Reactions proceeding via the reactive intermediate α-vinyl-*p*-xylylene. Contrasting orientations in the formation of cyclic dimers and polymer

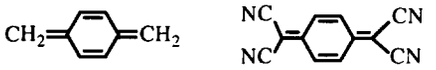
Gerald M. Brooke* and Martin F. Woolley
Chemistry Department, Science Laboratories, University of Durham, South Road, Durham DH1 3LE, UK
(Received 1 December 1991; revised 6 May 1992)

α-Vinyl-*p*-xylylene (**16**) has been shown to be an intermediate in the base-catalysed decomposition of both *p*-allylbenzyltrimethylammonium bromide (**17**) and *p*-methylcinnamyltrimethylammonium bromide (**19**). Cyclic dimers (**28**) and (**29**) (*EE* and *ZZ* isomers, respectively) are produced via the conjugatively extended vinyl head h′ to head h′ and tail to tail bond-forming reactions, which accompany a copolymer formed mainly via the contrasting head (vinyl-substituted head h *and* h′) to tail linking of α-vinyl-*p*-xylylene.

(Keywords: α-vinyl-*p*-xylylene; substituted 1,4-quinodimethane; orientation of dimerization and polymerization)

INTRODUCTION

p-Xylylene (**1**)[1] and its 7,7,8,8-tetracyano derivative [**2**, usually called tetracyanoquinodimethane (TCNQ)] represent extremes in the stability of 1,4-quinodimethane molecules.

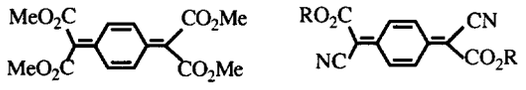


1 **2**

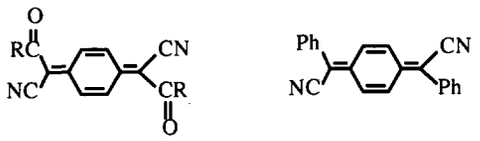
The former are highly reactive monomers, which rapidly form cyclic dimers (**3**), cyclic trimers (**4**) and linear polymers (**5**)[2], while the latter is a stable, easily handled compound which has not been polymerized by any type of initiation[3].

3, $n = 2$
4, $n = 3$ **5**

Between these two extremes, a variety of stable electrophilic 7,7,8,8-substituted quinodimethanes, **6**[3], **7**[4], **8**[5] and **9**[6], have been synthesized, the main interest in them being their spontaneous polymerizations with electron-rich alkenes to give strictly alternating copolymers via a chain growth mechanism.



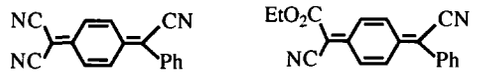
6 **7**



8 **9**

Some homopolymerization reactions, however, were readily induced (but only with compounds **7** and **8**) to give substituted poly(*p*-xylylene)s.

In 1990, the first unsymmetrically substituted 1,4-quinodimethanes, **10**[7] and **11**[8], were isolated.



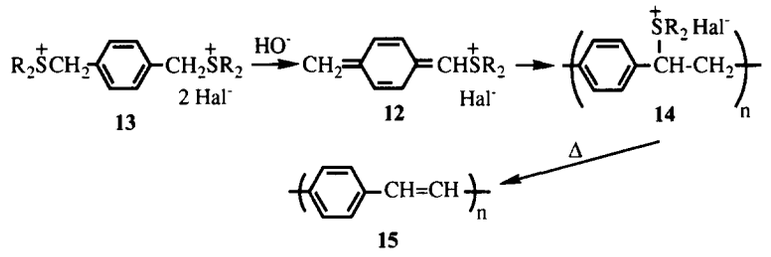
10 **11**

Homopolymerization of **10** with butyllithium gave a material recorded as having $M_n = 640$ (a value which lies between a dimer and trimer), while compound **11** with both butyllithium and potassium cyanide was reported to give homopolymer in 100% yield. However, no structural information was given for these homopolymers. High molecular weight alternating copolymers were obtained spontaneously at 60°C in chloroform between both **10** and **11** with a variety of alkenes. Two structures are possible for each alternating copolymer if the assumption is made that only head to tail linkages are formed; the one obtained from **10** and *p*-methylstyrene was determined by ^{13}C n.m.r. studies in conjunction with model compounds.

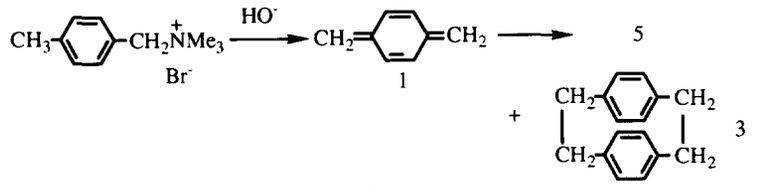
One of the most reactive unsymmetrical quinodimethane monomers studied is **12**[9,10] obtained via a base-induced elimination reaction from the salt **13**. It undergoes spontaneous polymerization to form the water soluble pre-polymer **14** which on heating gives poly(*p*-phenylenevinylene) (**15**, see *Scheme 1*). The tacit

