehyde,[4] but that starting material was not commercially available. Since a one-step synthesis of the 4-alkoxycinnamaldehydes **3** by a crossed aldol condensation was unattractive, a yield of 25% having been recorded for the preparation of 4-methoxycinnamaldehyde from anisaldehyde and ethanal,[5] a two-step procedure from the alkoxybenzaldehydes, involving the preparation of the 4-alkoxystyrenes **2**, followed by formylation with phosphorus oxychloride–*N,N*-dimethylformamide in the manner reported for styrene and 1-(4-methoxyphenyl)prop-1-ene[6] was adopted. The 4-alkoxystyrenes **2** were prepared by Wittig methylenation[7] of the 4-alkoxybenzaldehydes **1** using methyltriphenylphosphonium bromide and butyllithium, in tetrahydrofuran (THF). 4-(Butoxy)- and 4-(hexyloxy) styrenes had been reported previously, obtained by the dehydration of the corresponding 2-(4-alkoxyphenyl)ethanols.[8] Formylation of the styrenes **2** then gave the cinnamaldehydes **3**; the configuration of the double bond was in every case established as (*E*) on the basis of the proton–proton coupling constant, $J_{\alpha\beta}$, in the range 15–17 Hz.

Previous reports[9] on the preparation of 1,4-diarylbuta-1,3-dienes from (*E*)-cinnamaldehydes had revealed that the Wittig reaction gives mixtures in which the newly introduced double bond has been formed in both possible geometries, with the (*E,E*)-isomer predominating, whereas the Wadsworth–Emmons procedure gives essentially only the (*E,E*)-diene. Accordingly, for the preparation of the (*E,E*)-dienes **6** the Wadsworth–Emmons route was employed, as shown in Scheme 1. The phosphonates **5** were obtained from 4-substituted benzyl halides by the Arbuzov reaction.[10] The phosphonates **5** (X = F, Cl and Br) have been mentioned previously in the literature,[11] but no preparative details have been published. 4-Cyanobenzyl bromide was prepared by the bromination of 4-tolunitrile with *N*-bromosuccinimide.[12] 4-(Hexyloxy)benzyl alcohol **4** [X = $-OCH_2(CH_2)_4Me$; Y = OH] has been prepared[13] by the reduction of methyl 4-(hexyloxy)benzoate with sodium borohydride in the presence of potassium bromide in 1-(2-methoxyethoxy)-2-methoxyethane at 100 °C. Having available 4-(hexyloxy)benzaldehyde **1** (*n* = 4), the corresponding alcohol was prepared by reduction of the aldehyde with sodium borohydride. The alcohol **4** [X = $Me(CH_2)_4CH_2O$; Y = OH] reacted with hydrogen chloride in light petroleum (b.p. 60–80 °C), in a procedure modelled on a conversion of 4-methoxybenzyl alcohol into 4-methoxybenzyl bromide,[14] to give the desired benzyl chloride **4** [X = $CH_3(CH_2)_4CH_2O$; Y = Cl] as an unstable oil which was used immediately in the Arbuzov reaction. Condensation of (*E*)-4-(hexyloxy)cinnamaldehyde **3** (*n* = 4) with diethyl 4-cyanobenzylphosphonate **5** (X = CN) in THF in the presence of potassium *tert*-butoxide gave essentially a single diastereoisomer (> 95%; HPLC) of the desired diene. Recrystallisation afforded (*E,E*)-1-(4-cyanophenyl)-4-(4-hexyloxyphenyl)buta-

Table 1 Liquid crystal phases and transition temperatures for substituted phenyl hexyloxybuta-1,3-dienes **6**

R	X	Transitions (°C)
C_6H_{13}	F	K→127→S_B→160→S_A→166→N→174→I
C_6H_{13}	Cl	K→147→S_B→185→S_A→189→I
C_6H_{13}	Br	K→153→S_B→189→S_A→194→N→198→I
C_6H_{13}	CN	K→107→N→190→I
C_6H_{13}	OC_6H_{13}	K→187→N→194→I

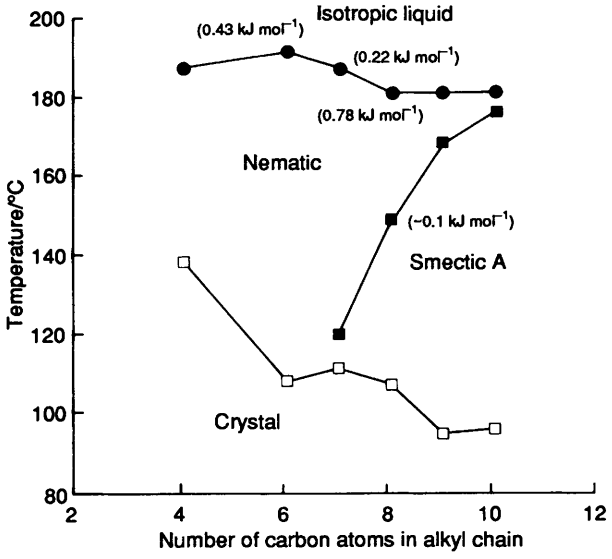
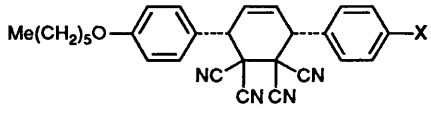


Fig. 1 Transition temperatures of 1-(4-cyanophenyl)-4-(4-alkoxyphenyl)buta-1,3-dienes; the figures on the graph indicate measured enthalpy changes for the transitions

1,3-diene **6** (n = 4; X = CN); the ^{1}H NMR spectrum (400 MHz in $CDCl_3$) showed separate alkenic signals at δ_H 6.58 and 6.72 (each 1 H, d, J 16 Hz) and at 6.83 and 7.03 (each 1 H, dd, J 10 and 16 Hz), clearly establishing the expected (*E*,*E*)-configuration. A series of other dienes **6** [n = 4; X = F, Br, Cl and $CH_3(CH_2)_4CH_2O$–] and (n = 2, 5, 8, 9 and 10; X = CN) was prepared similarly. The expected (*E*,*E*)-configuration was confirmed in a second case by the ^{1}H NMR spectrum of **6** (n = 4; X = Cl) which at 400 MHz exhibited resolved multiplets for all the dienic proton signals including single proton signals at δ 6.55 and 6.33 (d, J 15 Hz) and 6.79 and 6.90 (dd, J 15 and 10 Hz). All those dienes showed mesophases (see Table 1).

The preparation of **6** (n = 4; X = CN) was also studied using the Wittig approach. Reaction of 4-cyanobenzyl bromide **4** (X = CN; Y = Br) with triphenylphosphine gave the phosphonium salt, which was converted into the ylide with potassium *tert*-butoxide in dry THF. However, addition of 4-(hexyloxy)cinnamaldehyde **3** (n = 4) afforded a mixture of products. Column chromatography followed by medium pressure liquid chromatography (MPLC) gave two compounds in a combined yield of 70%. The first material eluted from the MPLC column was tentatively identified as the (*E*,*Z*)-isomer of 1-(4-cyanophenyl)-4-(4-hexyloxyphenyl)buta-1,3-diene. The slower moving material was identical with the (*E*,*E*)-isomer **6** (n = 4; X = CN) obtained from the Wadsworth–Emmons approach. The (*E*):(*Z*) ratio was shown by HPLC to be 7:3. It proved difficult to characterise the (*E*,*Z*)-isomer, since on standing it was converted into the (*E*,*E*)-isomer, a process which could be monitored by thin layer chromatography (TLC). Similar isomerisation has been reported[9b] for the (*E*,*Z*)-isomer of 1,4-diphenylbuta-1,3-diene. When freshly separated by MPLC, the (*E*,*Z*)-isomer, m.p. *ca.* 100 °C, unlike the (*E*,*E*)-isomer (for melting behaviour see Table 1) was not mesogenic, but the sample became so on standing, being converted into the (*E*,*E*)-isomer. The Wittig route was also used to prepare 1-(4-fluorophenyl)-4-(4-hexyloxyphenyl)buta-1,3-diene. The major product was mesogenic and was assumed to be the (*E*,*E*)-isomer **6** (n = 4; X = F). ^{1}H NMR spectrometry at 400 MHz in perdeuteriotetrahydrofuran did not permit an assignment of the configurations of both double bonds. ^{19}F NMR spectroscopy of the crude reaction product showed two signals; the minor signal was assigned as the fluorine atom in the (*E*,*Z*)-isomer which was not recovered after purification by MPLC.

