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Synthesis and Characterization of Stilbene Derivatives for Possible Incorporation as Smart Additives in Polymers Used as Packaging Films^{*}

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Several series of stilbene derivatives for possible use as smart additives in polymers used as packaging films have been prepared and characterized. Differential scanning calorimetry was performed on some of the stilbenes in order to determine any liquid crystal properties. Those compounds which had multiple phase transitions were also shown to have two liquid crystalline phases according to optical microscopy.

Introduction

One of the limitations of polymer films currently used for modified-atmosphere packaging is their limited permeation characteristics under varying environmental temperatures. Ideally, changes in the permeation rates of carbon dioxide and oxygen with temperature should be similar to the corresponding changes in respiration rate of the produce contained within. It has been shown previously that incorporation of liquid crystalline materials into a polymer matrix can improve dramatically the gas permeability properties of the film.¹ However, the transition temperatures involved in the reported cases were considerably above refrigeration temperatures. We have sought to address this problem by the use of liquid crystalline additives having transition temperatures slightly higher than typical storage temperatures $(0-10^{\circ}C)$. These liquid crystalline compounds would also need to be nontoxic since they will ultimately be in contact with the fresh produce. From the numerous compounds prepared previously,² it was thought that stilbenes may best suit the requirements of having liquid crystalline properties at low temperatures, especially if the structure included either branched alkyl chains or multisubstituted aromatic rings. Moreover, these compounds would have the added advantage of being potentially non-toxic. Therefore several series of substituted stilbenes were synthesized and examined for possible liquid crystal phase changes at temperatures close to those used for refrigeration.

Preparation of the Stilbene Derivatives

The synthesis of this class of compounds based entirely on a hydrocarbon skeleton, namely the 1-(3,5-dialkylphenyl)-2-(4-alkylphenyl)ethene series, was investigated. The most direct synthesis of a library of these stilbenes, which are *meta*-dialkylated in one of the aromatic rings, is via 1,3,5-tribromobenzene (1a), which has been trisfunctionalized by the sequential exchange of each bromide by using BuLi/Et₂O and reaction at each step with $Me_3M^{IV}Cl$ ($M^{IV} = Si$, Ge, Sn).³ Furthermore, 3,5-dibromophenyllithium has been coupled with CO₂, fluorinated esters, and ketones to give the resultant acylated adducts in good yield.⁴ For the present purpose, this route intended to use two sequential replacements of an aromatic bromide by treatment with butyllithium, each resultant aryl anion being trapped with an alkyl iodide to generate compounds of the type (1b) and then type (1c) bearing different hydrocarbon side chains $(\mathbf{R}^1 \text{ and } \mathbf{R}^2)$. Further treatment of the bromobenzene (1c) with BuLi followed by reaction with dimethylformamide and hydrolytic workup was expected to generate the formyl derivative (1d). This aldehyde can then undergo a Wittig reaction by treatment with the ylide formed from a suitably substituted *p*-alkylbenzyltriphenylphosphonium salt; this should lead directly to the desired stilbene derivatives (1e).

However, even after extensive experimentation involving the variation of a wide range of reaction parameters,⁵ treatment of (1a) with butyllithium in diethyl ether

 $^{^{\}ast}$ This paper is dedicated to Professor R. C. Cambie on the occasion of his retirement.



at -78° C followed by reaction with iodomethane, or 1-iodobutane, or 1-iodohexane afforded only 1,3dibromobenzene (1h). When tetrahydrofuran was used as solvent a complicated mixture was obtained from which only (1a), (1h) and 1-alkyl-2,4,5-tribromobenzene (from lithium–hydrogen exchange rather than lithium– bromide exchange) could be identified.⁴

Clearly an alkyl transfer reagent more efficient than an iodoalkane is required in order to allow coupling with the anion generated from (1a). A number of acyl transfer reagents such as acid chlorides, anhydrides and esters were therefore investigated.⁶ Although these would lead to the formation of aromatic ketones rather than arylalkane derivatives it was expected that subsequent reduction (e.g. Clemmensen) of the benzylic carbonyl could be achieved easily to form the required compounds (1c). Not unexpectedly, when an acid



chloride was used as electrophile the crude mixture contained only a small amount of the desired ketone (2), the alcohol (3) and its corresponding ester (4) being the major products. Compound (3) is clearly the product from reaction of (2) with 3,5-dibromophenyllithium; the alkoxide of (3) may react further *in situ* with 1 mol. equiv. of the acid chloride to give the ester (4) (Scheme 1).

A range of experiments was carried out in attempts to define the optimum conditions required for the formation of the desired ketones (2). In particular, changes to the reaction temperature, transmetallation of the aryllithium with either copper(I) bromide⁷ or manganese(II) bromide,⁸ excess of acid chloride, and inverse addition techniques, were investigated. Eventually the reproducible isolated yield of the aromatic ketones (2a) and (2b) was increased, but to only 50–60 and 25–30%, respectively. The latter yield is clearly inefficient for the start of a multistep synthesis. When an alkyl ester $(RCO_2C_2H_5, R = CH_3 \text{ or } C_5H_{11})$ or a symmetrical anhydride $[(C_5H_{11}CO)_2O]$ was used as electrophile, again only mixtures of (1h) and (2)-(4)were isolated, the highest yields of (2a) and (2b) being 42 and 32%, respectively.

In an alternative and successful approach the route outlined in Scheme 2 was undertaken. This sequence again relies on metal-halogen exchange of 1,3,5-tribromobenzene (1a) with butyllithium, the resultant monoanion being trapped with dimethylformamide to give, after hydrolytic workup, the formyl derivative (1f). The use of dimethylformamide as electrophile avoids the undesired formation of a ketone and products of its further reaction. Compound (1f) can now undergo a Wittig reaction to give the alkenyl derivative (10). Repetition of this sequence for the two bromine atoms remaining on the aromatic ring, including a step to hydrogenate the alkene double bonds, should lead to the 1-(3,5-dialkylphenyl)-2-(4alkylphenyl)ethene derivative (1t). It was recognized that the classic Wittig reaction conditions with a non-stabilized ylide would afford a mixture of E and Z isomers of the product stilbenes. However, the simplicity of the method was attractive, and samples of the pure stereoisomers could be separated chromatographically, potentially allowing individual assessment of each for liquid crystalline properties.

Therefore, a number of phosphonium salts of the type $\text{RCH}_2\text{PPh}_3^+\text{I}^-$ required for the first two Wittig steps were synthesized [R = H (93%), C_2H_5 (93%), C_3H_7 (91%), C_4H_9 (82%), C_5H_{11} (98%), C_6H_{13} (99\%)] by treatment of the corresponding alkyl iodide with triphenylphosphine. The 4alkylbenzyltriphenylphosphonium iodides required for the final Wittig step were synthesized⁹ from commercially available 4-alkylbenzaldehyde diethyl acetals in excellent overall yields (Scheme 3).

Treatment of (1a) with $BuLi/Et_2O$ at $-78^{\circ}C$ followed by quenching with dimethylformamide afforded



the desired dibromo aldehyde (1f) in 95% yield.⁴ Wittig reactions¹⁰ have been carried out by using a wide range of bases and solvents. The choice of solvent was critical to the yield of the 3,5-dibromo alkene in the present work; in diethyl ether the alkyltriphenylphosphonium salts were only sparingly soluble and their deprotonation with BuLi did not go to completion, leading to low yields of the expected products. The use of Bu^tOK– Bu^tOH solvate in diethyl ether is beneficial to the yield of some Wittig reactions.¹¹ However, use of this solvate for the generation of $C_6H_{13}CH=PPh_3$ and its coupling with (1f) did not lead to increased yields (31%) of the product (1m). Moreover, 3,5-dibromobenzenemethanol (1n) (43%) was also formed by hydride transfer from Although Bigot $et \ al.^{12}$ have reported the ylide. the formation of Wittig products when the reaction was carried out in either methanol or dioxan with K_2CO_3 as base, treatment of $C_7H_{15}PPh_3^+I^-/K_2CO_3$ in

methanol with 3,5-dibromobenzal dehyde (1f) returned only starting material. However, treatment of (1f) with $C_7H_{15}PPh_3^+I^-/BuLi$ in tetrahydrofuran afforded the desired alkenyl dibromo derivative (1m) as a clear oil in 95% yield.

R

C₂H₅

C₄H₉

C6H13

PPh3/C6H6

heat c. 5 h

(8a)

(8b)

(8c)

(8d) C₈H₁₇

Yield

98%

99%

NaBH₄/MeOH → OH

Yield

98%

94%

99%

93%

R

C₂H₅

C₄H₉

C6H13

 $C_{8}H_{17}$

/ Me₃SiCl/NaI MeCN/N₂

(9a)

(9b)

(9c)

(9d)

2 h

R Yield R Yield (11a) C_2H_5 99% (10a) C₂H₅ 98% (11b) C_4H_9 93% (10b) C_4H_9 93% (11c) (10c) C_6H_{13} 98% C_6H_{13} 97% (11d) C₈H₁₇ 97% (10d) C₈H₁₇ 98% Scheme 3 Reaction of (1m) with BuLi/Et₂O at -78° C followed by coupling with dimethylformamide gave the formyl derivative (5h) (89%), the yield depending critically on the molar ratio of BuLi used in the halogen exchange reaction. When 1.05 mol. equiv. of BuLi were used the yield of the aldehyde decreased dramatically (20-40%), the small excess of BuLi promoting competitive allylic deprotonation and then polymerization of the alkene.

The second Wittig reaction to form the bis(alkenyl)aryl bromide (5k) from the aldehyde (5h) was achieved in 96% yield by using the optimized procedure indicated earlier. The key intermediate (6f) was then synthesized (92%) by treatment of (5k) with BuLi/Et₂O followed by trapping of the anion with dimethylformamide and hydrolytic workup. The 3,5-bis(alkenyl)benzaldehydes (6f) showed the molecular ion at m/z 326 with an accurate mass measurement that was correct for C₂₃H₃₄O, and had ¹H and ¹³C n.m.r. data that were consistent with the proposed structure.

The mixture of E and Z isomers of the bis(alkenyl)aldehyde (6f) was coupled with $4-C_2H_5C_6H_4CH=PPh_3$ in tetrahydrofuran to afford a mixture of the isomeric stilbenes (12) (78%); this corresponds to an overall yield of 56% from (1a). Hydrogenation of the olefinic groups in (12) over Pd/C afforded 1-(3,5-dioctylphenyl)-2-(4ethylphenyl)ethane (13) (98%). This compound was isolated as a clear oil which showed the molecular ion at m/z 434 (C₃₂H₅₀), gave correct microanalytical data, and had ¹H and ¹³C n.m.r. spectra consistent with the proposed structure.