*To whom correspondence should be addressed

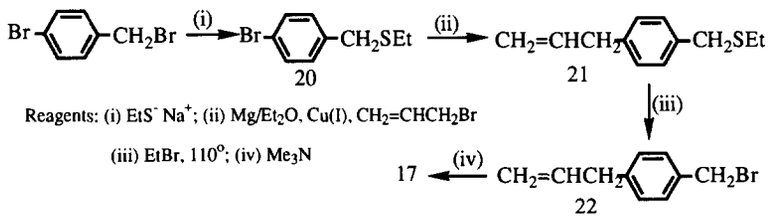
0032-3861/93/061282-07



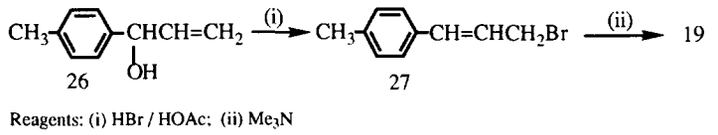
Scheme 1



Scheme 2

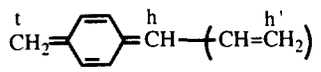


Scheme 3



Scheme 4

assumption in *Scheme 1* is that the polymerization process occurs 100% via head to tail reactions and the anionic mechanism recently proposed by Lahti *et al.* provides a rationale for this assumption[11]. In this paper we report the preparation and reactions of a new unsymmetrical *p*-xylylene compound (**16**).

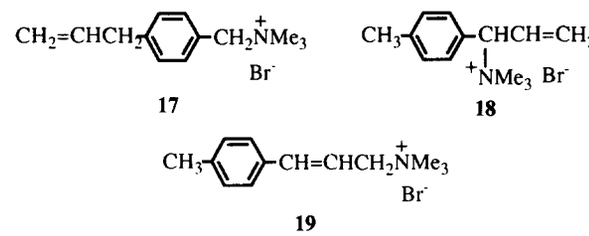


16

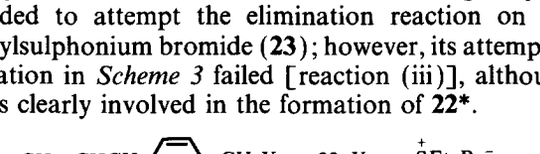
The special interest in this molecule lies in whether its polymerization involves, exclusively, reactions through h (with the vinyl group simply as a substituent), or whether reaction through h′, the conjugatively extended system, also occurs. The fundamental question of whether the polymerization of **16** involves only head to tail linking (h–t and/or h′–t) is also addressed.

SYNTHESES OF PRECURSOR MONOMERS

Winberg *et al.* developed a convenient route to *p*-xylylene, as shown in *Scheme 2*[12], and we envisaged that a similar base-induced elimination reaction with three monomer precursor trimethylammonium compounds, **17**, **18** and **19**, would provide alternative routes to the vinyl-extended *p*-xylylene (**16**).



The synthesis of **17** is shown in *Scheme 3*. Originally we intended to attempt the elimination reaction on the diethylsulphonium bromide (**23**); however, its attempted formation in *Scheme 3* failed [reaction (iii)], although it was clearly involved in the formation of **22***.

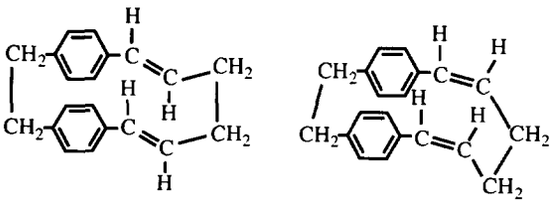


*Treatment of **22** with tetrahydrothiophen did give *p*-allylbenzyltetrahydrothiophenium bromide (**24**), but reaction with sodium hydroxide gave *p*-allylbenzyl alcohol (**25**) as the only identifiable product

not available for study. However, treatment of **27** with trimethylamine readily gave **19**.

POLYMERIZATION REACTIONS

Two methods were used to form the vinyl-substituted *p*-xylylene monomer **16** by effecting elimination reactions on the trimethylammonium compounds **17** and **19**. In the first method[12], treatment of both salts with hot aqueous sodium hydroxide gave polymeric material insoluble in organic solvents, accompanied by small amounts (~5%) of the cyclic dimer of **16**, namely **28**.



28

29

In the second polymerization method[14], the trimethylammonium salts **17** and **19** were first converted into the hydroxides using aqueous silver (I) oxide, and during the azeotropic distillation of the water from the mixtures using toluene, polymerization occurred. Small amounts of phenothiazine have been used previously in this method to reduce polymerization and enhance dimerization of the intermediate *p*-xylylene derivatives; in our hands its presence had little effect on the course of the reactions. Using this method with the *p*-allyl compound (**17**) and added phenothiazine, polymer (30%) again insoluble in organic solvents was obtained. The remaining material was a mixture of the *EE* isomer (**28**) and the *ZZ* isomer (**29**) in the ratio of 95:5, from which compound **28** was isolated in 67% yield. In the absence of phenothiazine, polymer insoluble in organic solvents amounted to 40%, the remaining material (60%) being entirely compound **28**.