The dienes **6** [n = 4; X = Br and X = $Me(CH_2)_4CH_2O$–] were extremely insoluble in the usual NMR solvents. They were further characterised by their adducts with tetracyanoethene, **7** [X = Br and $CH_3(CH_2)_4CH_2O$–]. Those were formed in good yield from the reactants in hot chloroform and were soluble in $CDCl_3$ at room temperature, allowing ^{1}H and ^{13}C NMR spectra to be recorded. Despite the presence of a transverse dipole, those tricyclic compounds were not mesogenic.



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Mesophase Properties.—The liquid crystal phases and transition temperatures for the compounds described in this paper were reported in our preliminary communication.[1] Phase types and transition temperatures were determined by optical microscopy, and differential scanning calorimetry (DSC) was also used to confirm the existence of phase transitions. Transition temperatures for the homologous series of 1-(4-cyanophenyl)-4-(alkoxyphenyl)-buta-1,3-dienes are illustrated in Fig. 1. Smectic A to nematic transition temperatures increase with increasing chain length as is usually observed, while the nematic to isotropic transition temperatures are almost independent of molecular length. Measured enthalpy changes for the transitions are consistent with the phase assignments.

The phase behaviour of the other mesogenic butadienes is summarised in Table 1; the proximity of the various mesophase transitions resulted in overlapping peaks in the DSC, which could not be deconvoluted into transitional enthalpy changes.

This work confirms that the diene group having an appropriate (*E*,*E*)-configuration can be a useful structural feature in promoting liquid crystallinity: such a group is another example of four centre linking groups already identified.[18] It is also clear from this work that a variety of different mesophases can be generated by different choices of substituents to the rings. The possibility of extending the conjugated length of a mesogen, and hence its dielectric, optical and shape anisotropy without using rigid aromatic rings has been demonstrated; the benefits of this are apparent in the relatively low viscosities of liquid crystal display mixtures using these materials.[2] A further interesting possibility arises from the (*E*,*E*):(*E*,*Z*) equilibrium, in which only the (*E*,*E*)-isomer is mesogenic. Photochemically induced changes between (*E*,*E*)- and (*E*,*Z*)-configurations will be accompanied by phase changes, and may be used in the development of wavelength sensitive optical sensors.

The diarylbutadienes **6** have potential as components in liquid crystal mixtures for display applications. In particular, the cyano-derivatives **6** (X = CN) combine a high dielectric and high optical anisotropy, but still retain a relatively low viscosity, in contrast with terphenyls of similar length. For example, admixture of diene **6** (n = 2, X = CN) with a commercial mixture of 1-alkyl-4-(4-cyanophenyl)cyclohexanes (PCHs) gave the results for viscosity, refractive index anisotropy and dielectric anisotropy listed in Table 2.

Table 2 Physical properties of butadiene **6** (n = 2, X=CN) mixtures added to PCH mixture

Weight (%)	Viscosity (centipoise)	Refractive index anisotropy	Dielectric anisotropy
0	29	0.14	10.4
10	28	0.15	10.7
15	29	0.15	11.2
25	31	0.17	12.3

Thus, a 25% addition of butadiene **6** (n = 2, X = CN) to the PCH mixture increases the birefringence and dielectric anisotropy by 20%, with only a 7% increase in viscosity.

Experimental

Air- or moisture-sensitive reactions were carried out in oven-dried glassware assembled under a positive pressure of oxygen-free nitrogen. Solvents were dried and purified according to literature methods.[15] Thin-layer chromatography (TLC) was used to monitor reactions and to establish the purity of samples; it was performed on aluminium sheets pre-coated with silica gel (Merck 60 F_{254}). The plates were inspected by UV light, and then developed by spraying with aqueous potassium permanganate. Column chromatography was performed using Merck Kieselgel 60 (230–400 mesh) silica gel as the stationary phase. Medium pressure liquid chromatography (MPLC) was carried out using a 9385 silica MPLC column and a UV detector set at 300 nm, with the solvent system indicated, at a flow rate of 20 cm^3 min^{-1}. High-performance liquid chromatography (HPLC) was performed, using injection samples of 10 mm^3, on a 3 micron Hypersil column with petroleum–dichloromethane (4:1) as the developing solvent at a flow rate of 2 cm^3 min^{-1}. Organic solutions were dried over anhydrous magnesium sulfate. Light petroleum is the fraction with b.p. 60–80 °C.

M.p.s were recorded on a hot stage apparatus, and are uncorrected. For solids showing liquid crystal phases the clearing temperature is given as the melting point in the Experimental section.

Low resolution mass spectrometry was carried out using a Kratos MS25 instrument. The method is specified as either electron impact (EI) or chemical ionisation by NH_4^+ (CI). Infrared spectra were recorded in a KBr pellet, or, for liquid samples, between NaCl plates or in chloroform solution using either Perkin-Elmer 457 or Perkin-Elmer 684 spectrophotometers. ^1H NMR spectra were recorded using Bruker WP80, Perkin-Elmer R34, Bruker AM250 or Bruker WH400 spectrometers, operating at 80, 220, 250 or 400 MHz respectively, for solutions in deuteriochloroform (unless otherwise stated). ^{13}C NMR spectra were recorded with either Bruker AM250 or Bruker WH400 instruments operating at 62.9 and 100.6 MHz respectively. ^{19}F and ^{31}P NMR spectra were recorded on a Bruker WP80 spectrometer at 75.4 and 32.4 MHz respectively. Chemical shifts were recorded in ppm from tetramethylsilane, employed as internal standard. Coupling constants (J) are given in Hz.

HPLC and MPLC were carried out by the University of Sheffield Chromatography Services and elemental analyses were performed by the University of Sheffield Microanalytical Services.

Materials. Methyllithium was standardised by titration against a solution of freshly recrystallised 4-biphenylmethanol in THF,[16] and butyllithium by titration against a solution of 2,5-dimethoxybenzyl alcohol in THF.[17]

The following compounds were prepared by literature procedures.[3,10a,12] 4-Cyanobenzyl bromide, m.p. 113–114 °C (lit.,[12] 115 °C); δ_H 7.65 and 7.53 (each 2 H, d, C_6H_4) and 4.50 (2 H, s, CH_2).