Having shown that a 3,5-bis(alkenyl)benzaldehyde does undergo Wittig coupling in good yield, we investigated methods of reducing the two double bonds in the subtended groups without destroying the aldehyde functionality. Hydrogenation of (6f) over Pd/C for 45 min afforded not only the desired aldehyde (7i) (23%)but also the methyl derivative (7g) (7%), and the hydroxymethyl derivative (7h) (70%). The alcohol (7h)was then reoxidized with pyridinium chlorochromate to give aldehyde (7i) (89%); this sequence affords (7i) in an overall yield of 85% from (6f). When the hydrogenation of (6f) was stopped after 2 mol. equiv. of hydrogen had been consumed a complicated mixture of products was obtained, including (¹H n.m.r.) compounds containing one double bond and a partially reduced aldehyde group, as well as the expected products. With the above hydrogenation/reoxidation sequence being used, (7c) and (7f) were each synthesized in 89% yield from their respective precursor, (6b) and (6d).

The aldehydes (7c), (7f) and (7i) were coupled with the ylides generated by treatment of (8a), (8b), (8c) and (8d) with BuLi. Typically, the 4alkylbenzyltriphenylphosphonium salts were treated with 1 mol. equiv. of BuLi in tetrahydrofuran at 0°C for 5 min, resulting in the formation of a deep red solution of the ylide. A solution of the aldehyde (7c), (7f) or (7i) in tetrahydrofuran was then added and the mixture was stirred at room temperature for 14 h, resulting in decolorization. Workup and chromatography afforded a mixture (85-90%) of the E (14a-j)and Z (15a-j) isomers of a 1-(3,5-dialkylphenyl)-2-(4alkylphenyl)ethene. The fractions were contaminated with a mixture of the E (16a–d) and Z (17a–d) isomers of their corresponding 1,2-bis(4-alkylphenyl)ethene derivatives. Analytically pure samples of all four components were obtained by repetitive p.l.c. on silica gel with hexanes as eluent. The 1,2-bis(4-alkylphenyl)ethene derivatives were shown to form by coupling of a

.OEt

H₃O⁺/CH₂Cl₂

PPh3+ I

4-alkylbenzylidenetriphenylphosphorane ylide with a 4-alkylbenzyltriphenylphosphonium iodide. Since the ylides were generated from the salts in the presence of a base (BuLi), the formation of the by-products could not be avoided.



Thermal and Optical Characterization

All of the stilbene derivatives prepared were examined for liquid crystallinity by means of differential scanning calorimetry (d.s.c.) between the temperatures of -100and $+100^{\circ}$ C. Surprisingly, the only compounds which exhibited any liquid crystalline behaviour were the *E* by-products (16b–d) of the coupling reaction between the respective aldehydes and ylides. The phase transition temperatures and the transition enthalpies (ΔH) are listed in Table 1. All other stilbene derivatives were liquid at ambient temperature. These results illustrate the difficulty that exists in predicting structure–activity correlations in potential liquid crystalline materials.

The actual phases of these liquid crystalline materials (16b–d) were determined by means of optical microscopy. All three of these stilbene derivatives exhibited both smectic and nematic phases (Table 1). For the 4,4'-dihexyl and 4,4'-dioctyl derivatives (16c, d) the type of smectic phase was identified as smectic



Table 1. Phase transition temperatures and enthalpies for the liquid crystalline compounds (16b–d)

Symbols: K, crystalline phase; S, smectic phase; N, nematic phase; I, isotropic phase

Cpd	R	К	S	Ν	Ι
		Transition	temperatures (°	C)	
(16b)	C_4H_9	А	22	110^{B}	
(16c)	C_6H_{13}	11	31	96	
(16d)	$\mathrm{C_8H_{17}}$	44 ^C	$46^{\rm C}$	96	
	Ti	ansition er	thalpies ΔH (J	$g^{-1})$	
(16b)	C_4H_9	Α	3.5	D	
(16c)	C_6H_{13}	$40 \cdot$	$5 9 \cdot 4$	$30 \cdot 9$	
(16d)	$\mathrm{C_8H_{17}}$	49.	$9^{\rm E}$ $20 \cdot 6^{\rm H}$	$= 34 \cdot 8$	

^A Could not be determined.

^B Determined from optical microscopy.

^C Peak temperatures recorded due to broad overlapping peaks.

^D Not recorded since determination of transition was by optical microscopy.

^E Partial transition enthalpies recorded due to broad overlapping peaks.

A by comparison of optical textures with those of other materials of known smectic A composition. The 4,4'-dibutyl derivative (16b), however, exhibited very unusual behaviour. D.s.c. traces for this compound reproducibly displayed only one transition between -100 and $+100^{\circ}$ C. The transition enthalpy for this peak $(3 \cdot 5 \text{ J g}^{-1})$ was not large enough to be a melting transition [cf. ΔH values for (16c,d) in Table 1 for K-S transitions]. Subsequently it was discovered by using optical microscopy that this ΔH appeared to indicate a smectic to nematic transition. The exact nature of the smectic phase could not be identified. Another unusual feature of the 4,4'-dibutyl derivative (16b) was the absence of a liquid crystalline to isotropic transition in the d.s.c. traces. Typically these transitions have a rather large enthalpy value [Table 1, ΔH values for (16c,d)]. Further d.s.c. traces for compound (16b) were run from -120 to $+300^{\circ}$ C, but only the one phase transition was exhibited. It was expected that, if a liquid crystalline to isotropic transition did exist in the temperature range examined, it would have been seen, especially since a possibly nematic phase existed. Surprisingly, the onset of the isotropic phase at 110°C could be seen clearly by optical microscopy, and at 120°C compound (16b) was completely isotropic in nature. That a transition from a liquid crystalline phase to an isotropic phase existed but was not detected by d.s.c. is extremely unusual.

Further work in this area will involve mixing (either through solutions or a melt) the liquid crystalline compounds (16b–d) in various ratios, either with each other or with some of the non-liquid crystalline stilbene derivatives. The aim will be to obtain eutectic mixtures with transitions that fall in the desired temperature range (0–10°C). Initial work on some mixtures has indicated significant lowering of some of the phase transition temperatures.

Experimental

For general experimental details see ref. 13. ¹H n.m.r. spectra were recorded at $400 \cdot 13$ MHz, and ¹³C n.m.r. spectra at $100 \cdot 62$ MHz on a Bruker AM400 instrument operating at $9 \cdot 2$ T. Multiplicities were determined from DEPT spectra. D.s.c. measurements were carried out under nitrogen by using a Polymer Laboratories PL DSC-12000 instrument with a scanning rate of 10° /min. Samples which showed transitions between -100 and $+100^{\circ}$ C were scanned a second time to eliminate thermal history. Data reported in Table 1 refer to heating runs other than the first. Identification of the particular liquid crystalline phases was performed by using an Olympus BHSM-L-2 microscope equipped with a Linkam THMS600 hot/cold stage and a Olympus long working distance objective (magnification $\times 20$).

General Procedure for Synthesis of the Triphenylphosphonium Salts

A solution of triphenylphosphine (1.00 mol. equiv.) and the alkyl or benzyl iodide (1.05 mol. equiv.) in anhydrous benzene was heated to reflux for 24 h. In the cases where the product was a solid the reaction mixture was filtered and the white salt washed several times with dry benzene. In the cases where the product was an oil the reaction mixture was separated in a separating funnel and the product washed several times with dry benzene to give, after drying under vacuum, pure RPPh₃I [R = CH₃ (93%), C₃H₇ (93%), C₄H₉ (91%), C₅H₁₁ (82%), C₆H₁₃ (98%), C₇H₁₅ (99%), CH₂C₆H₄C₂H₅ (99%), CH₂C₆H₄C₄H₉ (99%), CH₂C₆H₄C₆H₁₃ (98%)].

Hexyltriphenylphosphonium Iodide

Reaction of triphenylphosphine $(25 \cdot 0 \text{ g})$ and 1-iodohexane $(22\cdot 5~{\rm g})$ afforded after workup ${\rm C_6H_{13}PPh_3}^+\,{\rm I^-}$ $(44\cdot 3~{\rm g},\,98\%)$ as a viscous clear oil which on standing formed globular crys*tals*, m.p. 129–133°C (Found: $M^{+\bullet} - I$, 347·1931. $C_{24}H_{28}P^+$ requires m/z 347 1929). $\nu_{\rm max}$ (CH2Cl2) 3066, 3038, 2958, 2862, 1589, 1486, 1467, 1439 (intense), 1402, 1338, 1114 (intense), 997, 534, 508 cm⁻¹. $\delta_{\rm H}$ 0.82, t, J 6.7 Hz, 3H, $(CH_2)_5CH_3; 1 \cdot 17 - 1 \cdot 25, m, 4H, (CH_2)_3(CH_2)_2CH_3; 1 \cdot 53 - 25$ $1 \cdot 67$, m, 4H, CH₂(CH₂)₂C₃H₇; $3 \cdot 50 - 3 \cdot 71$, m, 2H, CH₂C₅H₁₁; $7 \cdot 67 - 7 \cdot 85$, m, 15H, CH (PPh₃). $\delta_{\rm C}$ 13 · 77, (CH₂)₅**C**H₃; 22 · 04, (CH₂)₄CH₂CH₃; 22.38, d, J 7.0 Hz, CH₂CH₂C₄H₉; 22.93, d, J 53·3 Hz, CH₂C₅H₁₁; 29·94, d, J 15·5 Hz, (CH₂)₂CH₂C₃H₇; $31 \cdot 03$, $(CH_2)_3 CH_2 C_2 H_5$; $117 \cdot 88$, d, J $85 \cdot 9 Hz$, 3C, $(C_{ipso})_3$; 130.44, d, J 12.5 Hz, 6C, (C_{meta})₆; 133.45, d, J 10.0 Hz, 6C, $({\rm C}_{ortho})_6;\,135\cdot01,\,{\rm d},\,J$ 2·3 Hz, 3C, $({\rm C}_{para})_3.~m/z$ (f.a.b.) 821 $((C_6H_{13}PPh_3)_2^{2+}I^-, 2\%), 681 (2), 363 (4), 347 (C_6H_{13}PPh_3^+, 100)_{13} (C_6H_{13}PPh_3^$ 100, 262 (⁺PPh₃, 7), 183 (5).