Pre-formation of the hydroxide salt from the cinnamyl derivative **19** and the azeotropic removal of water using toluene gave the *only* sample of polymer which was soluble in organic solvents. It was separated from other organic components as a solid (22%) by Soxhlet extraction with light petroleum, and purified by dissolution in tetrahydrofuran and reprecipitation in methanol. From the Soxhlet extracts were isolated the cyclic dimer **28** (25%) and the isomer **29** (0.25%).

RESULTS AND DISCUSSION

The isolation of compounds **28** and **29** from reactions involving both *p*-allylbenzyl- and *p*-methylcinnamyltrimethylammonium compounds (**17** and **19**, respectively) is clear evidence for the formation of the common intermediate α-vinyl-*p*-xylylene (**16**). The structure of these isomers rests primarily on the simplicity of their ^{1}H n.m.r. when comparing the absorptions of the protons in the alkene region with those found in related compounds, which showed clearly the presence of cinnamyl-type absorptions (as found in **19** and **27**) rather than allyl-type absorptions (as found in **17**, **21** and **22**). The presence of singlets in the region of 2.98 ppm for both **28** and **29** is also clear evidence of a plane of symmetry in the molecules and that head to head (and tail to tail) cyclic dimerization of **16** through t and the conjugatively extended vinyl group h′, had occurred. The stereochemistry about the double bonds in **28** is clearly *EE* ($J_{CH=CH}$ = 16.0 Hz), while in **29** is the *ZZ* isomer ($J_{CH=CH}$ = 11.2 Hz).

The cyclization of unsymmetrically substituted all-hydrocarbon *p*-xylylenes is a very rare reaction and the efficiency and particularly the modes of cyclization via the conjugatively extended head to head and tail to tail bond-forming reactions reported in this paper are of great significance as they suggested that concurrent polymerization of **16** might not necessarily be via a straightforward head to tail type reaction. Due to the complexity of the reaction product, however, the possibility of a double head h′ to tail cyclic dimerization of **16** having occurred to a small extent cannot be excluded.

The ^{1}H n.m.r. spectrum of the soluble polymer prepared from **19** as described above is shown in *Figure 1* and the COSY spectrum is given in *Figure 2*.

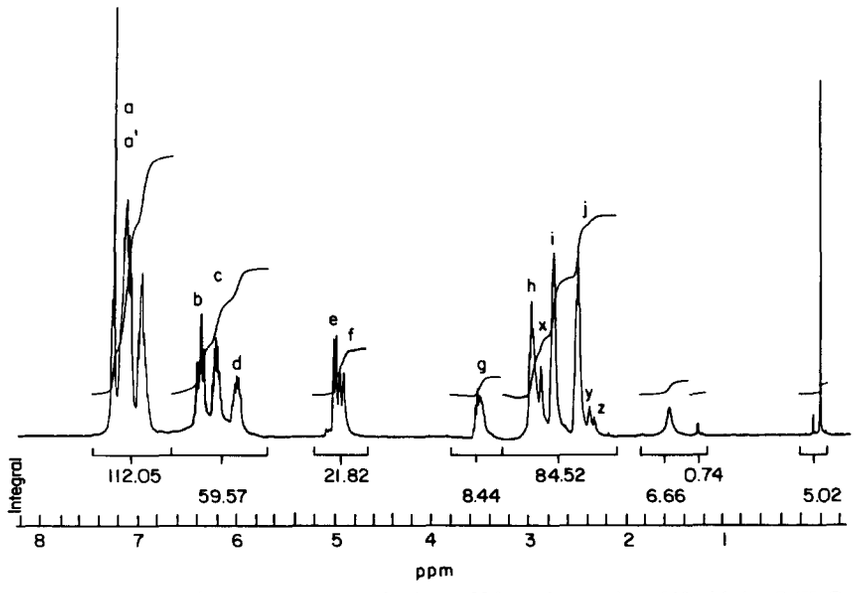


Figure 1 400 MHz ^{1}H n.m.r. spectrum of polymer **32** from the reaction of **19** with Ag_2O/H_2O

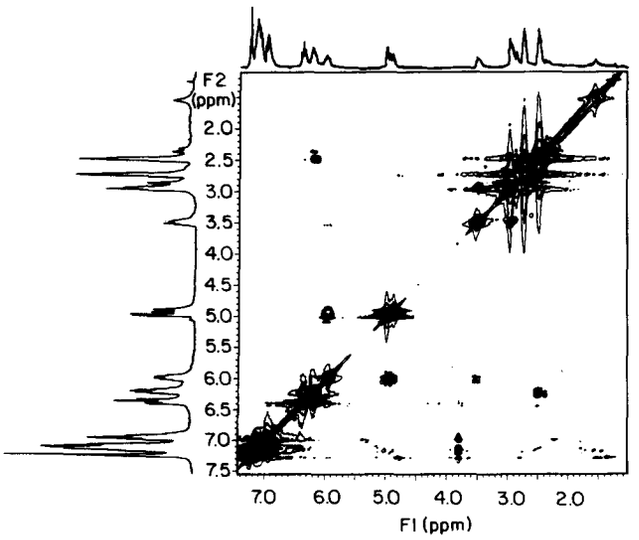
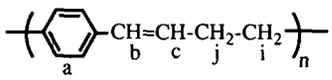


Figure 2 COSY spectrum of polymer **32** from the reaction of **19** with Ag_2O/H_2O

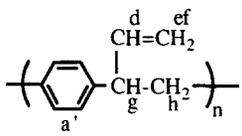
Absorptions b and c are due to the protons of a cinnamyl group; the protons represented by absorption c also couple to the protons represented by j, which in turn is coupled only with the protons represented by i.