Diethyl (4-cyanobenzyl)phosphonate, b.p. 204 °C at 4 mmHg, (lit.,[10a] 146–150 °C at 0.03 mmHg), (10.5 g, 77%); ν_{max}/cm^{-1} 2210 (CN); δ_H 7.62 (2 H, dd, $J_{H,H}$ 8.8, $J_{P,H}$ 1.5, aromatic), 7.43 (2 H, dd, $J_{H,H}$ 8.8, $J_{P,H}$ 2.5, aromatic), 4.05 (4 H, dq, $J_{H,H}$ 7, $J_{P,H}$ 7.5, 2 × OCH_2), 3.22 (2 H, d, $J_{P,H}$ 22.5, $C_6H_4CH_2$) and 1.26 (6 H, t, 2 × CH_3); δ_C 137.2 (1 C, d, $J_{P,C}$ 9.4, quaternary aromatic), 131.6 (2 C, d, J 2.5, aromatic), 130.1 (2 C, d, $J_{P,C}$ 9, aromatic), 118.1 (1 C, CN), 110.2 (1 C, d, $J_{P,C}$ 3.7, quaternary aromatic), 61.8 (2 C, d, $J_{P,C}$ 6.9, 2 × OCH_2), 33.5 (1 C, d, J 137.7, $C_6H_4CH_2$) and 15.8 (2 C, d $J_{P,C}$ 6.3, 2 × CH_3); m/z (CI) 254 (MH^+, 100%).

4-Butoxybenzaldehyde, δ_H 9.84 (1 H, s, CHO), 7.78 and 6.96 (each 2 H, d, C_6H_4), 4.00 (2 H, t, J 6.5, OCH_2), 1.77 (2 H, m, OCH_2CH_2), 1.48 (2 H, m, CH_3CH_2) and 0.96 (3 H, t, CH_3); δ_C 190.1, 163.9, 131.5, 129.5, 114.0, 67.7, 30.7, 18.8 and 13.4.

4-Hexyloxybenzaldehyde, δ_H 9.8 (1 H, s, CHO), 7.80 and 6.95 (each 2 H, d, C_6H_4), 4.0 (2 H, t, OCH_2), 1.80 (2 H, m, OCH_2CH_2), 1.50 [6 H, m, $CH_3(CH_2)_3$] and 0.90 (3 H, t, CH_3); δ_C 190.6, 164.2, 131.9, 129.7, 114.7, 68.4, 31.5, 29.0, 25.6, 22.5 and 13.9.

4-Heptyloxybenzaldehyde, δ_H 9.86 (1 H, s, CHO), 7.81 and 6.98 (each 2 H, d, C_6H_4), 4.05–3.99 (2 H, t, J 6.5, OCH_2), 1.80 (2 H, m, OCH_2CH_2), 1.38 [8H, m, $CH_3(CH_2)_4$] and 0.88 (3 H, t, CH_3); δ_C 190.5, 164.0, 131.8, 129.7, 114.7, 68.4, 31.6, 29.0, 28.9, 25.8, 22.5 and 13.9.

4-Octyloxybenzaldehyde, δ_H 9.88 (1 H, s, CHO), 7.82 and 6.99 (each 2 H, d, C_6H_4), 4.03 (2 H, t, 6.5, OCH_2), 1.80 (2 H, m, OCH_2CH_2), 1.39 [10 H, m, $CH_3(CH_2)_5$] and 0.88 (3 H, t, CH_3); δ_C 190.4, 164.2, 131.8, 129.8, 114.6, 68.3, 31.7, 29.2, 29.0, 28.9, 25.8, 22.5 and 13.4.

4-Nonyloxy- and 4-decyloxy-benzaldehydes were also prepared by literature procedures[3] and used immediately for the next stage of the synthesis, without spectroscopic characterisation. Here and elsewhere, all intermediates exhibited only those signals in their ^1H and ^{13}C NMR spectra consistent with the structures assigned.

Preparation of 4-Alkoxystyrenes.—General procedure. Butyllithium (9 mmol, 1.6 mol dm^{-3}) was added to a stirred slurry of methyltriphenylphosphonium bromide (4.4 g, 12.3 mmol) in THF (60 cm^3). After 0.5 h, a 4-alkyloxybenzaldehyde (6.4 mmol) in THF (20 cm^{-3}) was added. After 3 h, the reaction was quenched with methanol, ethanol or ice–water. The organic solvents were evaporated and the residue was taken up in chloroform and washed with water. The chloroform solution was dried and evaporated, and the residue was extracted several times with light petroleum. Column chromatography on the material extracted, using ethyl acetate–petroleum as the eluent, gave the 4-alkoxystyrene. In the case of compound **6** (n = 5) further purification by HPLC was necessary.

4-Butoxystyrene. The title compound was obtained as an oil (2.32 g, 59%); δ_H 7.35 and 6.94 (each 2 H, d, C_6H_4), 6.65 (1 H, dd, J 8, 11, vinyl), 5.59 (1 H, dd, J 18, 1, vinyl), 5.10 (1 H, dd, J 11, 1, vinyl), 3.95 (2 H, t, 6.5, OCH_2), 1.75 (2 H, m, OCH_2CH_2), 1.48 (2 H, m, CH_3CH_2) and 0.97 (3 H, t, CH_3); δ_C 127.3, 114.5, 111.2, 67.7, 31.3, 19.2 and 13.8; m/z (EI) 176 (M^+, 15%) and 120 (100%).

4-Hexyloxystyrene. The title compound was obtained as an oil (18.2 g, 91.8%); ν_{max}/cm^{-1} 1630 (C=C); δ_H 7.30 and 6.85 (each 2 H, d, C_6H_4), 6.6 (1 H, dd, J 17, 11, vinyl), 5.60 (1 H, d, J 17, vinyl), 5.10 (1 H, d, J 11, vinyl), 3.95 (2 H, t, OCH_2), 1.80 (2 H, m, OCH_2CH_2), 1.50 [6 H, m, $CH_3(CH_2)_3$] and 0.90 (3 H, t, CH_3); δ_C 159.0, 136.3, 130.2, 127.3, 114.4, 111.2, 68.0, 31.6, 29.2, 25.7, 22.6 and 14.0.

4-Heptyloxystyrene. The title compound was obtained as an oil (600 mg, 41%); δ_H 7.30 and 6.85 (each 2 H, d, C_6H_4), 6.63

(1 H, dd, *J* 17, 11, vinyl), 5.60 (1 H, d, *J* 17, vinyl), 5.20 (1 H, d, *J* 11, vinyl), 3.90 (2 H, t, OCH_2), 1.75 (2 H, m, OCH_2CH_2), 1.35 [8 H, m, $CH_3(CH_2)_4$] and 0.90 (3 H, t, CH_3); δ_C 159.0, 136.3, 130.3, 127.3, 114.5, 111.3, 68.1, 31.8, 29.3, 29.0, 26.0, 22.6 and 14.0.

4-*Octyloxystyrene*. The title compound was obtained as an oil (650 mg, 42%); δ_H 7.15 and 6.85 (each 2 H, d, C_6H_4), 6.57 (1 H, dd, *J* 18, 10, vinyl), 5.49 (1 H, d, *J* 18, vinyl), 5.00 (1 H, d, *J* 10, vinyl), 3.80 (2 H, t, OCH_2), 1.68 (2 H, m, OCH_2CH_2), 1.32 [10 H, m, $CH_3(CH_2)_5$] and 085 (3 H, t, CH_3); δ_C 159.0, 136.3, 130.3, 128.0, 114.5, 111.2, 68.0, 31.8, 29.4, 29.3, 29.2, 26.0, 22.6 and 14.0.

