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

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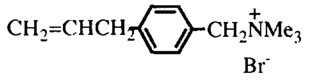
α-Phenyl-*p*-xylyene (**7**) has been shown to be an intermediate in the base-catalysed decomposition of both *p*-benzylbenzyltrimethylammonium bromide (**11**) and *p*-methylbenzhydryltrimethylammonium bromide (**12**). All the possible cyclic trimers of unsymmetrical linking are formed (i.e. phenyl-substituted head h to h and tail to tail links), which accompany a polymer formed mainly via the contrasting head to tail linking of α-phenyl-*p*-xylylene.

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

INTRODUCTION

In the previous paper[1] we described the preparation of two ammonium salts (**1** and **2**) and their conversion by base to products which showed clearly the intermediacy of the highly reactive vinyl-substituted *p*-xylylene derivative (**3**).



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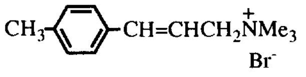

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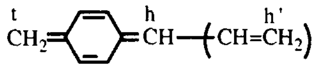

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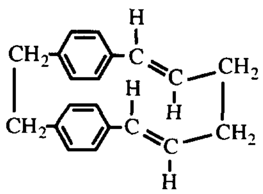
Among these products isolated were two cyclic dimers of **3**, namely compounds **4** and **5**, which were formed through the coupling of the two conjugatively extended heads h′ and the two tails t.



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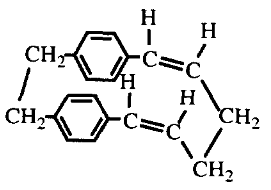

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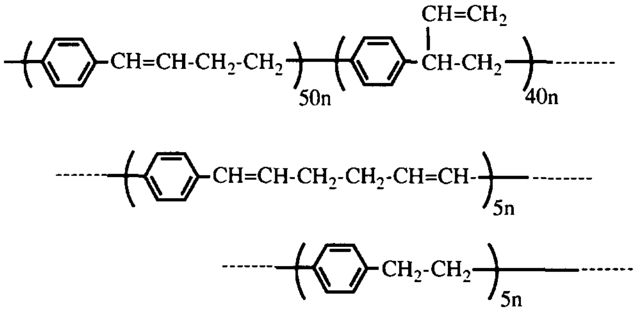
In one experiment a polymer was obtained which was soluble in organic solvents, the detailed ^{1}H n.m.r. of which revealed that a copolymer (**6**) had been formed which consisted of head to tail (h′–t) linkages (50%), head to tail (h–t) linkages (40%), and only 5% each of head to head (h′–h′) and tail to tail (t–t) linkages.



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In this paper we describe the preparation and properties of another unsymmetrical *p*-xylene, compound **7**. Once again, the special interest in this reactive intermediate was two-fold: first, whether the expected polymerization reactions would proceed with strictly head to tail coupling (the tacit assumption in the extensively studied polymerization reactions of xylylene derivatives of type **8**[2,3]); and second, whether the head moiety was h (with the phenyl group as a passive substituent) *or* whether it was h′, i.e. the *para* position in the phenyl substituent which is intimately involved as a group extending the conjugation of the *p*-xylylene structure*.

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*For the sake of simplicity, only the *para* position of the phenyl group is considered as the site of reaction of the conjugatively extended *p*-xylene, though the *ortho* positions are other possibilities

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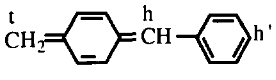

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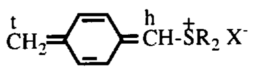

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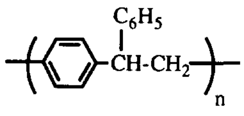
If coupling took place head to tail via head h, the polymer formed would be **9**, and if via head h′, it would be **10**.



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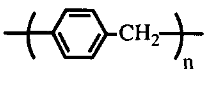

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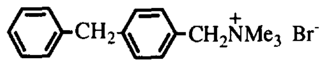
SYNTHESES OF PRECURSOR MONOMERS

Two trimethylammonium salts (**11** and **12**) were synthesized as alternative precursors to the phenyl-substituted *p*-xylylene (**7**).