30

Consequently, the structural feature **30** is present in the polymer, which shows clearly that some polymerization has occurred through the conjugatively extended head h′ in **16** with the tail t in another molecule of **16**.

The remaining absorptions d, e, f, g and h are also of interest. The COSY spectrum permits the unambiguous assignment of the protons at d, e and f to the three protons in a pendant vinyl group attached to an allylic carbon bearing the hydrogen represented by g.



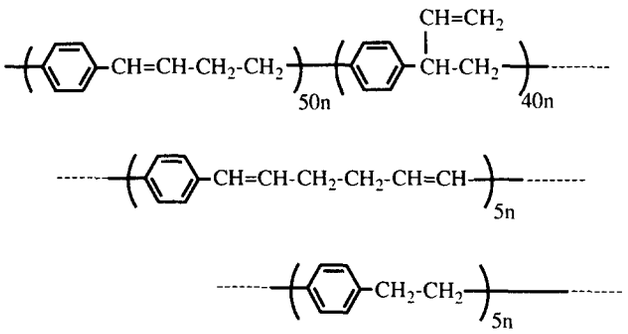
31

Protons at g and h are clearly on adjacent carbon atoms, so that another structural feature (**31**) is present in the polymer, the result of bond formation between the vinyl-substituted head h in **16** with the tail t in another molecule of **16**. The integrations of all the absorptions are in good agreement with the structural assignments; moreover the units **30** and **31** are present in the ratio 1.25:1.

The overwhelming evidence, therefore, is that the bulk of the polymer structure resulted from both the coupling of the vinyl-substituted head h to the tail t *and* the conjugatively extended head h′ to the tail t. This contrasts markedly with the mode of cyclic dimerization of **16** (h′ to h′ and t to t) which gives a significant yield (25%) of compound **28** formed concurrently with the polymer and prompted us to look more closely at the ^{1}H n.m.r. of the polymer to assess whether there were any other absorptions which might suggest *some* degree of head h′ to head h′ coupling and/or tail to tail coupling (both of these modes of coupling could occur independently). There are three extra peaks of reasonable significance to be accounted for: x, y and z, and if the chemical shifts of the protons in compounds **28** and **29** are used as models, then x (2.85 ppm) is due to the protons H in the $-C_6H_4-CH_2-CH_2-C_6H_4-$ unit (2.92 ppm in **28** and 2.87 ppm in **29**). The absorption y (2.35 ppm) is due to the protons H in the $-CH{=}CH-CH_2CH_2-CH{=}CH-$ unit in the double *EE* configuration (cf. the analogous protons at 2.42 ppm in **28**) as is shown in the high intensity COSY spectrum (*Figure 2*; protons represented by y couple with protons obscured by c). The aryl and alkene protons associated with these extra absorptions are also obscured by the resonances under a, and b and c, respectively. The absorption at z (2.32 ppm) is unaccounted for, but is clearly less significant than x and y.

All the polymers described in this paper had significantly low carbon analyses, particularly the solvent-insoluble materials. While this analysis was not as low for the soluble material discussed fully here, this state of affairs is not unusual in polymer chemistry where the proportion of carbon in hydrocarbon polymers is very high[15].

The distinction between the product of the polymerization being a copolymer or a mixture of homopolymers was resolved by the use of d.s.c., which showed only *one* glass transition temperature, characteristic of a random copolymer. Assuming that the only significant head to head coupling which occurs in the copolymer is h′ to h′ (as is found in compounds **28** and **29**; i.e. there is no h′ to h *or* h to h coupling), and taking into account the number of protons which each absorption in the ^{1}H n.m.r. represents, the proportions of the four different structural units present in copolymer **32** are as follows:



32

It has been shown that the cyclic dimer of *p*-xylylene (**3**) is converted into high molecular weight linear poly(*p*-xylylene) (**5**) by vacuum pyrolysis in the vapour phase at 600°C[16], and it was of interest to investigate the same reaction with compound **28**. It was argued that if the molecule reverted to monomer **16** again, then a polymer similar to the one prepared before in the liquid phase would be produced, whereas if polymerization occurred via a diradical formed by rupture of just one of the two $-CH_2-CH_2-$ bonds in **28** then extensive head to head (h′ – h′)/tail to tail (t – t) units would be found in the product. When the experiment was carried out at 580°C, compound **28** was merely isomerized to compound **29**, and essentially the same reaction occurred at 700°C.