4-*Nonyloxystyrene*. The *title compound* (2.86 g, 49%) had m.p. 27–30 °C (Found: C, 82.8; H, 10.4. $C_{17}H_{26}O$ requires C, 82.9; H, 10.6%); ν_{max}/cm^{-1} 1630 (C=C); δ_H 7.34 and 6.86 (each 2 H, d, C_6H_4), 6.66 (1 H, dd, *J* 18, 11, vinyl), 6.60 (1 H, d, *J* 18, vinyl), 5.11 (1 H, d, *J* 11, vinyl), 3.94 (2 H, t, *J* 6.5, OCH_2), 1.77 (2 H, m, OCH_2CH_2), 1.37 [12 H, m, $CH_3(CH_2)_6$] and 0.88 (3 H, t, CH_3); δ_C 159.0, 136.1, 130.3, 127.3, 114.5, 111.3, 68.1, 31.9, 29.5, 29.4, 29.3, 26.0, 22.6 and 14.1; *m/z* (EI) 246 (M^+, 10%) and 120 (100%).

4-*Decyloxystyrene*. The *title compound* (1.2 g, 24%) had m.p. 31–32 °C (from pentane) (Found: C, 83.2; H, 11.1. $C_{18}H_{28}O$ requires C, 83.0; H, 10.8%); δ_H 7.33 and 6.84 (each 2 H, d, C_6H_4), 6.69–6.62 (1 H, dd, *J* 18, 11, vinyl), 5.62–5.58 (1 H, d, *J* 18, vinyl), 5.12–5.10 (1 H, d, *J* 11, vinyl), 3.97–3.93 (2 H, t, *J* 6.5, OCH_2), 1.81–1.74 (2 H, m, OCH_2CH_2), 1.49–1.24 [14 H, m, $CH_3(CH_2)_7$] and 0.90–0.85 (3 H, t, CH_3); δ_C 159.0, 136.3, 130.3, 127.3, 114.5, 111.4, 68.1, 31.9, 29.6, 29.4, 29.3, 26.0, 22.7 and 14.1; *m/z* (EI) 260 (M^+; 55%) and 120 (100%).

Preparation of Alkoxycinnamaldehydes.—General method. Phosphorus oxychloride (10 mmol) was cautiously added to ice-cold, stirred *N,N*-dimethylformamide (DMF) (18 mmol). A 4-alkoxystyrene (4.6 mmol) in DMF (1 cm^3) was added to the solution and the mixture was then heated at 60–70 °C for 20 min. After cooling, a solution of sodium acetate (2 g) in water (30 cm^3) was cautiously added, and the reaction mixture was heated to 60–70 °C for a further 20 min. Chloroform was then added and the organic layer was washed with water, aqueous sodium hydrogen carbonate (until the washings were neutral), then with water. The solution was dried, evaporated, and the residue was purified by column chromatography using an ethyl acetate–light petroleum mixture as the eluent.

4-*Butoxycinnamaldehyde*. M.p. 31–32 °C (64%); δ_H 9.65 (1 H, d, *J* 7.5, CHO) 7.54 and 6.93 (each 2 H, d, C_6H_4), 7.44 (1 H, d, *J* 16, CH=CH–CHO), 6.60 (1 H, dd, *J* 16, 7.5, CH=CH–CHO), 4.00 (2 H, t, *J* 6.5, OCH_2), 1.79 (2 H, m, OCH_2CH_2), 1.50 (2 H, m, CH_3CH_2) and 0.98 (3 H, t, CH_3); δ_C 193.4, 161.8, 152.5, 130.2, 126.5, 115.0, 67.8, 31.0, 19.3 and 13.7; *m/z* (EI), 204 (M^+, 56%) and 147 (100%).

4-*Hexyloxycinnamaldehyde*. M.p. 30 °C (71%) (Found: C, 77.4; H, 8.95. $C_{15}H_{20}O_2$ requires C, 77.4; H, 8.7%); ν_{max}/cm^{-1} 1655 (enal); δ_H 9.62 (1 H, d, *J* 7.8, CHO), 7.48 and 6.91 (each 2 H, d, C_6H_4), 7.42 (1 H, *J* 16, CH=CH–CHO), 6.60 (1 H, dd, *J* 16, 7.8, CH=CH–CHO), 4.00 (2 H, t, OCH_2), 1.81 (2 H, m, OCH_2CH_2), 1.40 [6H, m, $CH_3(CH_2)_3$] and 0.90 (3 H, t, CH_3); δ_C 193.5, 161.8, 152.7, 130.3, 126.5, 126.3, 115.0, 68.2, 31.5, 29.1, 25.6, 22.5 and 14.0; *m/z* (EI) 232 ($M^{+\cdot}$, 29%) and 147 (100%).

4-*Heptyloxycinnamaldehyde*. M.p. 26 °C (71%); δ_H 9.66 (1 H, d, *J* 8, CHO), 7.52 and 6.94 (each 2 H, d, C_6H_4), 7.43 (1 H, d, *J* 15, CH=CH–CHO), 6.60 (1 H, dd, *J* 15, 8, –CH=CH–CHO), 4.00 (2 H, t, *J* 6.5, OCH_2), 1.80 (2 H, m, OCH_2CH_2), 1.40 [8 H, m, $CH_3(CH_2)_4$] and 0.90 (3 H, t, CH_3); δ_C 193.5, 161.8, 152.6, 130.6, 126.5, 126.4, 115.0, 68.2, 31.7, 29.1, 28.9, 25.9, 22.5 and 14.0; *m/z* (EI) 246 (M^+, 44%) and 147 (100%). *Phenitazone*: m.p. 121–123 °C (from ethanol) (Found: C, 78.6; H, 8.3; N, 3.65. $C_{24}H_{31}NO_2$ requires C, 78.86; H 8.54; N, 3.83%); ν_{max}/cm^{-1} 1640 (CH=CH–CH=N–); *m/z* (EI) 363 (M^+, 100%) and 260 (44%).

4-*Octyloxycinnamaldehyde*. The title compound was obtained as an oil (41%); δ_H 9.63 (1 H, d, *J* 7, CHO), 7.50 and 6.93 (each 2 H, d, C_6H_4), 7.43 (1 H, d, *J* 17, CH=CH–CHO), 6.58 (1 H, dd, *J* 17, 7, CH=CH–CHO), 4.00 (2 H, t, OCH_2), 1.78 (2 H, m, OCH_2CH_2), 1.40 [10 H, m, $CH_3(CH_2)_5$] and 0.88 (3 H, t, CH_3); δ_C 193.2, 161.7, 152.5, 130.1, 126.4, 126.2, 114.9, 68.1, 31.6, 29.1, 29.0, 28.9, 25.8, 22.4 and 13.9; *m/z* (EI) 260 (M^+, 260) 41%) and 148 (100%).

4-*Nonyloxycinnamaldehyde*. M.p. 36–37 °C (64%); δ_H 9.67 (1 H, d, *J* 8, CHO), 7.52 and 6.94 (each 2 H, d, C_6H_4), 7.50 (1 H, d, *J* 17, CH=CH–CHO), 6.61 (1 H, dd, *J* 17, 8, –CH=CH–CHO), 4.00 (2 H, t, *J* 6.5, OCH_2), 1.81 (2 H, m, OCH_2CH_2), 1.37 [12 H, m, $CH_3(CH_2)_6$] and 0.87 (3 H, t, CH_3); δ_C 193.5, 161.9, 152.6, 130.3, 126.6, 126.4, 115.1, 68.3, 31.8, 29.5, 29.3, 29.2, 29.1, 25.9, 22.6 and 14.0; *m/z* (+ EI) 274 (M^+ 28%), 148 (100%). *Phenitazone*: m.p. 120–122 °C (from ethanol); ν_{max}/cm^{-1} 1650 (CH=CH–CH=N–); (Found: C, 79.35; H, 8.95; N, 3.55. $C_{26}H_{35}NO_2$ requires C, 79.12; H, 8.69; N, 3.49%).