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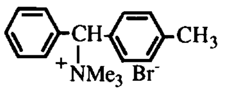

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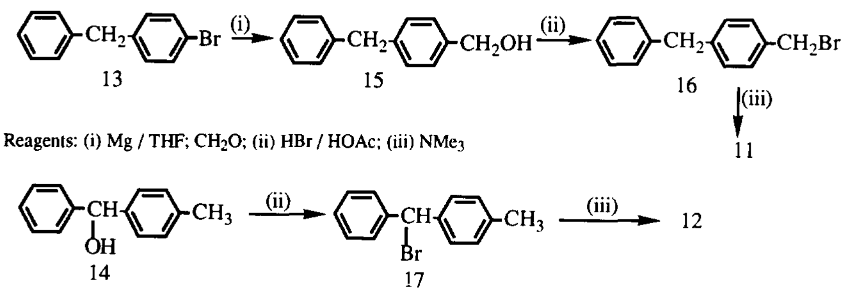
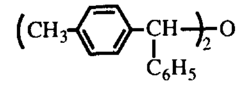
p-Benzylbromobenzene (**13**)[4] was the starting material used in a three-stage synthesis of **11** and *p*-methylbenzhydrol (**14**) was used for **12**. *Scheme 1* summarizes the reactions involved.



Reagents: (i) Mg / THF; CH_2O; (ii) HBr / HOAc; (iii) NMe_3

Scheme 1

The benzhydryl bromide (**17**) could only be obtained in ~94% purity (by g.l.c.); attempted purification by chromatography on silica resulted in its efficient conversion to the ether **18** (78%), and distillation gave **19**, presumably via a hydride abstraction reaction from a benzhydryl-type cation. The self coupling reaction of **17** with zinc gave the ethane derivative **20** used as a model for chemical shift assignments in interpreting n.m.r. data (see later).



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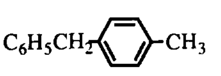

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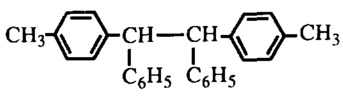

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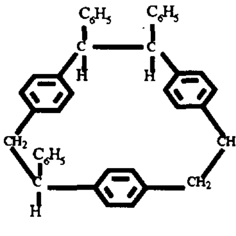
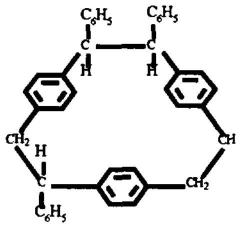
POLYMERIZATION REACTIONS

The trimethylammonium bromides (**11** and **12**) were first converted to the corresponding hydroxides using silver(I) oxide in water, and polymerizations carried out by azeotropically removing the water using toluene[5]. Organic solvent soluble products were obtained in both experiments and the polymer contents were separated from other organic materials by Soxhlet extraction with light petroleum. Further purification of the polymers was effected by dissolution in tetrahydrofuran and reprecipitation in methanol. Chromatography on silica was used to separate non-polymeric materials.

Five products were identified from the experiment using *p*-benzylbenzyltrimethylammonium bromide (**11**): polymer (32%); and two inseparable pairs of diastereomers (36% and 11%) which are either **21a** and **21b** or **22a** and **22b**, respectively, or vice versa (assignments unknown).



21a



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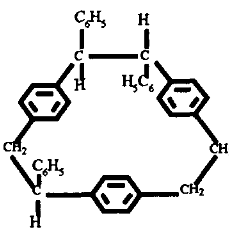

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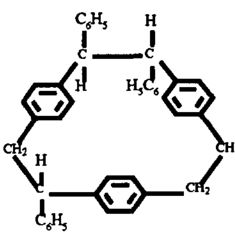