EXPERIMENTAL

N.m.r. spectra were recorded on a Brucker AMX 500 (^{1}H, 500.1385 MHz) and on a Varian 400 MHz (^{1}H, 399.952 MHz). Mass spectra were recorded on a VG 7070E mass spectrometer.

p-Allylbenzyltrimethylammonium bromide (***17***)

Preparation of p-*bromobenzyl ethyl sulphide* (***20***). Ethanolic sodium ethoxide, prepared by dissolving sodium (4.02 g, 0.17 mol) in dry ethanol (100 ml) was cooled to 0°C and treated over 15 min with ethanethiol (13 g, 0.20 mol). *p*-Bromobenzyl bromide (42.4 g, 0.17 mol) in hot ethanol (50 ml) was added with stirring over 30 min and the mixture heated under reflux for 1 h. The cooled mixture was acidified (2 M H_2SO_4), extracted with diethyl ether and the extracts dried ($MgSO_4$). Evaporation of the solvent gave the crude product (42.48 g) which was distilled to give *p*-bromobenzyl ethyl sulphide (**20**, 34.3 g, 88%); b.p. 92–95°C (0.08 mmHg). Found: C 46.97, H 4.53%; $C_9H_{11}BrS$ requires C 46.76, H 4.80%. δ_H ($CDCl_3$) 0.50 (t, $CH_2\underline{CH_3}$), 1.63 (q, $\underline{CH_2}CH_3$), 2.92 (s, Ar$\underline{CH_2}$S), 6.46 and 6.70 ppm (AB, $-C_6\underline{H_4}-$).

Preparation of p-*allylbenzyl ethyl sulphide* (***21***). Magnesium (25 g, 1.04 mol) in dry tetrahydrofuran (200 ml), activated using ethylene dibromide (0.5 ml), was treated under nitrogen with *p*-bromobenzyl ethyl sulphide (**20**, 94 g, 0.407 mol) in dry tetrahydrofuran (60 ml) over 1 h and the mixture heated under reflux for a further 1 h. The ethereal Grignard solution was then separated from unreacted magnesium by means of a steel canular. Copper(I) iodide (0.16 g, 0.84 mol) was added to the Grignard reagent followed by allyl bromide (40 ml, 0.462 mol) over 40 min with stirring, with a very exothermic reaction taking place. The brown reaction mixture was heated under reflux for 18 h. After cooling, the mixture was poured onto water, acidified (2 M H_2SO_4) and extracted with diethyl ether. The ether extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to give crude product which was distilled under reduced pressure to give *p*-allylbenzyl ethyl sulphide (**21**, 40.6 g, 52%); b.p. 118–120°C (1.5 mmHg). Found: C 75.31, H 8.40%; $C_{12}H_{16}BrS$ requires C 74.94, H 8.39%. δ_H ($CDCl_3$) 1.26 (t, $CH_2\underline{CH_3}$), 2.48 (q, $\underline{CH_2}CH_3$), 3.40 (d, $\underline{CH_2}CH{=}CH_2$), 3.72 (s, $C_6H_4\underline{CH_2}S$), 5.12 (m, CH=C$\underline{H_2}$), 5.97 (m, $\underline{CH}{=}CH_2$), 7.16 and 7.28 ppm (AB, $C_6\underline{H_4}$).

Preparation of p-*allylbenzyl bromide* (***22***). *p*-Allylbenzyl ethyl sulphide (**21**, 4.5 g, 23.4 mmol) and bromoethane (15 ml, 0.2 mol) were heated in a sealed tube at 150°C for 50 h. The crude product (4.0 g, 81%) was distilled through a Fischer-Spahltrohr column to afford *p*-allylbenzyl bromide (**22**, 1.83 g, 37%); b.p. 108–112°C (2.0 mmHg). Found: C 56.60, H 5.23%, M^+ 210/212; $C_{10}H_{11}Br$ requires C 56.90, H 5.25%, M^+ 210/212. δ_H ($CDCl_3$), 3.34 (d, $\underline{CH_2}CH{=}CH_2$), 4.42 (s, CH_2Br), 5.08 (m, CH=C$\underline{H_2}$), 5.90 (m, $\underline{CH}{=}CH_2$), 7.15 and 7.28 ppm (AB, $-C_6\underline{H_4}-$).

Preparation of p-*allylbenzyltetrahydrothiophenium bromide* (***24***). *p*-Allylbenzyl bromide (**22**, 0.52 g, 2.46 mmol) and tetrahydrothiophene (0.32 ml, 3.69 mmol) were mixed under nitrogen and within 30 min a white solid had formed. The hygroscopic solid was washed under nitrogen with light petroleum (b.p. 40–60°C) and dried *in vacuo* for 5 h to afford *p*-allylbenzyltetrahydrothiophenium bromide (**24**, 0.5 g, 68%). Found: C 55.94, H 6.67%; $C_{14}H_{19}BrS$ requires C 56.19, H 6.40%. δ_H ($CDCl_3$) 2.08 (m, $\underline{CH_2}CH_2S-$), 3.10 (d, $\underline{CH_2}CH{=}CH_2$), 3.25 (t, $CH_2\underline{CH_2}\underline{S}-$), 4.37 (s, $C_6H_4\underline{CH_2}\underline{S}$), 4.85 (m, CH=C$\underline{H_2}$), 5.69 (m, $\underline{CH}{=}CH_2$), 7.02 and 7.29 ppm (AB, $-C_6\underline{H_4}-$).