4-*Decyloxycinnamaldehyde*. M.p. 32–33 °C (lit.,[4] 32.5–34 °C); δ_H 9.66 (1 H, d, *J* 7, CHO), 7.51 and 6.93 (each 2 H, d, C_6H_4), 7.43 (1 H, d, *J* 17, CH=CH–CHO), 6.61 (1 H, dd, *J* 17, 7, CH=CH–CHO), 4.00 (2 H, t, *J* 6.5, OCH_2), 1.81 (2 H, m, OCH_2CH_2), 1.35 [14 H, m, $CH_3(CH_2)_7$] and 0.88 (3 H, t, CH_3); δ_C 193.6, 161.8, 152.8, 130.3, 126.5, 126.3, 115.0, 68.2, 31.9, 29.5, 29.33, 29.30, 29.1, 26.0, 22.7 and 14.1; *m/z* (EI) 188 (M^+, 57%) and 147 (100%).

4-*Hexyloxybenzyl Alcohol*.—Sodium borohydride (1.84 g, 48.5 mmol) was added to a stirred solution of 4-hexyloxybenzaldehyde (20 g, 97 mmol) in light petroleum (100 cm^3). After 4 h, ethanol (200 cm^3) was added and the solution was then heated at reflux for 45 min. Most of the solvent was evaporated, acetone (1000 cm^3) was added and the inorganic residues were allowed to precipitate. The mixture was filtered, the solvent evaporated, and the residue cooled to 4 °C whereupon it solidified. Recrystallisation from pentane afforded 4-hexyloxybenzyl alcohol, as a solid melting near room temperature (10.5 g, 52%); ν_{max}/cm^{-1} 3340 (OH); δ_H 7.20 and 6.80 (each 2 H, d, C_6H_4), 4.50 (2 H, s, $C_6H_4CH_2$), 3.90 (2 H, t, OCH_2), 2.30 (1 H, br s, OH), 1.73 (2 H, m, OCH_2CH_2), 1.35 [6 H, m, $CH_3(CH_2)_3$] and 0.85 (3 H, t, CH_3); δ_C 158.6, 132.8, 128.5, 114.4, 68.0, 31.5, 29.2, 25.6, 22.5 and 14.0.

4-*Hexyloxybenzyl Chloride*.—Light petroleum (200 cm^3) containing 4-(hexyloxy)benzyl alcohol (14.6 g, 70 mmol) was saturated with hydrogen chloride for 1 h. Magnesium sulfate was then added, and the resultant slurry stirred for 20 min. After filtration, the solvent was evaporated under reduced pressure to give 4-(hexyloxy)benzyl chloride as an unstable oil (12.65 g, 80%); δ_H 7.30 and 6.80 (2 H, d, C_6H_4), 4.46 (2 H, s, $C_6H_4CH_2$), 3.88 (2 H, t, *J* 6, OCH_2), 1.70 (2 H, m, OCH_2CH_2), 1.40 [6 H, m, $CH_3(CH_2)_3$] and 0.85 (3 H, t, CH_3); *m/z* (EI) 228 and 226 (M^+, 10 and 30%).

Preparation of Phosphonates.—General procedure. Triethyl phosphite (1 mol) was slowly added to the benzyl halide (1 mol) cooled in an ice bath. The mixture was subsequently heated under reflux for 1–16 h. The phosphonates were purified by distillation under reduced pressure.

Diethyl (4-Hexyloxybenzyl) phosphonate. The title compound was obtained as an oil (47%), b.p. 160–180 °C at 4 mmHg (Found: C, 61.55; H, 9.0. $C_{17}H_{29}O_4P$ requires C, 62.18; H 8.9%); ν_{max}/cm^{-1} 1615 (C=C, aromatic); δ_H 7.2 and 6.85 (each 2 H, m, C_6H_4), 4.05 (2 H, m, OCH_2CH_2), 4.02 (4 H, m, 2 × OCH_2CH_3), 3.10 (2 H, d, $J_{P,H}$ 21, $C_6H_4CH_2$), 1.77 (2 H, m, OCH_2CH_2), 1.40 [6 H, m, $CH_3(CH_2)_5$], 1.25 (3 H, t, CH_3CH_2O) and 0.90 [3 H, t,

$CH_3(CH_2)_5$]; δ_C 158.1 (1 C, d, $J_{P,C}$ 3,7, quaternary aromatic) 130.5 (2 C, d, $J_{P,C}$ 6.3, aromatic), 123.1 (1 C, d, $J_{P,C}$ 8.8, quaternary aromatic), 114.5 (2 C, d, $J_{P,C}$ 2.5, aromatic), 67.9 and 61.8 (2 C, d, $J_{P,C}$ 6.9, 2 × OCH_2CH_3), 33.6 (1 C, d, $J_{P,C}$ 138.9, $C_6H_4CH_2$), 31.2, 29.1, 25.6 and 22.4, [$CH_3(CH_2)_4$] and 16.2 (6 C, d, $J_{P,C}$ 6.3, 2 × OCH_2CH_3) and 13.8 [3 C, $CH_3(CH_2)_4$]; δ_P 25.5 *m/z* (EI) 329 [$(M + H)^+$, 15%], 191 (85%), 183 (82%) and 39 (100%).

Diethyl (4-Fluorobenzyl)phosphonate. The title compound was obtained as an oil (96%), b.p. 150 °C at 1 mmHg; ν_{max}/cm^{-1} 1610 (C=C, aromatic); δ_H 7.27 and 7.01 (each 2 H, d, C_6H_4), 4.02 (4 H, m, 2 × OCH_2), 3.13 (2 H, d, $J_{P,H}$ 21.5, $C_6H_4CH_2$) and 1.26 (6 H, t, *J* 7, 2 × CH_3); δ_C 161.9 (1 C, dd, aromatic) 131.2 (2 C, dd, aromatic), 127.3 (1 C, dd, aromatic) 115.1 (2 C, dd, aromatic), 62.0 (2 C, d, 2 × OCH_2), 32.8 (1 C, d, $C_6H_4CH_2$) and 16.2 (2 C, d, 2 × CH_3); *m/z* (+CI) 247 [$(M + H)^+$, 100%].

Diethyl (4-Chlorobenzyl)phosphonate. The title compound was obtained as an oil (59%), b.p. 162 °C at 2 mmHg; ν_{max}/cm^{-1} 1600 (C=C, aromatic); δ_H 7.26 (4 H, m, C_6H_4), 4.08, (4 H, m, 2 × OCH_2), 3.11 (2 H, d, $J_{P,H}$ 21.5, $C_6H_4CH_2$) and 1.25 (6 H, t, *J* 7, 2 × CH_3); δ_C 132.5 (1 C, d, $J_{P,C}$ 4.4, quaternary aromatic), 130.8 (1 C, d, $J_{P,C}$ 6.9, aromatic), 130.0 (1 C, d, $J_{P,C}$ 8.8, quaternary aromatic), 128.4 (1 C, d, $J_{P,C}$ 3.1, aromatic), 61.9 (2 C, d, $J_{P,C}$ 6.2, 2 × OCH_2), 32.9 (1 C, d, $J_{P,C}$ 138.9, $C_6H_4CH_2$) and 16.1 (2 C, d, $J_{P,C}$ 5.6, 2 × CH_3); *m/z* (CI) 263 [$(M + H)^+$, 100%].