4-Hexylbenzaldehyde (8c)

A solution of 4-hexylbenzaldehyde diethyl acetal (10 · 0 g, 37 · 9 mmol) in dichloromethane (100 ml) was treated with dilute HCl (3 drops, 2 mol l⁻¹) and water (1 · 4 ml, 75 · 8 mmol) at room temperature. After 2 · 5 h the reaction mixture was diluted with water and extracted with dichloromethane. Workup in the usual manner afforded (8c) (7 · 12 g, 99%) as a clear oil. $\nu_{\rm max}$ 2928, 2857, 2731, 1694 (C=O), 1606, 1575, 1466, 1386, 1305, 1168 cm⁻¹. $\delta_{\rm H}$ 0 · 88, br t, J 6 · 4 Hz, 3H, C₅H₁₀CH₃; 1 · 21-1 · 39, m, 6H, (CH₂)₂(CH₂)₃CH₃; 1 · 57-1 · 69, m, 2H, CH₂CH₂C₄H₉; 2 · 67, br t, J 7 · 4 Hz, 2H, CH₂C₅H₁₁; 7 · 32, br d, J 8 · 0 Hz, 2H, H3 and H5; 7 · 79, br d, J 8 · 1 Hz, 2H, H2 and H6; 9 · 96, s, 1H, CH=O. $\delta_{\rm C}$ 13 · 95, (CH₂)₅CH₃; 22.26, $(CH_2)_4 CH_2 CH_3$; 28.82, $(CH_2)_2 CH_2 C_3 H_7$; 30.93, CH₂CH₂C₄H₉; 31.54, $(CH_2)_3 CH_2 C_2 H_5$; 36.10, CH₂C₅H₁₁; 128.96, 2C, C 3 and C 5; 129.76, 2C, C 2 and C 6; 134.32, C 1; 150.35, C 4; 191.83, CH=O.

4-Hexylbenzenemethanol (9c)

Sodium borohydride $(3 \cdot 56 \text{ g}, 93 \cdot 7 \text{ mmol})$ was added in five equal portions to a solution of 4-hexylbenzaldehyde (8c) $(10 \cdot 0 \text{ g}, 37 \cdot 5 \text{ mmol})$ in methanol (100 ml) cooled to 0° C. After 1 h at 0°C the reaction mixture was allowed to warm to room temperature and was stirred for 12 h. Dilution with HCl (2 mol l^{-1}) followed by extraction with diethyl ether afforded after workup in the usual manner (9c) $(7 \cdot 12 \text{ g}, 99\%)$ as a clear oil. $\nu_{\rm max}$ 3333 (OH), 3012, 2926, 2855, 1514, 1464, 1417, 1335, 1017 cm⁻¹. $\delta_{\rm H}$ 0.88, t, J 6.5 Hz, 3H, (CH₂)₅CH₃; 1.20–1.39, m, 6H, $(CH_2)_2(CH_2)_3CH_3$; $1 \cdot 51 - 1 \cdot 68$, m, 2H, $CH_2CH_2C_4H_9$; $2 \cdot 41$, s, 1H, CH₂OH; $2 \cdot 58$, br t, J $7 \cdot 4$ Hz, 2H, CH₂C₅H₁₁; $4 \cdot 55$, s, 2H, CH₂OH; $7 \cdot 13$, br d, J $8 \cdot 1$ Hz, 2H, H2 and H6; 7.22, br d, J 8.1 Hz, 2H, H3 and H5. $\delta_{\rm C}$ 14.02, (CH₂)₅CH₃; 22.54, (CH₂)₄CH₂CH₃; 28.92, (CH₂)₂CH₂C₃H₇; $31 \cdot 67$, $(CH_2)_3 CH_2 C_2 H_5$; $35 \cdot 59$, $CH_2 C_5 H_{11}$; $64 \cdot 96$, $CH_2 OH$; 127.02, 2C, C3 and C5; 128.45, 2C, C2 and C6; 138.06, C1; $142 \cdot 27, C4.$

1-Hexyl-4-iodomethylbenzene (10c)

Chlorotrimethylsilane $(8 \cdot 01 \text{ g}, 74 \cdot 2 \text{ mmol})$ was added slowly to a mixture of sodium iodide (16.7 g, 0.11 mol) and 4hexylbenzenemethanol (9c) $(9 \cdot 89 \text{ g}, 44 \cdot 5 \text{ mmol})$ in acetonitrile (100 ml) cooled to 0° C. After 1 h at 0° C the reaction mixture was allowed to warm to room temperature and was stirred for 1 h after which time it was poured into water, and extracted with diethyl ether. The combined organic extracts were washed with water, saturated aqueous $Na_2S_2O_3$, and brine. Workup followed by flash chromatography on silica gel (hexanes/diethyl ether) afforded (10c) (10.9 g, 97%) as a clear oil which crystallized on standing to give white needles, m.p. 34–36°C. $\nu_{\rm max}$ 3022, 2955, 2925, 2855, 1612, 1509, 1464, 1378, 1156, 830 cm^{-1}. $\delta_{\rm H}$ 0·88, t, J6·7 Hz, 3H, (CH₂)₅CH₃; $1\cdot 22 - 1\cdot 38, \ m, \ 6H, \ (CH_2)_2 (CH_2)_3 CH_3; \ 1\cdot 50 - 1\cdot 68, \ m, \ 2H,$ $CH_2CH_2C_4H_9$; 2.55, br t, J 7.4 Hz, 2H, $CH_2C_5H_{11}$; 4.43, s, 2H, CH₂I; $7 \cdot 08$, br d, $J 8 \cdot 1$ Hz, 2H, H 3 and H 5; $7 \cdot 27$, br d, J $8 \cdot 1$ Hz, 2H, H2 and H6. $\delta_{\rm C}$ $6 \cdot 19$, CH₂I; $14 \cdot 07$, (CH₂)₅**C**H₃; $22 \cdot 56$, $(CH_2)_4 CH_2 CH_3$; $28 \cdot 95$, $(CH_2)_2 CH_2 C_3 H_7$; $31 \cdot 22$, $CH_2CH_2C_4H_9$; 31.67, $(CH_2)_3CH_2C_2H_5$; 35.67, $CH_2C_5H_{11}$; $128 \cdot 60, 2C, C3 and C5; 128 \cdot 81, 2C, C2 and C6; 136 \cdot 36, C4;$ $142 \cdot 80$, C1. m/z 301 (M^+ – H, 1%), 246 (M – CH₂=CHC₂H₅, 1), 231 $(M - C_5H_{11}, 3)$, 175 (M - I, 100), 117 (8), 104 (32), 91 (21), 78 (10), 43 (16).

4-Hexylbenzyltriphenylphosphonium Iodide (11c)

Reaction of triphenylphosphine $(8 \cdot 30 \text{ g}, 31 \cdot 2 \text{ mmol})$ with 1hexyl-4-iodomethylbenzene (10c) (10.6 g, 33.3 mmol) in refluxing benzene (100 ml) for 3 h afforded (11c) $(17 \cdot 9 \text{ g}, 98\%)$ as white microcrystalline rods, m.p. 147–150°Ć (Found: C, $65 \cdot 9$; H, $6 \cdot 0$; I, $22 \cdot 2$. C₃₁H₃₄IP requires C, $66 \cdot 0$; H, $6 \cdot 1$; I, $22 \cdot 5\%$. Found: m/z, 437.2397. C₃₁H₃₄P requires m/z, 437.2398). $\nu_{\rm max}$ (CH₂Cl₂) 3037, 2931, 2858, 1589, 1512, 1439 (intense), 1112 (intense), 998, 505 cm⁻¹. $\delta_{\rm H}$ 0.87, t, J 6.9 Hz, 3H, $(CH_2)_5 CH_3; 1 \cdot 20 - 1 \cdot 35, m, 6H, (CH_2)_2 (CH_2)_3 CH_3; 1 \cdot 47 - 100 CH_2 + 100$ $1 \cdot 56$, m, 2H, CH₂CH₂C₄H₉; $2 \cdot 51$, br td, $J \ 7 \cdot 8$, $1 \cdot 5$ Hz, 2H, CH₂C₅H₁₁; 5.12, d, J 13.9 Hz, 2H, CH₂PPh₃; 6.92-6.98, m, 4H, $C_6H_{13}C_6H_4CH_2PPh_3$; 7.60–7.70, m, 12H, $(H_{meta})_6$ and (Hortho)6, PPh3; 7.79, br tq, J 6.9, 1.9 Hz, 3H, (Hpara)3, PPh₃. $\delta_{\rm C}$ 13.63, (CH₂)₅**C**H₃; 22.09, (CH₂)₄**C**H₂CH₃; 28.29, $(CH_2)_2$ **C** $H_2C_3H_7$; 30·38, d, J 47·5 Hz, **C** H_2PPh_3 ; 30·69, $CH_2CH_2C_4H_9; 31 \cdot 12, (CH_2)_3CH_2C_2H_5; 34 \cdot 97, CH_2C_5H_{11};$ 116.98, d, J 85.7 Hz, 3C, $(C_{ipso})_3$; 123.14, d, J 8.6 Hz, C1; 128.50, d, J 2.8 Hz, 2C, C2 and C6; 129.83, d, $J = 12 \cdot 5 \text{ Hz}, 6C, (C_{meta})_6; 130 \cdot 74, d, J = 5 \cdot 3 \text{ Hz}, 2C, C = 3$ and C 5; 134.85, d, J 9.7 Hz, 6C, $(C_{ortho})_6$; 134.76, d, J 2.5 Hz, 3C, $(C_{para})_3$; 143.07, d, J 4.1 Hz, C 4. m/z (f.a.b.) 1001 ($(C_6H_{13}C_6H_4CH_2PPh_3)_2^{2+}$ I⁻, 1%), 588 (2), 437 ($C_6H_{13}C_6H_4CH_2PPh_3^+$, 100), 379 (4), 307 (9), 289 (5), 262 (+PPh_3, 10), 175 (9), 154 (22).

3,5-Dibromobenzaldehyde (1f)

A suspension of 1,3,5-tribromobenzene (1a) (10·0 g, 31·7 mmol) in diethyl ether (250 ml) at -78° C was treated dropwise with butyllithium (13·3 ml, 33·3 mmol). After 45 min dimethylformamide (6·95 g, 95·2 mmol) was added to the mixture, which was then stirred for a further 1 h. Dilution with HCl (100 ml, 2 mol l⁻¹) followed by workup in the usual manner afforded a cream-coloured solid which was purified by flash chromatography on silica gel (hexanes/diethyl ether) to give (1f) (7·92 g, 95%) as a white solid which crystallized from diethyl ether/hexanes as needles, m.p. 89–92°C. $\nu_{\rm max}$ 3076, 2836, 1707 (C=O), 1561, 1432 cm⁻¹. $\delta_{\rm H}$ 7·94, br d, J 1·7 Hz, 2H, H 2 and H 6; 7·92, br d, J 1·7 Hz, 1H, H 4; 9·91, s, 1H, CH=O. $\delta_{\rm C}$ 123·89, 2C, C 3 and C 5; 131·15, 2C, C 2 and C 6; 138·84, C 1; 139·51, C 4; 189·10, CH=O.