Preparation of p-*allylbenzyl alcohol* (***25***). *p*-Allylbenzyl bromide (**22**, 0.34 g, 1.59 mol) was treated with sodium hydroxide solution (10 ml, 1 M, 10 mmol) and heated under reflux for 3 h. After pouring onto water (25 ml) and acidifying (2 M H_2SO_4), the mixture was extracted with diethyl ether, the extracts dried ($MgSO_4$) and concentrated by rotary evaporation to give crude product (0.24 g), which was purified by chromatography on silica using diethyl ether in light petroleum (b.p. 40–60°C, 30 v/v%) as elutant to leave *p*-allylbenzyl alcohol (**25**, a liquid). Found: C 80.84, H 7.84%; $C_{10}H_{12}O$ requires C 81.04, H 8.16%. δ_H ($CDCl_3$) 2.09 (s, OH), 3.29 (d, $\underline{CH_2}CH{=}CH_2$), 4.52 (s, $-C_6H_4\underline{CH_2}O$), 5.01 (m, $\underline{CH}{=}CH_2$), 5.86 (m, $\underline{CH}{=}CH_2$), 7.08 and 7.18 ppm (AB, $-C_6\underline{H_4}-$); ν_{max}(neat) 3540–3120 cm^{-1} (broad, –OH).

Reaction of p-*allylbenzyltetrahydrothiophenium bromide* (***24***) *with sodium hydroxide*. *p*-Allylbenzyltetrahydrothiophenium bromide (**24**, 0.61 g, 2 mmol) in water (5 ml) was treated with sodium hydroxide solution (1 M, 5 ml) and the solution stirred and heated under reflux for 3.5 h. The mixture was poured onto water, acidified (2 M H_2SO_4) and extracted with dichloromethane. The organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave a viscous yellow oil (0.188 g). Column chromatography on silica using diethyl ether in light petroleum (b.p. 40–60°C, 30 v/v%) as elutant gave *p*-allylbenzyl alcohol (**25**, 0.0263 g, 9%) identified by i.r. comparison with an authentic sample.

Reaction of p-*allylbenzyl bromide* (***22***) *with trimethylamine*. *p*-Allylbenzyl bromide (**22**, 1.49 g, 7 mmol) in diethyl ether (10 ml) was treated with trimethylamine (3.0 g, 51 mmol) and left standing under nitrogen for 1 week. The white salt produced was filtered and washed under nitrogen with diethyl ether before drying *in vacuo* for 6 h to give *p*-allylbenzyltrimethylammonium bromide (**17**, 1.36 g, 71%) a hygroscopic salt containing water. Found: C, 55.76, H 7.21, N 4.75%; $C_{13}H_{20}BrN.0.5\,H_2O$ requires C 55.92, H 7.58, N 5.02%. δ_H ($CDCl_3$) 3.41–3.48 overlapping [s, $(CH_3)_3\overset{+}{N}$] and (d, $\underline{CH_2}CH{=}CH_2$), 5.02 (s, $\underline{CH_2}N^+-$), 5.08 (m, CH=C$\underline{H_2}$), 5.92 (m, $\underline{CH}{=}CH_2$), 7.25 and 7.58 ppm (AB, $-C_6\underline{H_4}-$).

p-*Methylcinnamyltrimethylammonium bromide* (***19***)

p-Methylcinnamyl bromide (**27**) was prepared by the method described previously (m.p. 59.5–60.5°C, lit.[13] 64–65°C). δ_H ($CDCl_3$) 2.32 (s, CH_3), 4.13 (d, CH_2Br), 6.32 (m, $C_6H_4CH_a{=}\underline{CH_b}$), 6.59 (m, $C_6H_4\underline{CH_a}{=}CH_b$, $J_{Ha,Hb}$ = 15.6 Hz) 7.10 and 7.26 ppm (AB, $-C_6\underline{H_4}-$). The bromide (**27**, 1.44 g, 6.82 mmol) in dry diethyl ether (15 ml), treated with trimethylamine (3.0 g, 50 mmol) was left standing under nitrogen for 21 h. The white precipitate was filtered and washed with diethyl ether to leave *p*-methylcinnamyltrimethylammonium bromide

hemihydrate (**19**, 1.0 g, 53%). Found: C 55.76, H 7.21, N 4.75%; $C_{13}H_{20}BrN.0.5H_2O$ requires C 55.92, H 7.58, N 5.02%. δ_H (D_2O) 2.32 (s, CH_3), 3.06 (s, $N^+(CH_3)_3$), 3.97 (d, $CH{=}CHCH_2N$), 4.81 (s, H_2O), 6.29 (m, $C_6H_4CH_a{=}CH_b$), 6.91 (m, $C_6H_4CH_a{=}CH_b$, $J_{Ha,Hb}$ = 15.6 Hz), 7.25 and 7.45 ppm (AB, $-C_6H_4-$).