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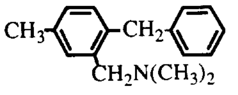
When the experiment was repeated under identical conditions using *p*-methylbenzhydryltrimethylammonium bromide (**12**), five products were again identified: polymer (12%) identical with the material prepared from **11** (except for slightly different values of M_n and M_w); one inseparable pair of diastereomers (17%) identical with the major inseparable pair of diastereomers formed from **11**; and an essentially equimolar mixture of isomers **23** and **24** (by g.l.c., 8%), the products of the two possible Sommelet–Hauser rearrangements brought about by a proton removal from one methyl group of the trimethylammonium functionality.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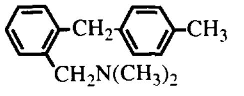
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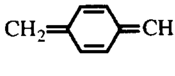
The ^1H n.m.r. spectrum of this mixture showed two CH_2–N groups and two CH_3–aryl groups but the CH_2 groups interlinking two pairs of aryl groups overlapped, as did the two $N(CH_3)_2$ groups.

RESULTS AND DISCUSSION

p-Xylylene (**25**) generated in the vapour phase by the pyrolysis of *p*-xylene readily polymerizes to give linear polymers (**26**)[6] but in cold hexane (−78°C) at high dilution conditions have been found for the efficient formation of the cyclic dimer (**27**) and the cyclic trimer (**28**)[7].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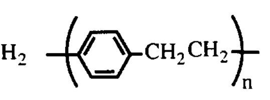
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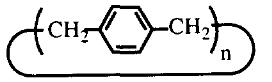
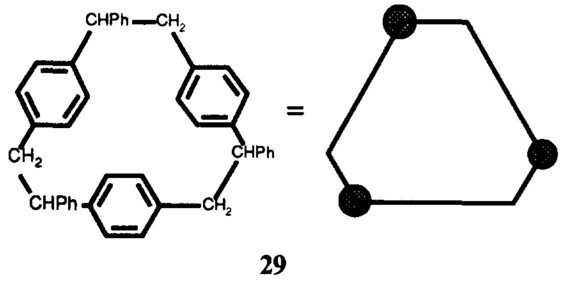

27, $n = 2$
28, $n = 3$

In the work described in this paper, two chromatographically pure samples were isolated and shown by mass spectrometry to be trimers of α-phenyl-*p*-xylylene (**7**). The complexity of the ^1H n.m.r. spectra showed immediately that *no* coupling between the head h′ and tail t in **7** had occurred [absorptions due to methylene groups in diarylmethanes (**10**) would have been expected at $\delta \sim 3.9$ ppm, as found in **19**], so that only coupling between the head h and tail t had occurred. Two basic cyclic trimers can be constructed if considerations of stereochemistry are ignored: three units joined head to tail (h–t, **29**) and the arrangement with one h–h coupling (and in consequence, one t–t coupling, **30**).



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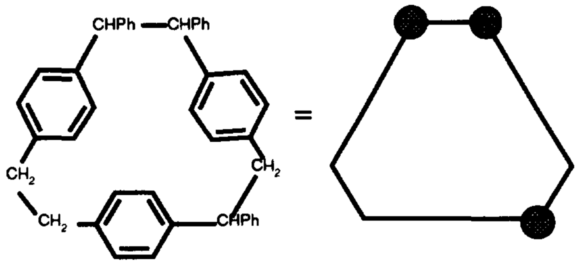

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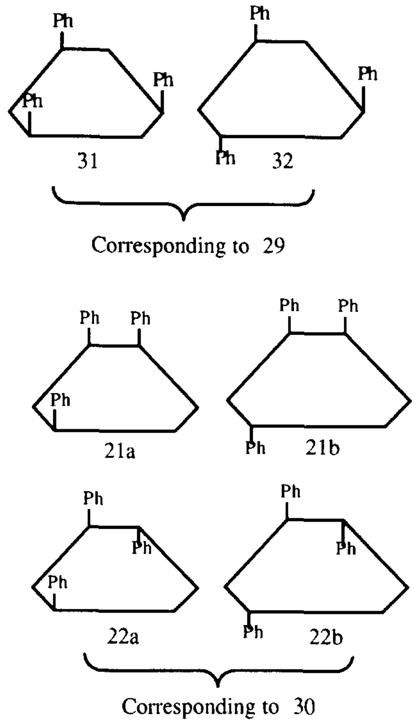
However, when the stereochemistry at each chiral centre in **29** and **30** is considered, the following six basic structures can be drawn (*Scheme 2*). (In reality, the mirror image of each structure should also be drawn since all the compounds will be racemates. For simplicity, however, only one enantiomer is drawn in each case.)