(E)- and (Z)-1-(3,5-Dibromophenyl)oct-1-ene (1m)

A solution of heptyltriphenylphosphonium iodide $(24 \cdot 4 \text{ g},$ $50 \cdot 0 \text{ mmol}$) in tetrahydrofuran (100 ml) was treated dropwise with butyllithium $(21 \cdot 0 \text{ ml}, 50 \cdot 0 \text{ mmol})$ at 0° C. After 15 min the reaction temperature was raised to 25° C during which time a dark red colour formed. The mixture was stirred for 3 h and a solution of 3,5-dibromobenzaldehyde (1f) $(6 \cdot 00 \text{ g}, 22 \cdot 7 \text{ mmol})$ in tetrahydrofuran (15 ml) was then added. After heating of the mixture under reflux for 12 h the solvents were removed under vacuum and the residue was extracted with dichloromethane. The combined organic fractions were washed with brine, dried (MgSO₄) and concentrated to yield a red oily residue which was extracted (Soxhlet) with hexanes. The resultant yellow oil was purified by flash chromatography on silica gel (hexanes) to give a mixture (95:5)of (E)- and (Z)-1-(3,5-dibromophenyl)oct-1-ene (1m) (7.43 g, 95%) as a pale yellow oil, Kugelrohr $115{-}125^{\circ}{\rm C}/0{\cdot}7~{\rm mmHg}$ (Found: C, $48 \cdot 8$; H, $5 \cdot 3$. $C_{14}H_{18}Br_2$ requires C, $48 \cdot 6$; H, 5·2%. Found: $M^{+\bullet}$, 343·9776. $C_{14}H_{18}^{79}Br_2$ requires $M^{+\bullet}$, 343·9734. Found: $M^{+\bullet}$, 345·9753. $C_{14}H_{18}^{79}Br_{18}^{81}Br$ requires $M^{+\bullet}$, 345 9755. Found: $M^{+\bullet}$, 347 9733. $C_{14}H_{18}^{-8}$ Br Br requires $M^{+\bullet}$, 347 9734). ν_{max} 3012, 2956, 2925, 2855, 1650, 1581, 1544, 1465, 1412, 1386 cm⁻¹. m/z 344/346/348 (M⁺, 12/28/12%), 260/262/264 (M - CH₂=CHC₄H₉, 50/100/50), $194/196 (M - Br - C_5H_{11}, 25/24), 182/184 (14/13), 128 (20),$ 115 (194/196 - Br, 82), 102 (18), 55 (12), 43 (32). E Isomer: $\delta_{\rm H}$ 0.89, br t, J 6.8 Hz, 3H, (CH₂)₅CH₃; 1.27–1.39, m, 6H, $(CH_2)_2(CH_2)_3CH_3$; 1·41–1·52, m, 2H, $CH_2CH_2C_4H_9$; 2·23, td, J 7·1, 5·5 Hz, 2H, CH=CHCH₂C₅H₁₁; 6·22-6·33, m, 2H, $CH = CHC_6H_{13}$; 7.39, d, J 1.7 Hz, 2H, H 2 and H 6; 7.46, t, J $1 \cdot 7 \text{ Hz}, 1 \text{H}, \text{H} 4. \ \delta_{\text{C}} 14 \cdot 08, (\text{CH}_2)_5 \mathbf{C} \text{H}_3; 22 \cdot 59, (\text{CH}_2)_4 \mathbf{C} \text{H}_2 \text{C} \text{H}_3;$ $28 \cdot 85$, $(CH_2)_2 CH_2 C_3 H_7$; $29 \cdot 04$, $(CH_2)_3 CH_2 C_2 H_5$; $31 \cdot 38$, $CH_2\textbf{C}H_2C_4H_9; \ 32\cdot95, \ \textbf{C}H_2C_5H_{11}; \ 122\cdot98, \ 2C, \ C\ 3 \ and \ C\ 5;$ 127.16, CH=CHC₆H₁₃; 127.61, 2C, C 2 and C 6; 131.87, C 4; $134 \cdot 62$, CH=**C**HC₆H₁₃; 141 $\cdot 60$, C1.

(E)- and (Z)-3-Bromo-5-(oct-1-enyl)benzaldehyde (5h)

A solution of a mixture (95:5) of (E)- and (Z)-1-(3,5-dibromophenyl)oct-1-ene (1m) $(4\cdot56 \text{ g}, 13\cdot2 \text{ mmol})$ in diethyl ether (100 ml) at -78°C was treated dropwise with butyllithium $(5\cdot80 \text{ ml}, 14\cdot5 \text{ mmol})$. After $1\cdot5$ h dimethylformamide $(3\cdot21 \text{ ml}, 39\cdot5 \text{ mmol})$ was injected into the reaction mixture which was then stirred for a further $1\cdot5$ h at -78°C . Quenching with HCl $(20 \text{ ml}, 2 \text{ mol} \text{ l}^{-1})$ followed by workup in the usual manner afforded a brown oil which was purified by flash chromatography on silica gel (hexanes/diethyl ether) to

give in order of increasing polarity: (i) a mixture (90:10) of (E)- and (Z)-1-(3-bromophenyl)oct-1-ene (5g) (0.18 g, 5%) as a clear oil, Kugelrohr 140–155°C/0.05 mmHg (Found: $M^{+\bullet}$, 266 0668. $C_{14}H_{19}^{79}Br$ requires $M^{+\bullet}$, 266 0670. Found: $M^{+\bullet}$, 268 0650. $C_{14}H_{19}^{81}Br$ requires $M^{+\bullet}$, 268 0650). ν_{max} 2956, 2926, 2854, 1592, 1561, 1469, 1422, 1384 cm⁻¹. m/z $266/268 (M^+, 25/24\%), 195/197 (M - C_5H_{11}, 14/13), 182/184$ $(M - CH_2 = CHC_4H_9, 80/79), 169 (10), 129 (14), 116 (100),$ 115 (51), 103 (10), 91 (12), 77 (10), 55 (25), 43 (28). EIsomer: $\delta_{\rm H}$ 0.92, t, J 6.9 Hz, 3H, (CH₂)₅CH₃; 1.25–1.38, m, 6H, (CH₂)₂(CH₂)₃CH₃; 1·44-1·50, m, 2H, CH₂CH₂C₄H₉; $2 \cdot 20$, qd, J $6 \cdot 8$ Hz, 2H, CH₂C₅H₁₁; $6 \cdot 18 - 6 \cdot 35$, m, 2H, $CH = CHC_6H_{13}$; 7.14, t, J 7.8 Hz, 1H, H5; 7.24, dt, J 7.9, 1.1 Hz, 1H, H6; 7.30, ddd, J7.9, 1.9, 1.2 Hz, 1H, H4; 7.48, t, J $1 \cdot 7 \text{ Hz}, 1\text{H}, \text{H} 2. \ \delta_{\text{C}} 14 \cdot 07, (\text{CH}_2)_5 \mathbf{C} \text{H}_3; 22 \cdot 60, (\text{CH}_2)_4 \mathbf{C} \text{H}_2 \text{C} \text{H}_3;$ $28\cdot 88, \ (\mathrm{CH}_2)_2 \textbf{C} \mathrm{H}_2 \mathrm{C}_4 \mathrm{H}_9; \ 29\cdot 17, \ (\mathrm{CH}_2)_3 \textbf{C} \mathrm{H}_2 \mathrm{C}_2 \mathrm{H}_5; \ 31\cdot 71,$ $CH_2CH_2C_4H_9$; 32.98, $CH_2C_5H_{11}$; 122.68, C3; 124.53, C6; $128 \cdot 34$, **C**H=CHC₆H₁₃; $128 \cdot 73$, C 2; $129 \cdot 53$, C 5; $129 \cdot 88$, C 4; $132 \cdot 86$, CH=**C**HC₆H₁₃; 140 · 11, C 1; and (ii) a mixture (95:5) of (E)- and (Z)-3-bromo-5-(oct-1-enyl)benzaldehyde (5h) $(3 \cdot 46 \text{ g},$ 89%) as a clear oil, Kugelrohr $110-120^{\circ}C/0.05$ mmHg (Found: C, $60 \cdot 8$; H, $6 \cdot 5$; Br, $27 \cdot 3$. C₁₅H₁₉BrO requires: C, $61 \cdot 0$; H, $6 \cdot 5$; Br, 27·1%. Found: $M^{+\bullet}$, 294·0612. $C_{15}H_{19}^{79}BrO$ requires $M^{+\bullet}$, 294·0619. Found: $M^{+\bullet}$, 296·0598. $C_{15}H_{19}^{81}BrO$ requires $\begin{array}{l} \mathrm{M}^{+\bullet}, \ 296\cdot0599). \ \nu_{\mathrm{max}} \ 2926, \ 2855, \ 2721, \ 1704 \ \mathrm{(C=O)}, \ 1591, \\ 1564, \ 1450, \ 1378 \ \mathrm{cm^{-1}}. \ \delta_{\mathrm{H}} \ 0.92, \ \mathrm{t}, \ J \ 6.9 \ \mathrm{Hz}, \ 3\mathrm{H}, \ \mathrm{(CH_2)_5CH_3}; \end{array}$ $1\cdot 25 - 1\cdot 39, \ m, \ 6H, \ (CH_2)_2 (CH_2)_3 CH_3; \ 1\cdot 44 - 1\cdot 53, \ m, \ 2H,$ $CH_2CH_2C_4H_9$; 2.26, tq, J 7.7, 1.5 Hz, 2H, $CH_2C_5H_{11}$; 6.37- $6 \cdot 48$, m, 2H, C**H**=C**H**C₆H₁₃; 7 \cdot 73, br t, J 1 \cdot 7 Hz, 1H, H4; $7 \cdot 76$ and $7 \cdot 83$, br t, $J \ 1 \cdot 7$ Hz, 1H each, H2 and H6; $9 \cdot 96$, s, 1H, CH=O. δ_C 14.05, (CH₂)₅CH₃; 22.54, (CH₂)₄CH₂CH₃; $28 \cdot 85, \ (CH_2)_2 \textbf{C} H_2 C_3 H_7; \ 28 \cdot 99, \ (CH_2)_3 \textbf{C} H_2 C_2 H_5; \ 31 \cdot 65,$ $CH_2CH_2C_4H_9$; 32.97, $CH_2C_5H_{11}$; 123.40, C3; 125.60, C6; $127 \cdot 20$, **C**H=CHC₆H₁₃; $130 \cdot 25$, C 2; $134 \cdot 24$, C 4; $134 \cdot 96$, $CH = CHC_6H_{13}$; 138.01, C1; 140.93, C5; 190.78, CH=O. m/z 296/294 (M⁺, 20/19%), 210/212 (M - CH₂=CHC₄H₉, 100/98), 197(10), 145 (8), 128 (18), 116 (95), 102 (10), 89 (8), 77 (10), 63 (10), 55 (21), 43 (40), 41 (32).