Diethyl (4-Bromobenzyl)phosphonate. The title compound was obtained as an oil (42%), b.p. 162 °C at 0.4 mmHg; ν_{max}/cm^{-1} 1600 (C=C, aromatic); δ_H 7.43 and 7.17 (each 2 H, d, C_6H_4), 4.02 (4 H, m, 2 × OCH_2), 3.1 (2 H, d, $J_{P,H}$ 21.5, $C_6H_4CH_2$) and 1.25 (6 H, t, *J* 7.5, 2 × CH_3); δ_C 131.4 (2 C, d, $J_{P,C}$ 3.1, aromatic) 130.6 (1 C, d, $J_{P,C}$ 9.4, quaternary aromatic), 120.7 (1 C, d, $J_{P,C}$ 4.4, quaternary aromatic), 62.1 (2 C, d, $J_{P,C}$ 6.9, 2 × OCH_2), 33.0 (1 C, d, $J_{P,C}$, 138.4, $C_6H_4CH_2$) and 16.2 (2 C, d, $J_{P,C}$ 6.3, 2 × CH_3); δ_P 26.8; *m/z* (CI) 309 and 307 (M^+, 98 and 100%).

Preparation of Dienes by the Wadsworth–Emmons Reactions.—General procedure. Potassium *tert*-butoxide (4 mmol) was added to a stirred solution of the phosphonate (4 mmol) in dry THF (100 cm^3). The resultant yellow solution was allowed to stir for 10 min before the addition of a solution of the cinnamaldehyde (2.15 mmol) in dry THF (100 cm^3). The solution was then heated at reflux for 20 min before cooling and the addition of methanol or water (100 cm^3) to quench the reaction. The organic solvents were evaporated to leave a residue, which {except for **6** [*n* = 4; X = $-OCH_2(CH_2)_4CH_3$]} was dissolved in chloroform or dichloromethane. The organic layer was separated, washed with water, dried, and the solvent evaporated. For **6** (*n* = 4; X = CN, F, Br; *n* = 5, 7 and 8; X = CN) the crude product was purified by washing it through a silica column with chloroform or dichloromethane followed by crystallisation from dichloromethane–pentane. For **6** (*n* = 2 and 6, X = CN) the crude product was purified by crystallisation from chloroform, followed by column chromatography using dichloromethane as the eluent. For **6** (*n* = 4; X = Cl) the crude product was purified by crystallisation from chloroform. For **6** [*n* = 4; X = $-OCH_2(CH_2)_4CH_3$] the crude product was obtained after quenching the reaction with water by concentration of the reaction mixture (see above) followed by filtration. The solid was washed with water, and ethyl acetate–light petroleum and crystallised from chloroform.

1-(4-*Cyanophenyl*)-4-(4-*hexyloxyphenyl*)*buta*-1,3-*diene*. M.p. 190 °C (31%) (Found: C, 83.45; H, 7.78; N, 4.15. $C_{23}H_{25}NO$ requires C, 83.34; H, 7.60; N, 4.22%); ν_{max}/cm^{-1} 2220 (CN) and 1600 (C=C, aromatic); δ_H(400 MHz) 7.59, 7.48, 7.38 and 6.88 (each 2 H, d, 2 × C_6H_4), 7.03 and 6.83 (each 1 H, dd, *J* 16, 10, CH=C*H*–C*H*=CH), 6.71 and 6.58 (each 1 H, d, *J* 16 C*H*=CH–CH=C*H*), 3.98 (2 H, t, *J* 6.5, OCH_2), 1.79 (2 H, m, OCH_2CH_2), 1.41 [1 H, m, $CH_3(CH_2)_3$] and 0.92 (3 H, t, CH_3); δ_C 159.3, 142.1, 135.2, 133.2, 132.3, 129.3, 129.2, 127.9, 126.4, 126.1, 119.1, 114.7, 109.9, 68.1, 31.6, 29.2, 25.7, 22.6 and 14.0; *m/z* (EI) 331 (M^+, 100%) and 247 (67%).

1-(4-*Fluorophenyl*)-4-(4-*hexyloxyphenyl*)*buta*-1,3-*diene*. M.p. 174 °C (27%) (Found: C, 81.1; H, 7.85. $C_{22}H_{25}FO$ requires C, 81.44; H, 7.7%); δ_H(400 MHz; C_4D_8O) 7.44, 7.35 and 7.03 (each 2 H, d, aryl), 6.89 (5 H, m, 3 diene and 2 aryl protons), 6.59 (1 H, dd, *J* 15, 10, diene), 3.95 (2 H, t, OCH_2), 1.75 (2 H, m, OCH_2CH_2), 1.40 [6 H, m, $CH_3(CH_2)_3$] and 0.9 (3 H, t, CH_3); δ_C (C_4D_8O) 163.0 (1 C, d, *J* 245.9), 160.0 and 135.2 (2 C, d, *J* 3.1), 133.5, 130.9, 130.8, 130.5, 130.4, 128.6, 128.5, 128.3, 127.7, 116.0 (2 C, d, *J* 21.9), 115.3, 66.6, 32.4, 30.1, 26.5, 23.4 and 14.2; δ_F −115.2 (1 F, tt, *J* 8.5, 5.5); *m/z* (EI) 324 (M^+; 100%) and 240 (57%).

1-(4-*Chlorophenyl*)-4-(4-*hexyloxyphenyl*)*buta*-1,3-*diene*. M.p. 189 °C (34%) (Found: C, 77.25; H, 7.55; Cl, 10.45. $C_{22}H_{25}ClO$ requires C, 77.51; H, 7.39, Cl, 10.39%); ν_{max}/cm^{-1} 1600 (C=C, aromatic); δ_H(400 MHz) 7.35 (4 H, m, aryl), 7.28 and 6.86 (each 2 H, m, aryl), 6.86 and 6.80 (each 1 H, dd, *J* 15, 10, CH=C*H*–C*H*=CH), 6.63 and 6.55 (each 1 H, d, *J* 15, C*H*=CH–CH=C*H*), 4.0 (2 H, t, *J* 6.5, OCH_2), 1.6 (2 H, m, OCH_2CH_2), 1.45–1.30 [6H, m, $CH_3(CH_2)_3$] and 0.9 (3 H, t, CH_3); *m/z* (EI) 342 and 340 (M^+, 33 and 100%) and 255 (83%).

1-(4-*Bromophenyl*)-4-(4-*hexyloxyphenyl*)*buta*-1,3-*diene*. M.p. 198 °C, (52%) (Found: C, 68.35; H, 6.4; Br, 20.75. $C_{22}H_{25}BrO$ requires C, 68.57; H, 6.54; Br, 20.73%); ν_{max}/cm^{-1} 1600 (C=C, aromatic); *m/z* (EI) 386 and 384 (M^+, 99 and 100%).

1,4-*Bis*(4-*hexyloxyphenyl*)*buta*-1,3-*diene*. M.p. 194 °C (51%) (Found: C, 82.7; H, 9.4. $C_{28}H_{38}O_2$ requires C, 82.6; H, 9.42%); *m/z* (EI) 406 (M^+, 100%).

1-(4-*Butoxyphenyl*)-4-(4-*cyanophenyl*)*buta*-1,3-*diene*. M.p. 186 °C (45%) (Found: C, 83.25; H, 7.05; N, 4.65. $C_{21}H_{21}NO$ requires C, 83.13; H, 6.97; N, 4.61%); δ_H(250 MHz) 7.58, 7.47, 7.37 and 6.87 (each 2 H, d, 2 × C_6H_4), 7.04 (1 H, dd, *J* 16.5, 9.5, diene), 6.67 (3 H, m, diene), 3.96 (2 H, t, *J* 6.5, OCH_2), 1.62 [4 H, $CH_3(CH_2)_2$] and 0.89 (3 H, t, CH_3); δ_C 159.5, 142.2, 135.3, 133.3, 132.4, 129.4, 129.3, 128.0, 126.5, 126.2, 119.1, 114.8, 110.0, 67.8, 31.3, 19.2 and 13.8; *m/z* (EI) 303 (M^+, 82%), 247 (52%) and 230 (100%).