Scheme 2

The 500 MHz ^1H n.m.r. spectrum of the major cyclic trimer (isolated in 36% yield) produced from **11** is shown in *Figure 1*. The spectrum can be divided into three distinct regions: (i) 2.5–3.5 ppm; (ii) 4.0–5.0 ppm; and (iii) 6.5–7.5 ppm. The relative values of the integrated spectrum in these regions, (i):(ii):(iii) = 2:1:9, show clearly (the protons referred to are underlined) that (i) is due to $-\underline{CH_2}-$, (ii) is due to $-\underline{CH}(C_6H_5)-$ and (iii) is due to $-C_6\underline{H}_4-$ plus $C_6\underline{H}_5-$, i.e. all the protons found in the monomer repeat unit **7**, albeit in different environments. The expanded ^1H n.m.r. spectrum excluding the aromatic protons is shown in *Figure 2*. The integrated spectrum shows that there are twice as many protons in B (total relative integration 31) as there are in the combined absorptions of C and D (total relative integration 15.5). The chemical shifts of the absorptions in B (~4.6 ppm) are very close to the methine protons in the model compound 1,2-di-(*p*-tolyl)-1,2-diphenylethane (**20**, 4.72 ppm), so that the AB system (relative integration 18) and the overlapping 'singlet' (relative integration 13) are each due to pairs of protons (underlined) in $-\underline{CH}(C_6H_5)-\underline{CH}(C_6H_5)-$ in two slightly different environments (and therefore in two different compounds) caused by the different stereochemistry of an associated $-\underline{CH}(C_6H_5)-CH_2-$ group in a remoter part of the same molecule, the single protons (underlined) of which have absorptions at C (relative integration 8.5) and D (relative integration 7), respectively. Moreover, since the integrations of the protons in peak B relative to the combined integration of peaks C and D are precisely 2:1, there are no

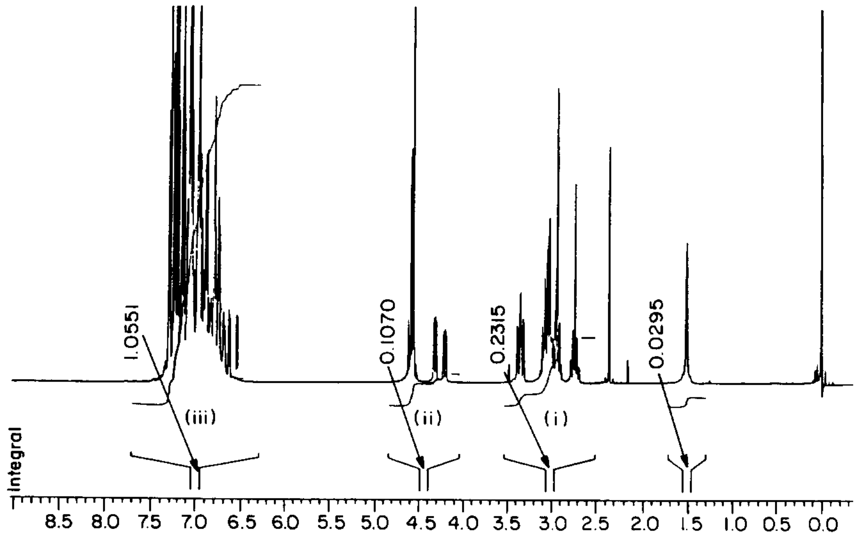


Figure 1 500 MHz ^1H n.m.r. spectrum of the cyclic trimer of **7** isolated in 36% yield from the reaction of **11** with Ag_2O/H_2O