Use of a mixture (36:64) of (E)- and (Z)-1-(3,5-dibromophenyl)oct-1-ene (1m) $(3 \cdot 56 \text{ g}, 10 \cdot 3 \text{ mmol})$ gave in order of increasing polarity: (i) a mixture (35:65) of (E)- and (Z)-1-(3-bromophenyl)oct-1-ene (5g) $(0\cdot 10 \text{ g}, 4\%)$ as a clear $C_{14}H_{19}^{79}Br$ requires $M^{+\bullet}$. oil (Found: $M^{+\bullet}$, 266.0668. 266.0670. Found: $M^{+\bullet}$, 268.0650. $C_{14}H_{19}^{81}Br$ requires $M^{+\bullet}$, 268.0650). $\nu_{\rm max}$ 2956, 2926, 2855, 1592, 1556 cm⁻¹. m/z $266/268 (M^+, 21/20\%), 195/197 (M - C_5H_{11}, 10/10), 182/184$ $(M - CH = CHC_4H_9, 10/10), 169 (10), 129 (11), 116 (100), 115$ (52), 103 (10), 91 (12), 77 (12), 55 (23), 43 (30). Z Isomer: $\delta_{\rm H} = 0.88$, t, J 7.1 Hz, 3H, (CH₂)₅CH₃; 1.25–1.38, m, 6H, $(CH_2)_2(CH_2)_3CH_3$; 1.44–1.50, m, 2H, $CH_2CH_2C_4H_9$; 2.28, qd, J 7.4, 1.8 Hz, 2H, CH₂C₅H₁₁; 5.71, dt, J 11.7, 7.3 Hz, 1H, $CH = CHC_6H_{13}$; 6.18–6.35, m, 1H, $CH = CHC_6H_{13}$; 7.17– 7.22, m, 2H, H4 and H5; 7.32-7.37, m, 1H, H6; 7.41, br s, 1H, H2. $\delta_{\rm C}$ 14.06, (CH₂)₅**C**H₃; 22.62, (CH₂)₄**C**H₂CH₃; $28\cdot 55, \ (CH_2)_2 \textbf{C} H_2 C_3 H_7; \ 28\cdot 96, \ (CH_2)_3 \textbf{C} H_2 C_2 H_5; \ 29\cdot 79,$ $\mathrm{CH}_{2}\textbf{C}\mathrm{H}_{2}\mathrm{C}_{4}\mathrm{H}_{9}; \ 31 \cdot 70, \ \textbf{C}\mathrm{H}_{2}\mathrm{C}_{5}\mathrm{H}_{11}; \ 122 \cdot 22, \ \mathrm{C}\ 3; \ 127 \cdot 29, \ \mathrm{C}\ 6;$ $127 \cdot 35$, **C**H=CHC₆H₁₃; $129 \cdot 35$, C 2; $129 \cdot 92$, C 5; $131 \cdot 56$, C 4; $134 \cdot 67$, CH=**C**HC₆H₁₃; 139 \cdot 90, C1; and (ii) a mixture (36:64) of (E)- and (Z)-3-bromo-5-(oct-1-enyl)benzaldehyde (5h) $(2 \cdot 72 \text{ g},$ 90%) as a clear oil, Kugelrohr $110-120^{\circ}C/(0.05 \text{ mmHg})$ (Found: C, 60.8; H, 6.5; Br, 27.3. C₁₅H₁₉BrO requires C, 61.0; H, 6.5; Br, 27.1%. Found: $M^{+\bullet}$, 294.0612. $C_{15}H_{19}^{79}BrO$ requires , 294.0619. Found: $M^{+\bullet}$, 296.0598. $C_{15}H_{19}^{81}BrO$ M^+ requires M^+•, 296 0599). $\nu_{\rm max}$ 2926, 2855, 2721, 1704 (C=O), 1591, 1564, 1450, 1378 cm⁻¹. m/z 296/294 (M⁺, 20/19%), 210/212 (M - CH₂=CHC₄H₉, 100/98), 197 (10), 145 (8), 128 (18), 116 (95), 102 (10), 89 (8), 77 (10), 63 (10), 55 (21), 43 (40),41 (32). Z Isomer: $\delta_{\rm H}$ 0.91, t, J 7.1 Hz, 3H, (CH₂)₅CH₃; $1\cdot 26-1\cdot 39,\ m,\ 6H,\ (CH_2)_2(CH_2)_3CH_3;\ 1\cdot 43-1\cdot 54,\ m,\ 2H,$ $CH_2CH_2C_4H_9$; 2.32, qd, J 7.3, 1.8 Hz, 2H, $CH_2C_5H_{11}$;

5.84, dt, J 11.6, 7.4 Hz, 1H, CH=CHC₆H₁₃; 6.34–6.50, m, 1H, CH=CHC₆H₁₃; 7.66, br t, J 1.7 Hz, 1H, H4; 7.70 and 7.88, br t, J 1.7 Hz, 1H each, H2 and H6; 9.97, s, 1H, CH=O. $\delta_{\rm C}$ 14.01, (CH₂)₅CH₃; 22.54, (CH₂)₄CH₂CH₃; 28.49, (CH₂)₂CH₂C₃H₇; 28.85, (CH₂)₃CH₂C₂H₅; 29.59, CH₂CH₂C₄H₉; 31.60, CH₂C₅H₁₁; 123.01, C3; 126.14, C6; 128.58, CH=CHC₆H₁₃; 130.04, C2; 136.29, C4; 137.08, CH=CHC₆H₁₃; 137.73, C1; 140.63, C5; 190.72, CH=O.

1-Bromo-3,5-bis(oct-1-enyl)benzene (5k)

A solution of heptyltriphenylphosphonium iodide (10.7 g, $22 \cdot 0 \text{ mmol}$) in tetrahydrofuran (50 ml) was treated dropwise with butyllithium (8.80 ml, 22.0 mmol) at 0°C. After 15 min the reaction mixture was allowed to warm to room temperature during which time a dark red colour formed. The mixture was stirred for 3 h and was then treated with a solution of a mixture (85:15) of (E)- and (Z)-3-bromo-5-(oct-1-enyl)benzaldehyde (5h) (2.95 g, 10.0 mmol) in tetrahydrofuran (10 ml). After heating under reflux for 12 h the solvents were removed under vacuum and the residue was extracted with dichloromethane. The combined organic fractions were washed with brine, dried $(MgSO_4)$ and concentrated to yield a red oily residue which was extracted (Soxhlet) with hexanes. The resultant yellow oil was purified further by flash chromatography on silica gel (hexanes) to give a mixture of three isomers of 1-bromo-3,5-bis(oct-1-enyl)benzene (5k) (3.61 g, 96%) as a pale yellow oil, Kugelrohr 140–150°C/0.04 mmHg (Found: C, 70.0; H, 8.9. $C_{22}H_{33}Br$ requires C, 70.0; H, 8.9%. Found: $M^{+\bullet}$ 376 · 1766. $C_{22}H_{33}^{79}Br$ requires $M^{+\bullet}$, 376 · 1766. Found: $M^{+\bullet}$, 378 · 1746. $C_{22}H_{33}^{81}Br$ requires $M^{+\bullet}$, 378 · 1745). m/z $376/378 \ (M^+,\ 88/90\%),\ 319/321 \ (M-C_4H_9,\ 8/7),\ 292/294$ $(M - CH_2 = CHC_4H_9, 14/13), 280/282 (14/14), 240 (5), 226$ (50), 210 (30), 155 (100), 142 (57), 129 (57), 115 (37), 111(18), 97 (10), 69 (48), 55 (50), 43 (62). $\nu_{\rm max}$ 3010, 2956, 2926, 2855, 1591, 1557, 1466, 1378 cm⁻¹.

3,5-Bis(oct-1-enyl)benzaldehyde (6f)

A solution of a mixture of three stereoisomers of 1-bromo-3,5bis(oct-1-enyl)benzene (5k) (1.65 g, 4.38 mmol) in tetrahydrofuran (20 ml) at -78° C was treated dropwise with butyllithium (1.93 ml, 4.81 mmol), forming a deep red-brown solution. After 1.5 h dimethylformamide (1.15 ml, 1.31 mmol) was injected into the reaction mixture which was then stirred for a further 1.5 h at -78° C. Quenching with HCl (5 ml, 2 mol l⁻¹) followed by workup and flash chromatography on silica gel (hexanes/diethyl ether) gave in order of increasing polarity: (i) a mixture of stereoisomers of 1,3-bis(oct-1-enyl)benzene (6e) (72 mg, 5%) as a clear oil, Kugelrohr $140-150^{\circ}C/0.05 \text{ mmHg}$ (Found: $M^{+\bullet}$, 298.2663. $C_{22}H_{34}$ requires $M^{+\bullet}$, 298.2661). $\nu_{\rm max}$ 2927, 2857, 2855, 1457, 1384, 909 cm⁻¹. m/z 298 (M⁺ 74%), 283 $(M - CH_3, 4)$, 255 $(M - C_3H_7, 4)$, 241 $(M - C_4H_9, 4)$ 9), 227 $(M - C_5H_{11}, 20)$, 214 $(M - CH_2 = CHC_4H_9, 18)$, 202 (11), 155 (10), 143 (32), 129 (100), 117 (30), 111 (20), 105 (10),91 (18), 69 (45), 55 (40), 43 (52); (ii) a mixture of stereoisomers of 3,5-bis(oct-1-enyl)benzaldehyde (6f) $(1 \cdot 30 \text{ g}, 92\%)$ as a clear oil, Kugelrohr 165–175°C/0·1 mmHg (Found: C, 84·6; H, $10 \cdot 4$. C₂₃H₃₄O requires C, 84 \cdot 6; H, 10 \cdot 5\%. Found: M^{+•} 326 · 2610. C₂₃H₃₄O requires M^{+•}, 326 · 2610). $\nu_{\rm max}$ 3010, 2926, 2855, 2719, 1703 (C=O), 1593, 1462, 1379 cm⁻¹. m/z $326 (M^+, 100\%), 287 (10), 269 (5), 255 (M - C_5H_{11}, 10), 242$ $(M - CH_2 = CHC_4H_9, 18), 230$ (10), 158 (40), 143 (30), 129 (78), 117 (18), 91 (12), 69 (22), 55 (28), 43 (40); and (iii) a clear oil (50 mg) consisting of several components of which only the mixture of stereoisomers of 3,5-bis(oct-1-enyl)benzoic acid (6g) could be identified (Found: $M^{+\bullet}$, $342 \cdot 2553$. $C_{23}H_{34}O_2$ requires M^{+•}, 342 · 2559). $\nu_{\rm max}$ 3440 (OH), 2926, 2855, 1699 (C=O), 1598, 1456, 1384, 1143 cm⁻¹. m/z 342 (M⁺, 28%), $313 (M - C_2H_5, 10), 295 (313 - H_2O, 5), 257 (20), 245 (42),$

230 (27), 215 (20), 174 (10), 160 (100), 145 (15), 129 (27), 117 (32), 95 (20), 69 (20), 55 (32), 43 (42).