POLYMERIZATION REACTIONS

Using p-*allylbenzyltrimethylammonium bromide* (*17*)

Method 1[12]. *p*-Allylbenzyltrimethylammonium bromide (**17**, 3.18 g, 11.7 mmol) in water (10 ml) was added over 30 min to a refluxing solution of sodium hydroxide (41 g, 1.03 mol) in water (55 ml) and refluxing was continued for a further 15 min. After cooling the mixture, insoluble polymeric material was filtered off and washed with water before drying *in vacuo*. Extraction of the polymer in a Soxhlet apparatus with hot dichloromethane allowed insoluble polymer (1.97 g) to be isolated. Found: C 85.32, H 7.68%; $(C_{10}H_{10})_n$ requires C 92.3, H 7.7%. The aqueous filtrate was acidified (2 M H_2SO_4), extracted with dichloromethane and *all* the organic extracts combined, dried ($MgSO_4$) and solvent evaporated to leave 0.17 g of a complex mixture (by t.l.c.). Column chromatography of this material on silica (15 cm × 3 cm) using carbon tetrachloride as elutant enabled one component (0.08 g, $R_f = 0.15$) to be isolated from the mixture. Recrystallization from carbon tetrachloride gave *E,E*-[6,2]-paracyclophan-1,5-diene (**28**, 0.06 g, 3.9%); m.p. 147–150°C. Found: C 92.31, H 7.78%, M^+ 260.1526; $C_{20}H_{20}$ requires C 92.26, H 7.74%, M^+ 260.1565. δ_H ($CDCl_3$) 2.42 (m, $CH{=}CH{-}CH_2$), 2.92 (s, $C_6H_4CH_2$), 5.50 (m, $C_6H_4CH_a{=}CH_b$), 5.90 (d, $C_6H_4CH_a{=}CH_b$, $J_{Ha,Hb}$ = 16.0 Hz), 6.51 and 6.77 ppm (AB, $-C_6H_4-$); ν_{max} (KBr disc) 968 cm^{-1} (*trans* CH=CH bend).

Method 2[14]. (1) With polymerization inhibitor. *p*-Allylbenzyltrimethylammonium bromide (**17**, 4.3 g, 0.016 mol) in water (120 ml) was treated with silver(I) oxide (4.0 g, 0.017 mol; from reaction of silver nitrate with sodium hydroxide) and mechanically stirred for 2.25 h. The silver bromide precipitate was filtered and washed with water (40 ml) to leave a solution of *p*-allylbenzyltrimethylammonium hydroxide (160 ml, 0.1 M). This solution was mixed with toluene (175 ml) and phenothiazine (0.10 g, 0.5 mmol) and mechanically stirred under reflux whilst azeotropically removing water by means of a Dean–Stark apparatus. After 3 h all the water had been removed and no more trimethylamine was evolved. The hot toluene solution was filtered to remove insoluble material (0.62 g, 30%) and concentrated by rotary evaporation to leave crude product (1.57 g). The ^1H n.m.r. of this material showed it was a mixture of *E,E*-[6,2]-paracyclophan-1,5-diene (**28**, 95%) and *Z,Z*-[6,2]-paracyclophan-1,5-diene (**29**, 5%) (see later) and, surprisingly, no soluble polymer. Column chromatography of a portion of this mixture (0.304 g) on alumina using light petroleum (b.p. 40–60°C) as elutant gave *E,E*-[6,2]-paracyclophan-1,5-diene (**28**, 0.27 g, representing 67% overall yield; m.p. 147–150°C), identified by ^1H n.m.r. spectroscopy.

(2) Without polymerization inhibitor. *p*-Allylbenzyltrimethylammonium bromide (**17**, 5.46 g, 0.02 mol) in water (150 ml) was treated with silver(I) oxide (8 g, 0.034 mol; from reaction of silver nitrate with sodium hydroxide) and stirred at room temperature for 1.5 h. The silver(I) bromide precipitate was filtered off and washed with water (50 ml) to leave a solution of *p*-allylbenzyltrimethylammonium hydroxide (200 ml, 0.1 M). Toluene (150 ml) was added and the water removed azeotropically over 3.5 h under reflux using a Dean–Stark apparatus. The hot toluene solution was filtered to remove insoluble polymeric material (1.05 g, 40%) and the filtrate concentrated by rotary evaporation to leave *E,E*-[6,2]-paracyclophan-1,5-diene (**28**, 1.58 g, 60%), identified by ^1H n.m.r. spectroscopy.

Using p-*methylcinnamyltrimethylammonium bromide* (*19*)

Method 1[12]. *p*-Methylcinnamyltrimethylammonium bromide hemihydrate (**19**, 0.596 g, 2.2 mmol) in water (10 ml) was added dropwise over 30 min to a refluxing solution of sodium hydroxide (15 g, 0.38 mol) in water (20 ml) and refluxing continued for 1.5 h. The insoluble polymeric material was filtered off, washed with water and hot dichloromethane and dried *in vacuo* (0.158 g, 57%). Found: C 84.21, H 7.06%; the sought-after polymer $(C_{10}H_{10})_n$ would require C 92.3, H 7.7%. The aqueous filtrate was acidified (2 M H_2SO_4) and extracted with dichloromethane and the combined organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to leave crude soluble product (0.12 g). Column chromatography of this product on silica using carbon tetrachloride as elutant gave *E,E*-[6,2]-paracyclophan-1,5-diene (**28**, 0.015 g, 5%) as the fastest moving component in a complex mixture ($R_f = 0.15$), identified by ^1H n.m.r. and i.r. spectroscopy.