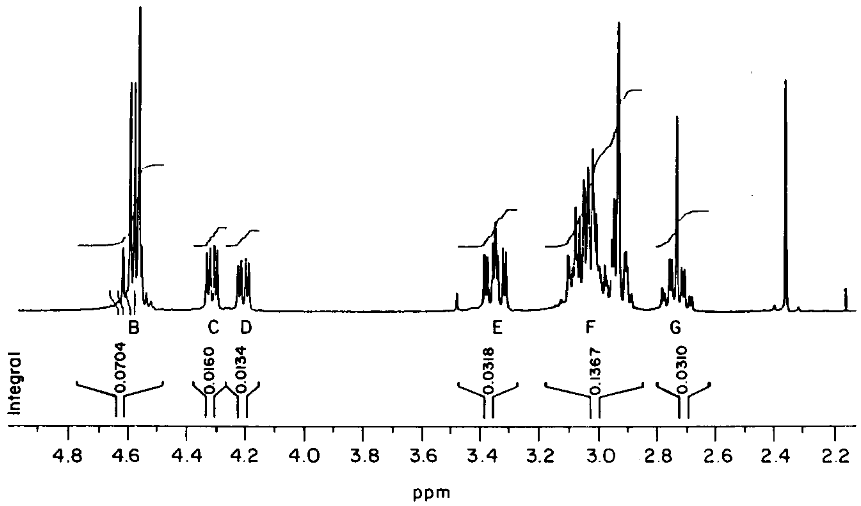


Figure 2 Expanded 500 MHz ^1H n.m.r. spectrum of the cyclic trimer of **7** isolated in 36% yield from the reaction of **11** with Ag_2O/H_2O

diastereomers present in the material studied corresponding to the basic structure (**29**) [i.e. no isomers (**31** and **32**) which *only* contain the $-CH(C_6H_5){-}CH_2{-}$ unit] since they would obviously alter the ratio of the absorptions in B relative to C and D. The ^1H n.m.r. spectrum (*Figure 1*) is therefore that of an inseparable mixture of diastereomers having the basic structure **30**; the individual compounds are either the pairs **21a** and **21b** or **22a** and **22b** present to the extent of 1.3:1 (average of 18:13 and 8.5:7).

The COSY spectrum of the major cyclic trimer (isolated in 36% yield) is shown in *Figure 3* and has enabled further assignments of the absorptions to be made. The multiplet E is a pair of overlapping doublet of doublets; the one centred at 3.362 ppm is due to one proton (from the integrated spectrum) which coupled with the single proton represented by the doublet of doublets C, whilst the other at 3.326 ppm coupled with the single proton represented by the doublet of doublets D. Therefore the proton (underlined) in a $-C\underline{H}(C_6H_5){-}CH_2{-}$ unit at C and D in the two

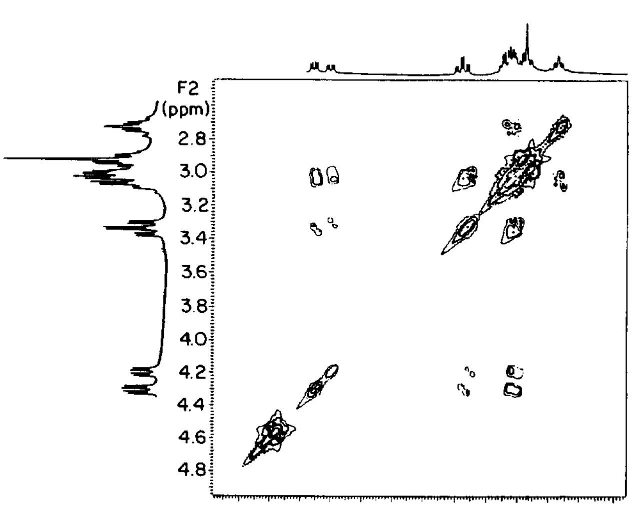


Figure 3 COSY ^1H n.m.r. spectrum of the cyclic trimer of **7** isolated in 36% yield from the reaction of **11** with Ag_2O/H_2O