1-[3,5-Bis(oct-1-enyl)phenyl]-2-(4-ethylphenyl)ethene (12)

A suspension of 4-ethylbenzyltriphenylphosphonium iodide $(3 \cdot 89 \text{ g}, 7 \cdot 66 \text{ mmol})$ in tetrahydrofuran (70 ml) was treated dropwise with butyllithium (3.06 ml, 7.66 mmol) at 0° C. After 5 min the deep red mixture was allowed to warm to room temperature and was treated with a solution of a mixture of stereoisomers of 3,5-bis(oct-1-enyl)benzaldehyde (6f) $(1 \cdot 10 \text{ g})$ 3.48 mmol) in tetrahydrofuran (10 ml). The reaction mixture was heated under reflux for 2 h after which time it was concentrated under vacuum and extracted with dichloromethane. The combined organic fractions were washed with brine, dried (MgSO₄) and concentrated to yield a red oily residue which was extracted (Soxhlet) with hexanes. The resultant yellow oil was purified by flash chromatography on silica gel (hexanes) to give a mixture of isomers of the *ethene* (12) $(1 \cdot 31 \text{ g}, 88\%)$ as a pale yellow oil. A portion $(0 \cdot 10 \text{ g})$ was purified further by p.l.c. on silica gel to give the title compound (mixture of isomers) (89 mg, 89%) as a clear oil, Kugelrohr $200-225^{\circ}\text{C}/0.8 \text{ mmHg}$ (Found: C, $89 \cdot 6$; H, $10 \cdot 2$. C₃₂H₄₄ requires C, $89 \cdot 7$; H, $10 \cdot 4\%$. Found: $M^{+\bullet}$, 428.3439. $C_{32}H_{44}$ requires $M^{+\bullet}$, 428.3443). m/z 428 (M $^+,\,100\%),\,413$ (M - CH_3, 2), 386 (2), 371 (3), 357 (2), 259 (7), 119 (20), 91 (8), 55 (7), 43 (15). $\nu_{\rm max}$ 3007, 2958, 2926, 2854, 1585, 1511, 1458, 1385 cm⁻

Reduction of 3,5-Bis(oct-1-enyl)benzaldehyde (6f) with $Pd-C/H_2$

A solution of the aldehyde (6f) (0.11 g, 0.34 mmol) in ethanol (10 ml) was stirred with palladium on carbon (10%), 18 mg, $16 \cdot 9 \,\mu$ mol) under a hydrogen atmosphere for 45 min. The reaction mixture was then filtered through Celite and concentrated under vacuum to give a clear oil which was purified by flash chromatography on silica gel (hexanes/diethyl ether) to give in order of increasing polarity: (i) 1-methyl-3,5-dioctylbenzene (7g) as a clear oil (8 mg, 7%), Kugelrohr 150–155°C/0·1 mmHg (Found: C, 87·2; H, 12·9. $C_{23}H_{40}$ requires C, 87·3; H, 12·7%. Found: $M^{+\bullet}$, 316·3123. $C_{23}H_{40}$ requires $M^{+\bullet}$, 316·3130). ν_{max} 3012, 2926, 2855, 1604, 1459, 1384 cm⁻¹. $\delta_{\rm H}$ 0·88, t, J 7·0 Hz, 6H, 3-(CH₂)₇CH₃ and $5-(CH_2)_7CH_3$; $1\cdot 20-1\cdot 38$, m, 20H, $3-(CH_2)_2(CH_2)_5CH_3$ and $5-(CH_2)_2(CH_2)_5CH_3$; $1\cdot 54-1\cdot 63$, m, 4H, $3-CH_2CH_2C_6H_{13}$ and 5-CH₂CH₂C₆H₁₃; $2 \cdot 29$, s, 3H, 1-CH₃; $2 \cdot 53$, br t, J $7 \cdot 6$ Hz, 4H, 3-CH₂C₇H₁₅ and 5-CH₂C₇H₁₅; 6.79, br s, 1H, H4; 6.81, br s, 2H, H2 and H6. $\delta_{\rm C}$ 14·10, 2C, 3-(CH₂)₇**C**H₃ and 5-(CH₂)₇CH₃; 21.33, 1-CH₃; 22.68, 2C, 3-(CH₂)₆CH₂CH₃ and 5-(CH₂)₆CH₂CH₃; 29.28, 2C, 3-(CH₂)₄CH₂C₃H₇ and $5-(CH_2)_4$ **C** $H_2C_3H_7$; 29.49, 4C, $3-(CH_2)_2$ **C** $H_2C_4H_9$ and $5-(CH_2)_2$ CH₂CH₂C₄H₉; $31 \cdot 62$, 2C, $3-CH_2$ CH₂C₆H₁₃ and 5- $CH_2CH_2C_6H_{13}$; 31.91, 2C, 3- $(CH_2)_5CH_2C_2H_5$ and 5- $(CH_2)_5$ CH₂C₂H₅; 35.92, 2C, 3-CH₂C₇H₁₅ and 5-CH₂C₇H₁₅; 125.59, C4; 126.47, 2C, C2 and C6; 137.52, C1; 142.80, 2C, C3 and C5. m/z 316 (M⁺, 52%), 301 (M – CH₃, 3), $273 \ (M-C_{3}H_{7}, \ 8), \ 259 \ (M-C_{4}H_{9}, \ 10), \ 245 \ (M-C_{5}H_{11},$ 4), 231 $(M - C_6H_{13}, 9)$, 218 $(M - CH_2 = CHC_5H_{11}, 100)$, 203 $(218 - CH_3, 10), 175 (218 - C_3H_7, 2), 161 (218 - C_4H_9, 8), 147$ $(218 - C_5H_{11}, 8), 133 (218 - C_6H_{13}, 10), 119 (218 - C_7H_{15}, 10), 110 (218 - C_7H_{15}, 10), 10 (218 - C_7H_{1$ 96), 105 (218 – C₈H₁₇, 50), 91 (18), 71 (C₅H₁₁⁺, 10), 57 (C₄H₉⁺, 18), 43 (C₃H₇⁺, 30); (ii) *3,5-dioctylbenzaldehyde* (7i) as a clear oil (26 mg, 23%), Kugelrohr $160-165^{\circ}C/0.05$ mmHg (Found: C, $83 \cdot 3$; H, $11 \cdot 6$. $C_{23}H_{38}O$ requires C, $83 \cdot 6$; H, 11.6%. Found: $M^{+\bullet}$, 330.2914. $C_{23}H_{38}O$ requires $M^{+\bullet}$, 330·2923). $\nu_{\rm max}$ 2926, 2855, 2717, 1703 (C=O), 1602, 1461, 1385 cm^{-1}. $\delta_{\rm H}$ 0·88, t
,J7·0 Hz, 6H, 3-(CH2)7CH3 and $5-(CH_2)_7CH_3$; $1\cdot 21-1\cdot 39$, m, 20H, $3-(CH_2)_2(CH_2)_5CH_3$ and $5-(CH_2)_2(CH_2)_5CH_3$; $1\cdot 58-1\cdot 69$, m, 4H, $3-CH_2CH_2C_6H_{13}$ and 5-CH₂CH₂C₆H₁₃; 2.65, br t, J 7.5 Hz, 4H, 3-CH₂C₇H₁₅ and 5-CH₂C₇H₁₅; 7.26, br d, J 1.6 Hz, 1H, H4; 7.51, br d, J

1.5 Hz, 2H, H 2 and H 6; 9.97, s, 1H, 1-C(O)H. δ_C 14.06, 2C, 3-(CH₂)₇CH₃ and 5-(CH₂)₇CH₃; 22.63, 2C, 3-(CH₂)₆CH₂CH₃ and 5-(CH₂)₆CH₂CH₃; 29.22, 2C, 3-(CH₂)₄CH₂C₃H₇ and $5-(CH_2)_4$ **C** $H_2C_3H_7$; 29.40, 4C, $3-(CH_2)_2(CH_2)_2C_4H_9$ and $5-(CH_2)_2(CH_2)_2C_4H_9$; $31\cdot 29$, 2C, $3-CH_2C_4H_2C_6H_{13}$ and 5-CH₂CH₂C₆H₁₃; 31.84, 2C, 3-(CH₂)₅CH₂C₂H₅ and 5-(CH₂)₅-CH₂C₂H₅; 35.59, 2C, 3-CH₂C₇H₁₅ and 5-CH₂C₇H₁₅; 127.13, 2C, C2 and C6; 135.01, C4; 136.61, C1; 143.81, 2C, C3 and C 5; $192 \cdot 88$, C(O)H. m/z 330 (M⁺, 79%), 232 (100), 220 (10), 217 (22), 204 (12), 133 (28), 117 (12), 105 (78), 91 (32), 79 (10), 71 ($C_5H_{11}^+$, 14), 57 ($C_4H_9^+$, 37), 43 ($C_3H_7^+$, 52); and (iii) 3,5dioctylbenzenemethanol (7h) a clear oil (80 mg, 70%), Kugelrohr $165-170^{\circ}C/0.1 \text{ mmHg}$ (Found: C, 83.2; H, 12.4. $C_{23}H_{40}O$ requires C, 83 · 1; H, 12 · 1%. Found: $M^{+\bullet}$, 332 · 3075. $C_{23}H_{40}O$ requires M^{+•}, 332·3079). $\nu_{\rm max}$ 3333 (OH), 2926, 2854, 1604, 1456, 1384 cm⁻¹. $\delta_{\rm H}$ 0.88, t, J 7.1 Hz, 6H, 3-(CH₂)₇CH₃ and $5-(CH_2)_7CH_3$; $1\cdot 21-1\cdot 37$, m, 20H, $3-(CH_2)_2(CH_2)_5CH_3$ and $5-(CH_2)_2(CH_2)_5CH_3$; $1\cdot 58-1\cdot 65$, m, 4H, $3-CH_2CH_2C_6H_{13}$ and 5-CH₂CH₂C₆H₁₃; 1.77, s, 1H, 1-CH₂OH; 2.58, br t, J 8.0 Hz, 4H, $3-CH_2C_7H_{15}$ and $5-CH_2C_7H_{15}$; 4.65, br s, 2H, $1-CH_2OH$; 6.93, br s, 1H, H4; 7.00, br s, 2H, H2 and H6. $\delta_{\rm C}$ 14.09, 2C, $3-(CH_2)_7$ CH₃ and $5-(CH_2)_7$ CH₃; $22 \cdot 66$, 2C, $3-(CH_2)_6$ CH₂CH₃ and $5-(CH_2)_6CH_2CH_3$; 29.26, 2C, $3-(CH_2)_4CH_2C_3H_7$ and $5-(CH_2)_4CH_2C_3H_7$; 29.43, 4C, $3-(CH_2)_2(CH_2)_2C_4H_9$ and $5-(CH_2)_2(CH_2)_2C_4H_9$; 31.55, 2C, $3-CH_2CH_2C_6H_{13}$ and 5- $CH_2CH_2C_6H_{13}$; 31.89, 2C, 3-(CH₂)₅ $CH_2C_2H_5$ and (CH₂)₅- $CH_2C_2H_5$; 35.92, 2C, 3- $CH_2C_7H_{15}$ and 5- $CH_2C_7H_{15}$; 65.55, 1-CH₂OH; 124.38, 2C, C 2 and C 6; 127.95, C 4; 140.68, C 1; 143.24, 2C, C 3 and C 5. m/z 332 (M^+ , 80%), 314 (M - H₂O, 4), 301 (M-CH₂OH, 9), 275 (M-C₄H₉, 10), 259 (8), 234 (65), 219 (15), 204 (31), 189 (10), 173 (5), 159 (11), 135 (35),105 (100), 91 (30), 79 (10), 71 ($C_5H_{11}^+$, 18), 57 ($C_4H_9^+$, 30), $43 (C_3H_7^+, 48).$

Oxidation of 3,5-Dioctylbenzenemethanol (7h)

A solution of the alcohol (7h) (0.11 g, 0.33 mmol)in dichloromethane (10 ml) was treated with pyridinium chlorochromate (0.11 g, 0.50 mmol) at room temperature under a nitrogen atmosphere. After 3 h the reaction mixture was filtered through Celite and purified by flash chromatography on silica gel (hexanes/diethyl ether) to give 3,5-dioctylbenzaldehyde (7i) as a clear oil (0.11 g, 89%).