1-(4-*Cyanophenyl*)-4-(4-*heptyloxyphenyl*)*buta*-1,3-*diene*. M.p. 186 °C (Found: C, 83.2; H, 7.85; N, 4.25. $C_{24}H_{27}NO$ requires C, 83.43; H, 7.87; N, 4.05%); ν_{max}/cm^{-1} 2220 (CN); δ_H(250 MHz) 7.58, 7.47, 7.38 and 6.87 (each 2 H, d, 2 × C_6H_4), 7.05 (1 H, dd, *J* 16.5, 9.5, diene), 6.69 (3 H, m, diene), 3.60 (2 H, t, *J* 6.5, OCH_2), 1.79 (2 H, m, OCH_2CH_2), 1.39 [8H, m, $CH_3(CH_2)_4$] and 0.89 (3 H, t, CH_3); δ_C 159.5, 142.2, 135.3, 133.4, 129.5, 129.3, 128.0, 126.2, 119.1, 114.9, 110.1, 68.2, 31.8, 29.3, 29.0, 26.0, 22.6 and 14.0; *m/z* (EI) 345 (M^+, 100%) and 247 (84%).

1-(4-*Cyanophenyl*)-4-(4-*octyloxyphenyl*)*buta*-1,3-*diene*. M.p. 180 °C (35%) (Found: C, 83.2; H, 8.15; N, 3.95. $C_{25}H_{29}NO$ requires C, 83.52; H, 8.13; N, 3.89%); ν_{max}/cm^{-1} 2230 (–CN); δ_H 7.56, 748, 7.38 and 6.88 (each 2 H, d, 2 × C_6H_4), 7.04, (dd, diene), 6.69 (3 H, m, diene), 3.98 (2 H, t, *J* 6.5, OCH_2), 1.78 (2 H, m, OCH_2CH_2), 1.39 [10 H, m, $CH_3(CH_2)_5$] and 0.89 (3 H, t, CH_3); δ_C 159.5, 142.2, 135.3, 133.4, 129.5, 129.3, 128.0, 126.2, 119.1, 114.9, 110.1, 68.2, 31.8, 29.3, 29.0, 26.0, 22.6 and 14.0; *m/z* (EI) 345 (M^+, 100%) and 247 (84%).

1-(4-*Cyanophenyl*)-4-(4-*nonyloxyphenyl*)*buta*-1,3-*diene*. M.p. 180 °C (40%) (Found: C, 83.65; H, 8.45; N, 3.6. $C_{26}H_{31}NO$ requires C, 83.59; H, 8.36; N, 3.75%); δ_H(250 MHz) 7.59, 7.48, 7.38 and 6.88 (each 2 H, d, 2 × C_6H_4), 7.04 (1 H, dd, *J* 16.5, 9.5, diene), 6.68 (3 H, m, diene), 3.97 (2 H, t, *J* 6.5. OCH_2), 1.78 (2 H, m, OCH_2CH_2), 1.38 [12 H, m, $CH_3(CH_2)_6$] and 0.89 (3 H, t, CH_3); δ_C 159.3, 142.1, 135.2, 133.2, 132.3, 129.3, 129.2, 127.9,

126.4, 126.1, 119.1, 114.7, 109.9, 68.1, 31.9, 29.5, 29.4, 29.2, 26.0, 22.7 and 14.1; *m/z* (EI) 373 (M^+, 100%), 247 (92%).

1-(4-*Cyanophenyl*)-4-(4-*decyloxphenyl*)*buta*-1,3-*diene*. M.p. 180 °C (57%) (Found: C, 83.6; H, 8.65; N, 3.5. $C_{27}H_{33}NO$ requires C, 83.67; H, 8.65; N, 3.61%); ν_{max}/cm^{-1} 2220 (–CN); δ_H(250 MHz) 7.60, 748, 7.36 and 6.88 (each 2 H, m, 2 × C_6H_4), 7.04 (1 H, dd, *J* 16.5, 9.5, diene), 6.69 (3 H, m, diene), 3.97 (2 H, t, *J* 6.5, OCH_2), 1.79 (2 H, m, OCH_2CH_2), 1.38 [14 H, m, $CH_3(CH_2)_7$] and 0.87 (3 H, t, CH_3); δ_C(250 MHz) 159.3, 142.1, 135.2, 133.2, 132.4, 129.3, 129.2, 127.9, 126.4, 126.1, 119.1, 114.7, 109.9, 68.1, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7 and 14.1; *m/z* (EI) 387 (M^+, 100%) and 247 (57%).

Preparation of (4-*Cyanobenzyl*)*triphenylphosphonium Bromide*.—4-Cyanobenzyl bromide (20 g, 102 mmol) and triphenylphosphine (26.8 g, 102 mmol) were heated in refluxing toluene (100 cm^3) for 1.5 h. After cooling the liquid was decanted and fresh toluene (30 cm^3) was added. The mixture was heated to boiling point and then left to cool slowly. The solid was collected by filtration and dried under vacuum for 24 h, to give *the salt* (36.8 g, 79%) as a white powder m.p. > 305 °C (Found: C, 68.2; H, 4.4; Br, 17.4; N, 2.8. $C_{26}H_{21}BrNP$ requires C, 68.13; H, 4.61; Br, 17.43; N, 3.05%); ν_{max}/cm^{-1} 2215 (–CN); $\delta_P(CD_3OD)$ 22.9; *m/z* (CI) 378 (100%) ($C_{26}H_{21}NP^+$ requires *m/z* 378).

Preparation of Dienes by the Wittig Reaction.—General procedure. Potassium *tert*-butoxide (63 mmol) was added to a vigorously stirred slurry of the phosphonium salt (63.3 mmol) in dry THF (200 cm^3). The resultant solution was stirred for a further 0.5 h and 4-(hexyloxy)cinnamaldehyde (32 mmol) in dry THF (200 cm^3) was then added. After the mixture had been stirred for 16 h, a molar excess of water was added and the solution was stirred for a further 0.5 h. The organic solvents were then removed under reduced pressure and the resultant aqueous solution was extracted three times with chloroform. The combined chloroform extracts were dried and the solvent evaporated to give a solid.

Reaction of 4-(*hexyloxy*)*cinnamaldehyde with the ylide prepared from* (4-*cyanobenzyl*)*triphenylphosphonium bromide*. Column chromatography, using chloroform–light petroleum (1:4) as the eluent, afforded a green solid which was separated into three components by MPLC [dichloromethane–light petroleum (35:65)]. The first material eluted had no absorption in the UV region corresponding to a 1,4-diarylbutadiene, and was not investigated further; the second and third components (combined yield 70%) were identified as the (*E,Z*)- and (*E,E*)-forms of 1-(4-*cyanophenyl*)-4-(4-*hexyloxyphenyl*)*buta*-1,3-*diene*. The (*E,E*)-isomer was identical with the product obtained by the Wadsworth–Emmons reaction. The ratios of the two forms [(*Z*):(*E*); 7:3] were determined by HPLC. (E,Z)-1-(4-*Cyanophenyl*)-4-(4-*hexyloxyphenyl*)*buta*-1,3-*diene* had m.p. *ca.* 100 °C (Found: C, 83.2; H, 7.9; N, 4.35. $C_{23}H_{25}NO$ requires C, 83.33; H, 7.6; N, 4.25%) and in daylight, during a few days, was completely transformed into the (*E,E*)-form.