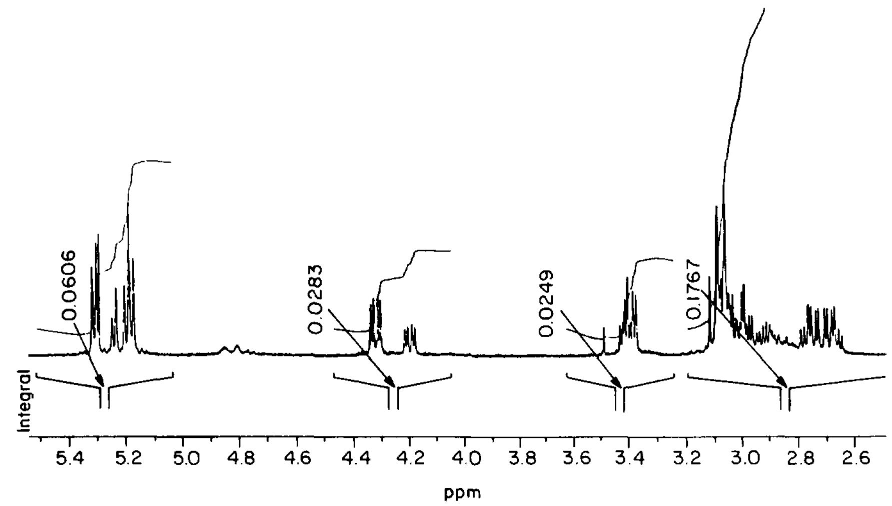
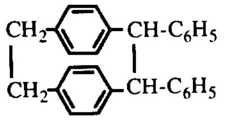


Figure 4 500 MHz ^1H n.m.r. spectrum of the cyclic trimer of 7 isolated in 11% yield from the reaction of **11** with Ag_2O/H_2O

diastereomers in the mixture is associated with one proton (underlined) in E of the same structural unit $-CH(C_6H_5)-C(\underline{H})H-$. The multiplet G, from its relative integration, is due to overlapping absorptions caused by one proton from each of the two diastereomers present in the mixture which are coupled only with protons in the broad region F, and is the proton (underlined) in the $-CH_2C(H)\underline{H}-$ unit of each diastereomer. The broad region F, therefore, is due to the four remaining protons (underlined) in the following structural units which were present in each of the two diastereomers: $-\underline{CH_2}C(\underline{H})H-$ and $-CH(C_6H_5)C(H)\underline{H}-$.

The 500 MHz ^1H n.m.r. spectrum of the minor cyclic trimer (isolated in 11% yield from **11**) is shown in the expanded aliphatic region in *Figure 4* and is very similar to that of the major cyclic trimer (*Figure 2*) showing that it had the same basic structure (**30**). It, too, was an inseparable mixture of diastereomers, present in the ratio of 2:1. The most significant differences between the two spectra, however, are the chemical shifts of the two pairs of protons (underlined) in the $-C\underline{H}(C_6H_5)-C\underline{H}(C_6H_5)-$ group which in this minor component occur at 5.15–5.35 ppm (cf. 4.60–4.66 ppm). Clearly, the big differences in shifts of these vicinal hydrogens is a direct consequence of the relative stereochemistry of the vicinal phenyl groups, which can be either *syn* (as in **21a** and **21b**) or *anti* (as in **22a** and **22b**). The lack of basic model compounds has not enabled us to distinguish even this fundamental difference between the different pairs of compounds. The assignment of the stereochemistry within each pair is an even greater problem to be solved.

In 1957 Bersch reported that the decomposition of *p*-benzylbenzylammonium hydroxide gave a polymer (no details given) and a cyclic dimer (**33**, m.p. 277–279°C)[8]. Moreover, the self coupling of **34** with silver produced an isomer of **33**, so it was suggested that the two isomers differed only in the *syn–trans* relationship of the C_6H_5 groups. No structural determination details were given. Later it was argued that the product from the trimethylammonium compound could have been **35**[9]. The melting point of the 'dimer' prepared by Bersch is very close to that of the major cyclic trimer mixture described in this work (269–272°C).