General Procedure for the Synthesis of 1-(3,5-Dialkylphenyl)-2-(4-alkylphenyl)ethene

A suspension of the 4-alkylbenzyltriphenylphosphonium iodide (10 mmol) in tetrahydrofuran (70 ml) was treated with butyllithium (10 mmol) at 0°C. After 5 min the deep orange-red reaction mixture was allowed to warm to room temperature and a solution of 3,5-dialkylbenzaldehyde (5 mmol) in tetrahydrofuran (10 ml) was added. The mixture was stirred at room temperature for 14 h after which time the solvents were removed under vacuum and the residue was extracted with dichloromethane. Workup as above (Soxhlet; hexanes) and flash chromatography on silica gel (hexanes) gave a clear oil which consisted of a mixture of the E and Z isomers of a 1-(3,5-dialkylphenyl)-2-(4-alkylphenyl)ethene (85-90%), and the E and Z isomers of a 1,2-bis(4-alkylphenyl)ethene. This mixture was separated into its components by repetitive p.l.c. on silica gel to give analytically pure samples. Two sets of representative spectroscopic data are listed below.

(Z)-1-(3,5-Dihexylphenyl)-2-(4-octylphenyl)ethene (15h) and Its E Isomer (14h)

The Z isomer (15h) was a clear *oil* (Found: $M^{+\bullet}$, 460 · 4086. C₃₄H₅₂ requires $M^{+\bullet}$, 460 · 4069). ν_{max} 2956, 2927, 2855, 1595, 1463, 1384 cm⁻¹. $\delta_{\rm H}$ 0 · 88, t, J 7 · 0 Hz, 6H, 3'-(CH₂)₅CH₃ and 5'-(CH₂)₅CH₃; 0 · 89, t, J 6 · 9 Hz, 3H, 4''-(CH₂)₇CH₃; 1 · 22–1 · 35, m, 22H, 3'-(CH₂)₂(CH₂)₃CH₃, 5'-(CH₂)₂(CH₂)₃CH₃ and

4''-(CH₂)₂(CH₂)₅CH₃; 1·46–1·53, m, 4H, 3'-CH₂CH₂C₄H₉ and 5'-CH₂CH₂C₄H₉; 1.56-1.61, m, 2H, 4"-CH₂CH₂C₆H₁₃; $2 \cdot 46$, br t, J $7 \cdot 9$ Hz, 4H, 3'-CH₂C₅H₁₁ and 5'-CH₂C₅H₁₁; 2.55, br t
, J $7.9\,\mathrm{Hz},\,2\mathrm{H},\,4^{\prime\prime}\text{-}\mathrm{C}\mathbf{H}_{2}\mathrm{C}_{7}\mathrm{H}_{15};\,6.51,\,\mathrm{br}$ s, 2H, H12.55, bit t, $J' = 12, 211, 4 = 0.12 \times 113, 0.01, 0.0$ $(CH_2)_5$ CH₃ and 4''-(CH₂)₇CH₃; 22.61, 2C, 3'-(CH₂)₄CH₂CH₃ and $5' - (CH_2)_4 CH_2 CH_3$; $22 \cdot 67$, $4'' - (CH_2)_6 CH_2 CH_3$; $28 \cdot 99$, 2C, 3'-(CH₂)₂CH₂C₃H₇ and 5'-(CH₂)₂CH₂C₃H₇; 29.28, 4"- $(CH_2)_4$ CH₂C₃H₇; 29·35, 4''-(CH₂)₃CH₂C₄H₇; 29·49, 4''- $(CH_2)_2 CH_2 C_5 H_{11};$ 31.38, 2C, 3'-CH₂ $CH_2 C_4 H_9$ and 5'- $CH_2CH_2C_4H_9; 31.44, 4''-CH_2CH_2C_6H_{13}; 31.76, 2C, 3' ({\rm CH}_2)_3 {\bm C} {\rm H}_2 {\rm C}_2 {\rm H}_5 ~{\rm and}~ 5' {\rm -} ({\rm CH}_2)_3 {\bm C} {\rm H}_2 {\rm C}_2 {\rm H}_5;~ 31 {\rm \cdot} 90,~ 4'' {\rm -} ({\rm CH}_2)_5 {\rm \cdot} {\bm C} {\rm H}_2 {\rm C}_2 {\rm H}_5;~ 35 {\rm \cdot} 72,~ 2{\rm C},~ 3' {\rm \cdot} {\bm C} {\rm H}_2 {\rm C}_5 {\rm H}_{11} ~{\rm and}~ 5' {\rm \cdot} {\bm C} {\rm H}_2 {\rm C}_5 {\rm H}_{11};~ 35 {\rm \cdot} 84,$ 4''-**C**H₂C₇H₁₅; 126.21, 2C, C 2' and C 6'; 127.45, C 4'; 128.09, 2C, C 2" and C 6"; 128.78, C 3" and C 5"; 129.71, C 2; 130.00, C1; 134·74, C1''; 137·17, C1'; 141·80, C4''; 142·60, 2C, C3' and C5'. m/z 460 (M⁺, 100%), 416 (M - C₃H₈, 2), 390 $(M - CH_2 = CHC_3H_7, 10), 361 (M - C_7H_{15}, 4), 319 (4), 277$ $(8), 207 (9), 179 (4), 129 (4), 105 (8), 57 (C_4H_9^+, 9), 43$ $(C_3H_7^+, 18).$

The *E* isomer (14h) was a clear *oil* (Found: $M^{+\bullet}$, 460 · 4083. $C_{34}H_{52}$ requires $M^{+\bullet}$, 460 · 4069). ν_{max} 3019, 2956, 2926, 2854, 1596, 1512, 1465, 1378 cm⁻¹. $\delta_{\rm H}$ 0.88(5), t, J 7.0 Hz, 6H, 3'-(CH₂)₅CH₃ and 5'-(CH₂)₅CH₃; 0.88(9), t, J 6.9 Hz, 3H, 4''-(CH₂)₇CH₃; 1.20-1.37, m, 22H, $3' - (CH_2)_2 (CH_2)_3 CH_3$, $5' - (CH_2)_2 (CH_2)_3 CH_3$ and 4'' - $(CH_2)_2(CH_2)_5CH_3$; 1.56–1.68, m, 6H, 3'-CH₂CH₂C₄H₉, 5'- $CH_2CH_2C_4H_9$ and 4"- $CH_2CH_2C_6H_{13}$; 2.59, t, J 7.6 Hz, 4H, $3'-CH_2C_5H_{11}$ and $5'-CH_2C_5H_{11}$; 2.60, t, J 7.4 Hz, 2H, 4''-CH₂C₇H₁₅; 6·84, d, J 1·2 Hz, H4'; 7·02 and 7·08, d, J 16·3 Hz, 1H each, H1 and H2; 7·14, d, J $1 \cdot 2$ Hz, 2H, H 2' and H 6'; $7 \cdot 16$, d, J $8 \cdot 1$ Hz, 2H, H 3'' and H 5''; 7.42, br d, J 8.0 Hz, 2H, H 2'' and H 6''. $\delta_{\rm C}$ $14 \cdot 10, 3C, 3' - (CH_2)_5 CH_3, 5' - (CH_2)_5 CH_3 and 4'' - (CH_2)_7 CH_3;$ 22.61, 2C, 3'-(CH₂)₄CH₂CH₃ and 5'-(CH₂)₄CH₂CH₃; 22.67, 4''-(CH₂)₆**C**H₂CH₃; 28.99, 2C, 3'-(CH₂)₂**C**H₂C₃H₇ and 5'- $(CH_2)_2$ **C** $H_2C_3H_7$; 29·10, 4''-(CH_2)_4**C** $H_2C_3H_7$; 29·27, 4''- $(CH_2)_3$ **C** $H_2C_4H_9$; 29·35, 4''- $(CH_2)_3$ **C** $H_2C_4H_9$; 29·49, 4''- $(CH_2)_2$ CH₂C₅H₁₁; 31.38, 2C, 3'-CH₂CH₂C₄H₉ and 5'- $CH_2CH_2C_4H_9$; 31.53, 4"- $CH_2CH_2C_6H_{13}$; 31.75, 2C, 3'- $(CH_2)_3$ **C** $H_2C_2H_5$ and 5'- $(CH_2)_3$ **C** $H_2C_2H_5$; 31.90, 4''- $(CH_2)_5$ - $CH_2C_2H_5$; 35.72, 4"- $CH_2C_7H_{15}$; 35.99, 2C, 3'- $CH_2C_5H_{11}$ and 5'-**C**H₂C₅H₁₁; 123.92, 2C, C 2' and C 6'; 126.33, 2C, C 2'' and C6''; 127.96, C4'; 128.08, C1; 128.18, C2; 128.70, 2C, C3''and C5"; 135.02, C1"; 137.33, C1'; 142.39, C4"; 143.15, 2C, C3' and C5'. m/z 460 (M⁺, 100%), 432 (M - CH₂=CH₂, 2), 390 $(M - CH_2 = CHC_3H_7, 10)$, 361 $(M - C_7H_{15}, 4)$, 319 (4), 207 (11), 129 (4), 105 (8), 57 ($C_4H_9^+$, 9), 43 ($C_3H_7^+$, 12).