Method 2[14]. *p*-Methylcinnamyltrimethylammonium bromide hemihydrate (**19**, 20.51 g, 0.076 mol) in water (115 ml) was treated with freshly prepared silver(I) oxide (25 g, 0.108 mol; from reaction of silver nitrate with sodium hydroxide) and mechanically stirred for 2.5 h. The precipitated silver(I) bromide and excess silver(I) oxide were filtered off and washed with water to give a solution of *p*-methylcinnamyl trimethylammonium hydroxide (175 ml, 0.043 M). Toluene (250 ml) and phenothiazine (1 g, 5 mmol) were added to the solution and water removed azeotropically over 5 h under reflux using a Dean–Stark apparatus. The hot toluene solution was filtered to remove insoluble material (0.35 g) and the filtrate concentrated by rotary evaporation to leave crude product (11.5 g). Soxhlet extraction of this material with light petroleum (b.p. 80–100°C) left polymeric material (**32**, 2.1 g, 22%) which was dissolved in tetrahydrofuran and reprecipitated into methanol. Found: C 87.96, H 7.39%; $(C_{10}H_{10})_n$ requires C 92.3, H 7.7%. $M_n = 1.44 \times 10^4$; $M_w = 7.43 \times 10^4$; M_w/M_n = 5.15. δ_H ($CDCl_3$), see *Figure 1*.

The cooled Soxhlet extracts yielded a white precipitate (3.43 g, 36%) which was recrystallized from light petroleum (b.p. 80–100°C) and sublimed twice to give *E,E*-[6,2]-paracyclophan-1,5-diene (**28**, 2.5 g, 25%), identified by ^1H n.m.r. spectroscopy.

Column chromatography on alumina of the petroleum-soluble material from the Soxhlet extracts using light petroleum (b.p. 40–60°C) as elutant produced an impure sample of *Z,Z*-[6,2]-paracyclophan-1,5-diene (**29**, 20 mg), identified by ^1H n.m.r. spectroscopy (see below).

Pyrolysis of E,E-[*6,2*]-*paracyclophan-1,5-diene* (***28***)

E,E-[6,2]-paracyclophan-1,5-diene (**28**, 0.182 g, 0.7 mmol) was sublimed at ~250°C (0.01 mmHg) and passed through a furnace maintained at 580°C into a cool tube held at room temperature. The oily material that collected was sublimed at 40°C and recrystallized from light petroleum to give *Z,Z*-[6,2]-paracyclophan-1,5-diene (**29**); m.p. 70.5–71.5°C. Found: C 91.88, H 7.54%; $C_{20}H_{20}$ requires C 92.26, H 7.74%. δ_H ($CDCl_3$) 1.96 (m, $CH{=}CH{-}CH_2$), 2.87 (s, $C_6H_4CH_2$), 5.55 (m, $C_6H_4CH_a{=}CH_b$), 6.34 (d, $C_6H_4CH_a{=}CH_b$, $J_{Ha,Hb}$ = 11.25 Hz), 6.58 and 6.72 ppm (AB, $-C_6H_4-$).

ACKNOWLEDGEMENTS

We thank the SERC for financial support (to MFW) and Drs A. M. Kenwright and R. S. Matthews for n.m.r. measurements.

REFERENCES

1 Swarc, M. *Nature* 1947, **160**, 403
2 Errede, L. A. and Cassidy, J. P. *J. Am. Chem. Soc.* 1960, **82**, 3653
3 Iwatsuki, S. and Itoh, T. *Macromolecules* 1980, **13**, 983
4 Hall Jr, H. K., Brandt, M. W. and Mulvaney, J. E. *Macromolecules* 1988, **21**, 1553
5 Iwatsuki, S., Itoh, T., Sato, T. and Higucki, T. *Macromolecules* 1987, **20**, 2651
6 Brandt, M. W., Mulvaney, J. E. and Hall Jr, H. K. *J. Polym. Sci. A* 1989, **27**, 1957
7 Itoh, T. and Hall Jr, H. K. *Macromolecules* 1990, **23**, 2836
8 Ramezanian, M., Itoh, T., Padias, A. and Hall Jr, H. K. *Macromolecules* 1990, **23**, 3545
9 Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.* 1984, **25**, 327
10 Gagnon, D. R., Capistran, J. D., Lenz, R. W. and Antoun, S. *Polymer* 1987, **28**, 567
11 Lahti, P. M., Modarelli, D. A., Denton III, F. R., Lenz, R. W. and Karasz, F. E. *J. Am. Chem. Soc.* 1988, **110**, 7258
12 Winberg, H. E., Fawcett, F., Mochel, W. E. and Theobald, C. W. *J. Am. Chem. Soc.* 1960, **82**, 1428
13 Burton, H. and Ingold, C. K. *J. Chem. Soc.* 1928, 904
14 Filler, R. and Cantrell, G. L. *J. Fluorine Chem.* 1986, **30**, 399
15 Feast, W. J. and Millichamp, I. S. *Polym. Commun.* 1983, **24**, 102
16 Gorham, W. F. *J. Polym. Sci. A* 1966, **4**, 3028