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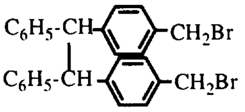

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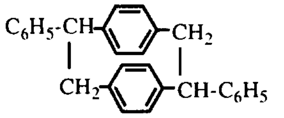

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The experiments described in this paper show very clearly that *all* the possible cyclic trimers of α-phenyl-*p*-xylylene (**7**), when linked unsymmetrically, are formed. However, due to the complexity of the reaction products, the possibility of the symmetrically linked cyclic trimers of **7** (i.e. **31** and **32**) also being formed cannot be excluded.

The 400 MHz ^1H n.m.r. spectrum of the polymer produced from both precursor monomers (**11** and **12**) is shown in *Figure 5* and is relatively simple compared with those shown in *Figures 1–3*. The major absorptions at 3.19, 4.05 and 6.74–7.25 ppm were present in the ratio 2:1:9, showing that head to tail (h–t) polymerization was the main course of reaction. However, a closer look at the spectrum reveals a number of smaller absorptions, and it was of interest to examine whether these could be due to some head to head and/or tail to tail coupling of the reactive intermediate **7** (both of these modes could occur independently), since such processes had clearly been identified in the formation of the two pairs of diastereomeric cyclic trimers described above. The peak at 4.64 ppm was assigned to protons (underlined) in a head to head unit $-C\underline{H}(C_6H_5)-C\underline{H}(C_6H_5)-$ found in the major cyclic trimer (but not the minor cyclic trimer) while the peak at 2.7 ppm corresponded closely to the protons (underlined) in a tail to tail unit $-C_6H_4-\underline{CH_2CH_2}-C_6H_4-$. No assignments could be made to the peaks at 3.05, 3.45 and 3.95 ppm. The integrated n.m.r. of the polymer indicated that 97% consists of head to tail coupling, the remaining 3% resulting from head to head/tail to tail coupling, as is

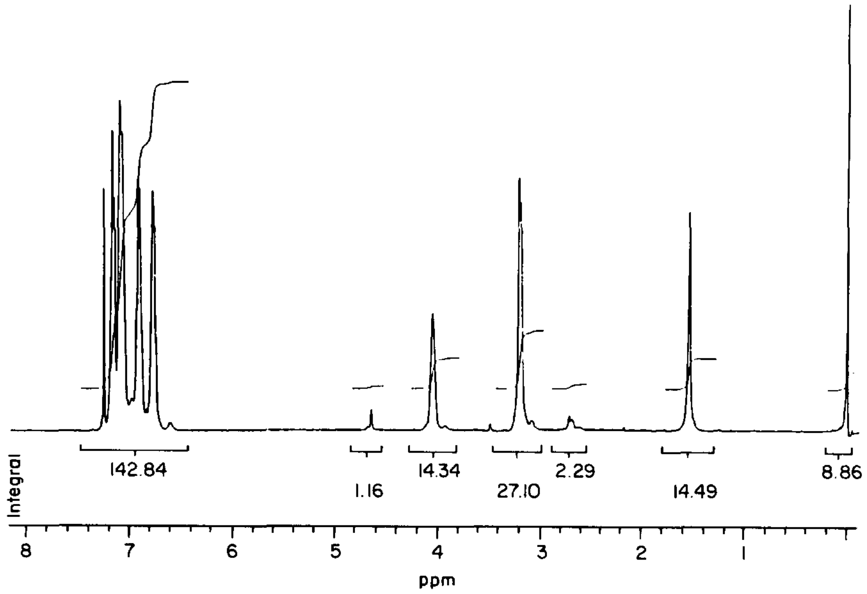
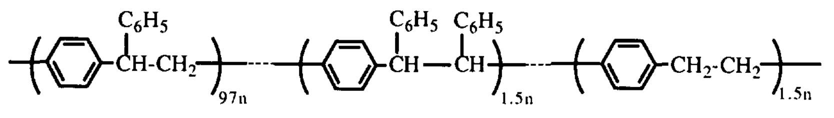


Figure 5 400 MHz ^1H n.m.r. spectrum of polymer **36** obtained from the reaction of **11** with Ag_2O/H_2O



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shown in structure **36**. The polymer had a low carbon analysis, but this is not unusual in polymer chemistry where the proportion of carbon in hydrocarbon polymers is very high[10].