Reaction of 4-(*hexyloxy*)*cinnamaldehyde with the ylide prepared from* (4-*fluorobenzyl*)*triphenylphosphonium bromide*. Column chromatography using chloroform–light petroleum (3:8) as the eluent gave a solid, δ_F −115.80 and −115.68 which ran as a single material on TLC. The impurity responsible for the signal at δ_F −115.68 was removed by preparative MPLC (THF), giving (*E,E*)-1-(4-fluorophenyl)-(4-hexyloxy)-phenylbuta-1,3-diene, identical with the material from the Wadsworth–Emmons reaction.

3-(4-*Bromophenyl*)-6-(4-*hexyloxyphenyl*)-4,4,5,5-*tetracyanocyclohex*-1-*ene*.—1-(4-Bromophenyl)-4-(4-hexyloxyphenyl)-buta-1,3-diene (65 mg, 0.17 mmol) and tetracyanoethene (32 mg, 0.20 mmol) were heated in dichloromethane (5 cm^3) at reflux for 1 h. After cooling the mixture was filtered. Evaporation of the filtrate afforded a residue which after column chromatography using dichloromethane as the eluent gave 3-(4-*bromophenyl*)-6-(4-*hexyloxyphenyl*)-4,4,5,5-*tetracyanocyclohex*-1-*ene*, m.p. 112–114 °C (from ethanol) (83 mg, 95%) (Found: C, 65.3; H, 4.7; Br, 15.65; N, 10.85. $C_{28}H_{25}BrNO$ requires C, 65.49; H 4.90; Br, 15.56; N, 10.91%); δ_H 7.64 and 6.98 (each 2 H, d, C_6H_4), 7.44 (4 H, m, C_6H_4), 6.28 (2 H, m, C*H*=C*H*), 4.39 (2 H, s, benzylic), 3.98 (2 H, t, OCH_2), 1.80 (2 H, m, OCH_2CH_2), 1.42 [6H, m, $CH_3(CH_2)_3$] and 0.91 (3 H, t, CH_3); δ_C 160.7, 132.3, 132.0, 131.7, 131.4, 127.7, 125.8, 124.9, 123.4, 114.9, 111.7, 111.6, 109.4, 109.2, 68.2, 46.5, 46.3, 43.4, 42.8, 31.5, 29.1, 25.6, 22.5 and 13.9; *m/z* (EI) 514 [$(M + H)^+$, 43%] and 386 (100%).

3,6-*Bis*-(4-*hexyloxyphenyl*)-4,4,5,5-*tetracyanocyclohex*-1-*ene*.—1,4-Bis-(4-hexyloxyphenyl)buta-1,3-diene (1.0 g, 2.46 mmol) and tetracyanoethene (0.35 g, 2.73 mmol) were heated in dichloromethane (30 cm^3) at reflux for 2 h. After cooling the mixture was filtered and the solvent evaporated. Column chromatography, using dichloromethane as the eluent, gave 3,6-*bis*-(4-*hexyloxyphenyl*)-4,4,5,5-*tetracyanocyclohex*-1-*ene*, m.p. 90–91 °C, (1.22 g, 93%) (Found: C, 76.3; H, 7.15; N, 10.58. $C_{34}H_{38}N_4O_2$ requires C, 76.37; H, 7.16; N, 10.48%); δ_H 7.46 and 6.98 (each 4 H, d, 2 × C_6H_4), 6.26 (2 H, d C*H*=C*H*), 4.38 (2 H, s, benzylic), 3.99 (4 H, t, *J* 6, 2 × OCH_2), 1.85 (4 H, m, 2 × OCH_2CH_2), 1.44 [12 H, m, 2 × $CH_3(CH_2)_3$] and 0.92 (6 H, t, 2 × CH_3); δ_C 165.0, 131.7, 126.8, 123.7, 114.8, 111.9, 109.4, 68.1, 46.4, 43.2, 31.5, 29.0, 25.6, 22.5 and 14.0; *m/z* (CI) 552 [$(M + NH_4)^+$, 38%] and 407 (100%).

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References

1 R. Brettle, D. A. Dunmur, N. J. Hindley and C. M. Marson, *Jpn. Pat. Filing No.* 3-139999, 1991; Hitachi Research Laboratories, private communication.
2 R. Brettle, D. A. Dunmur, N. J. Hindley and C. M. Marson, *J. Chem. Soc., Chem. Commun.*, 1992, 411.
3 (*a*) C. Weygand and R. Gabler, *J. Prakt Chem.*, 1940, **155**, 332; (*b*) G. W. Gray and B. Jones, *J. Chem. Soc.*, 1954, 1467; (*c*) T. Nogradi, L. Vargha, G. Ivanovics and I. Koczka, *Acta Chim. Acad., Sci. Hung.*, 1954, **4**, 303; (*d*) H. Edgerson, R. L. Hull and J. R. Fisher, *J. Am. Pharm., Assoc. Sci. Ed.*, 1959, **48**, 320.
4 T. Nishimura, S. Yoshi, H. Toku, K. Hasegawa and D. Nagaki, *Kitasato Arch., Exp. Med.*, 1975, **48**, 165.
5 J. M. Van der Zanden, *Recl. Trav. Chim. Pays-Bas*, 1941, **60**, 291.
6 C. J. Schmidle and P. G. Barnett, *J. Amr. Chem. Soc.* 1956, **78**, 3209.
7 J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis*, Academic Press, New York, 1979.
8 G. S. Kolesnikov and G. N. Pogosyan, *Izv. Akad. Nauk, Armyan SSSR, Khim. Nauk*, 1957, **10**, 131.
9 (*a*) L. F. Fieser, *Organic Experiments*, D. C. Heath, Boston, 1965, 119; (*b*) G. Markl and A. Merz, *Synthesis*, 1973, 295; (*c*) C. Piechucki, *Synthesis*, 1976, 187; (*d*) I. Hughes and R. A. Raphael, *Tetrahedron Lett.*, 1983, **24**, 1441; Md. A. Hashem, P. Weyerstahl and B. S. Green, *Tetrahedron*, 1984, **40**, 203.
10 (*a*) F. Kagan, R. D. Bohenmeyer and R. E. Stube, *J. Am. Chem. Soc.*, 1959, **81**, 3026; (*b*) A. Franke, G. Mattern and W. Traber, *Helv. Chim. Acta*, 1975, **58**, 268.
11 (*a*) B. Christina, G. Fulvio and C. Alberto, *Eur. J. Med. Chem.*, 1987,

22, 437; (*b*) W. F. Chamberlain and W. M. Haskins, *J. Econ. Entomol.*, 1951, **44**, 177.
12 M. Julia and F. Chastrette, *Bull. Soc. Chim. Fr.*, 1962, 2247.
13 H. Moeller and S. Wallat, *Ger. Pat.* DE, 3,332,505, 1985.
14 H. Stephen and C. Weizman, *J. Chem. Soc.*, 1914, **105**, 1152.
15 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1983.
16 E. Juaristi, A. Martinez-Richa, A. Garcia-Rivera and J. S. Cruz-Sanchez, *J. Org. Chem.*, 1983, **48**, 2603.
17 M. R. Winkle, J. M. Lansinger and R. C. Ronald, *J. Chem. Soc., Chem. Commun*, 1980, 87.
18 (*a*) S. M. Kelly, J. Funfschilling and F. Leenhouts, *Liq. Cryst.*, 1991, **10**, 243; (*b*) S. M. Kelly, *Liq. Cryst.*, 1991, **10**, 261; (*c*) S. M. Kelly, *Liq. Cryst.*, 1991, **10**, 273.

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