(Z)-1,2-Bis(4-octylphenyl)ethene (17d) and Its E Isomer (16d)

The Z isomer (17d) was a clear *oil* (Found: $M^{+\bullet}$, 404 · 3445. C₃₀H₄₄ requires M^{+•}, 404·3443). $\nu_{\rm max}$ 2956, 2926, 2854, 1596, 1512, 1464, 1384 cm⁻¹. $\delta_{\rm H}$ 0.87, t, J 6.5 Hz, 6H, $4'\text{-}(\mathrm{CH}_2)_7\mathrm{C}\textbf{H}_3 \ \text{and} \ 4''\text{-}(\mathrm{CH}_2)_7\mathrm{C}\textbf{H}_3; \ 1\cdot22\text{-}1\cdot35, \ m, \ 20\mathrm{H}, \ 4'\text{-}$ $(CH_2)_2(CH_2)_5CH_3$ and $4''-(CH_2)_2(CH_2)_5CH_3$; 1.55–1.62, m, 4H, 4'-CH₂CH₂C₆H₁₃ and 4''-CH₂CH₂C₆H₁₃; $2 \cdot 55$, br t, J 7.9 Hz, 4H, 4'-CH₂C₇H₁₅ and 4''-CH₂C₇H₁₅; 6.51, br s, 2H, H 1 and H 2; 7.03, br d, J 8.0 Hz, 4H, H 3', H 5', H 3'' and H5''; 7.18, dt, J 8.2, 1.8 Hz, 4H, H2', H6', H2''and H 6". $\delta_{\rm C}$ 14.10, 2C, 4'-(CH₂)₇CH₃ and 4"-(CH₂)₇CH₃; 22.68, 2C, 4'-(CH₂)₆CH₂CH₃ and 4"-(CH₂)₆CH₂CH₃; 29.28, 2C, $4' - (CH_2)_4 CH_2 C_3 H_7$ and $4'' - (CH_2)_4 CH_2 C_3 H_7$; 29.34, 2C, $4' - (CH_2)_3 CH_2 C_4 H_9$ and $4'' - (CH_2)_3 CH_2 C_4 H_9$; 29.49, 2C, 4'-(CH₂)₂**C**H₂C₅H₁₁ and 4''-(CH₂)₂**C**H₂C₅H₁₁; 31·36, 2C, $4'-CH_2\textbf{C}H_2C_6H_{13} \ \, \text{and} \ \ 4''-CH_2\textbf{C}H_2C_6H_{13}; \ \ 31\cdot 91, \ \ 2C, \ \ 4' (CH_2)_5$ **C** $H_2C_2H_5$ and 4''- $(CH_2)_5$ **C** $H_2C_2H_5$; 35.73, 2C, 4'- $CH_2C_7H_{15}$ and 4"- $CH_2C_7H_{15}$; 128.18, 4C, C2', C6', C2"

and C6''; 128.72, 4C, C3', C5', C3'' and C5''; 129.53, 2C, C1 and C2; 134.75, 2C, C1' and C1''; 141.78, 2C, C4' and C4. m/z 404 (M⁺, 100%), 361 (M – C₃H₇, 2), 318 (3), 305 (M – C₇H₁₅, 20), 291 (M – C₈H₁₇, 2), 207 (22), 192 (5), 179 (4), 129 (5), 105 (8), 57 (C₄H₉⁺, 9), 43 (C₃H₇⁺, 10).

The *E* isomer (16d) was an oily wax (Found: $M^{+\bullet}$, 404.3443. $C_{30}H_{44}$ requires $M^{+\bullet}$, 404.3443). ν_{max} 2954, 2918, 2848, 1463, 1384 cm⁻¹. $\delta_{\rm H}$ 0.88, t, J 7.1 Hz, 6H, 4'-(CH₂)₇CH₃ and 4''-(CH₂)₇CH₃; 1·27-1·31, m, 20H, 4'- $(CH_2)_2(CH_2)_5CH_3$ and 4''- $(CH_2)_2(CH_2)_5CH_3$; 1.57–1.64, m, 4H, 4'-CH₂CH₂(CH₂)₅CH₃ and 4''-CH₂CH₂C₆H₁₃; $2 \cdot 59$, br t, J 7.6 Hz, 4H, 4'-CH₂C₇H₁₅ and 4''-CH₂C₇H₁₅; 7.04, br s, 2H, H1 and H2; $7 \cdot 15$, br d, J $8 \cdot 2$ Hz, 4H, H3', H5' H3" and H5"; 7.41, br d, J 8.2 Hz, 4H, H2', H6', H2" and H6". $\delta_{\rm C}$ 14.09, 2C, 4'-(CH₂)₇CH₃ and 4"-(CH₂)₇CH₃; 22.66, 2C, 4'-(CH₂)₆CH₂CH₃ and 4''-(CH₂)₆CH₂CH₃; 29.26, 2C, 4'-(CH₂)₄CH₂C₃H₇ and 4''-(CH₂)₄CH₂C₃H₇; 29.32, 2C, 4'-(CH₂)₃**C**H₂C₄H₉ and 4''-(CH₂)₃**C**H₂C₄H₉; 29.48, 2C, 4'-(CH₂)₂**C**H₂C₅H₁₁ and 4''-(CH₂)₂**C**H₂C₅H₁₁; 31.44, 2C, 4'-CH₂CH₂C₆H₁₃ and 4''-CH₂CH₂C₆H₁₃; 31.88, 2C, 4'- $(CH_2)_5$ **C** $H_2C_2H_5$ and 4''- $(CH_2)_5$ **C** $H_2C_2H_5$; 35.72, 2C, 4'- $CH_2C_7H_{15}$ and 4"- $CH_2C_7H_{15}$; 126.29, 4C, C2', C6', C2" and C6''; 127.70, 2C, C1 and C2; 128.70, 4C, C3', C5' C3" and C5"; 134.97, 2C, C1' and C1"; 142.39, 2C, C4 and C 4". m/z 404 (M⁺, 100%), 376 (M - C₂H₄, 2), 348 $(M - CH_2 = CHC_2H_5, 3), 305 (M - C_7H_{15}, 18), 291 (M - C_8H_{17}, 30), 200 (M - C_8H_{17}, 30), 200 (M - C_8H_{17}, 30))$ 2), 207 (18), 192 (5), 179 (4).

The *E* and *Z* isomers of the 1,2-bis(4-alkylphenyl)ethene were shown to have formed by condensation of a 4-alkylbenzyltriphenylphosphonium iodide in the presence of butyllithium. Typically, treatment of the 4-alkylbenzyltriphenylphosphonium iodide (10 mmol) with butyllithium (10 mmol) in tetrahydrofuran (30 ml) at room temperature for 14 h afforded a mixture (3:2) of the *E* and *Z* isomers of the 1,2-bis(4-alkylphenyl)ethene (20–70%).

Reduction of 1-[3,5-Bis(oct-1-enyl)phenyl]-2-(4ethylphenyl)ethene (12)

A solution of the ethene (12) (0.57 g, 1.33 mmol) in ethanol/hexanes (1:1, 90 ml) was stirred with palladium on carbon (10%, 71 mg, $66 \cdot 6 \mu mol$) under a hydrogen atmosphere for $3 \cdot 5$ h. The mixture was then filtered through Celite and the solvents were removed under vacuum to give 1-(3,5-dioctylphenyl)-2-(4-ethylphenyl)ethane (13) as a clear oil (0.57 g, 98%), Kugelrohr $210-215^{\circ}\text{C}/0.1 \text{ mmHg}$ (Found: $\nu_{\rm max}$ 3011, 2926, 2854, 1602, 1514, 1456, 1378, 1061 and 709 cm⁻¹. $\delta_{\rm H}$ 0.88, br t, J 6.5 Hz, 6H, 3'-(CH₂)₇CH₃ and 5'-(CH₂)₇CH₃; 1.23, t, J 7.7 Hz, 3H, 4"-CH₂CH₃; 1.23- $1 \cdot 38$, m, 20H, 3'-(CH₂)₂(CH₂)₅CH₃ and 5'-(CH₂)₂(CH₂)₅CH₃; $1 \cdot 56 - 1 \cdot 63$, m, 4H, 3'-CH₂CH₂C₆H₁₃ and 5'-CH₂CH₂C₆H₁₃; $2 \cdot 54$, br t, J $7 \cdot 9$ Hz, 4H, 3'-CH₂C₇H₁₅ and 5'-CH₂C₇H₁₅; $2 \cdot 62$, t, J $7 \cdot 6$ Hz, 2H, 4"-CH₂CH₃; $2 \cdot 81 - 2 \cdot 92$, m, 4H, $({\rm H\,1})_2$ and $({\rm H\,2})_2;~6\cdot82,~{\rm br}$ s, 3H, and $7\cdot11,~{\rm br}$ s, 4H, ${\rm H\,2''},~{\rm H\,3''},~{\rm H\,5''},~{\rm H\,6''},~{\rm H\,2'},~{\rm H\,4'}$ and H $6'.~\delta_{\rm C}$ 14 $\cdot11,~2{\rm C},~3' (CH_2)_7$ CH₃ and 5'- $(CH_2)_7$ CH₃; 15.56, 4''-CH₂CH₃; 22.69, 2C, 3'-(CH₂)₆CH₂CH₃ and 5'-(CH₂)₆CH₂CH₃; 28.46, 4"-CH₂CH₃; 29.31, 2C, 3'-(CH₂)₄CH₂C₃H₇ and 5'-(CH₂)₄CH₂C₃H₇; 29.48, 2C, 3'-(CH₂)₃CH₂C₄H₉ and 5'-(CH₂)₃CH₂C₄H₉; 29.51, 2C 3'-(CH₂)₂CH₂C₅H₁₁ and 5'-(CH₂)₂CH₂C₅H₁₁; 31.63, 2C, $3'-CH_2CH_2C_6H_{13}$ and $5'-CH_2CH_2C_6H_{13}$; 31.93, 2C, $3'-CH_2CH_2C_6H_{13}$; 31.93, 3C, $3'-CH_2CH_2C_6H_{13}$; 3C, $3'-CH_2CH_2C_6H_2C_6H_{13}$; 3C, $3'-CH_2CH_2C_6H_$ $(CH_2)_5$ **C** $H_2C_2H_5$ and 5'-(CH_2)_5**C** $H_2C_2H_5$; 35.99, 2C, 3'- $CH_2C_7H_{15}$ and 5'- $CH_2C_7H_{15}$; 37.70 and 38.14, C1 and C2; $125 \cdot 84$, 2C, C2' and C6'; $126 \cdot 14$, C4'; $127 \cdot 73$, 2C, C2'' and C6''; 128.35, 2C, C3'' and C5''; 139.26, C1''; 141.61, C4''; 141.67, C1'; 142.77, 2C, C3' and C5'. m/z 434 (M⁺, 24%),

392 (M – CH₂=CHCH₃, 10), 350 (M – CH₂=CHC₄H₉, 2), 336 (M – CH₂=CHC₅H₁₁, 8), 315 (14), 302 (2), 237 (2), 217 (22), 203 (8), 145 (3), 133 (12), 118 (100), 105 (10), 91 (9), 69 (8), 43 (C₃H₇⁺, 10).

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Supplementary Data

Experimental text including spectroscopic characterization data for the compounds [RPPh₃I (R = CH₃, C₃H₇, C₄H₉, C₅H₁₁, C₇H₁₅), (1g–o), (2a,b), (3a,b), (4b), (5a,b,d,f–j), (6b–d), (7a,c–f), (8b), (9a,b,d), (10a,b,d), (11a,b,d), (14a–g,i,j), (15a–g,i,j), (16a–c) and (17a–c)] referred to in this paper. Copies are available, until 31 December 2002, from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.

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