EXPERIMENTAL

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

Preparation of p-*benzylbenzyltrimethylammonium bromide (11)*

Preparation of p-*benzylbenzyl alcohol (15)*. Magnesium (2.8 g, 0.116 mol) in dry tetrahydrofuran (25 ml), activated using ethylene dibromide (20 drops), was treated over 0.5 h with *p*-benzylbromobenzene (**13**, 10 g, 0.04 mol)[4] in dry tetrahydrofuran (10 ml) and heated under reflux for a further 1 h. Paraformaldehyde (4.5 g, 0.155 mol) was decomposed at 180–200°C and the resulting formaldehyde gas passed over the ice-cooled Grignard reagent through a heated wide-bored tube by means of a stream of nitrogen. After stirring at room temperature for 1 h, the mixture was poured onto ice, acidified (2 M H_2SO_4) and extracted with diethyl ether. The organic extracts were dried ($MgSO_4$) and concentrated by rotary evaporation to give crude product (9.4 g). After trituration with light petroleum (b.p. 30–40°C) a white solid was obtained (7.5 g) which was recrystallized from light petroleum (b.p. 30–40°C) to give *p*-benzylbenzyl alcohol (**15**, 4.6 g, 57%); m.p. 44.0–45.0°C. Found: C 84.48, H 7.11%, M^+ 198; $C_{14}H_{14}O$ requires C 84.81, H 7.12%, M^+ 198. δ_H ($CDCl_3$) 1.76 (b, OH), 3.97 (s, CH_2), 4.62 (s, CH_2OH), 7.17 and 7.26 ppm (AB, $-C_6H_4-$ and $-C_6H_5$); ν_{max} (nujol) 3250 cm^{-1} (OH).

Preparation of p-*benzylbenzyl bromide (16)*. *p*-Benzylbenzyl alcohol (**15**, 4.1 g, 0.021 mol) was treated with HBr in glacial acetic acid (30 ml, 45 w/v%) and stirred at 45°C for 2 h. The bulk of the acid was removed *in vacuo* (0.05 mmHg) at room temperature before fractional distillation to give *p*-benzylbenzylbromide (**16**, 4.8 g, 89%); b.p. 98–102°C (0.05 mmHg); m.p. 35.5–36.5°C (from light petroleum, b.p. 40–60°C). Found: C 64.11, H 4.88%, M^+ 260/262; $C_{14}H_{13}Br$ requires C 64.39, H 5.02%, M^+ 260/262. δ_H ($CDCl_3$) 3.89 (s, CH_2), 4.36 (s, CH_2Br), 7.12 and 7.22 ppm (AB, $-C_6H_4-$ and $-C_6H_5$).

Reaction of p-*benzylbenzyl bromide (16) with trimethylamine*. *p*-Benzylbenzyl bromide (**16**, 0.643 g, 2.46 mmol) in dry diethyl ether (10 ml) was treated with trimethylamine and left standing under nitrogen for 1 day. The resulting white solid was washed by decantation with dry diethyl ether before drying *in vacuo* and gave *p*-benzylbenzyltrimethylammonium bromide (**11**, 0.52 g, 66%). Found: C 63.45, H 6.92, N 4.34%; $C_{17}H_{22}BrN$ requires C 63.75, H 6.92, N 4.37%. δ_H ($CDCl_3$) 3.38 (s, $N^+(CH_3)_3$), 3.98 (s, CH_2), 5.02 (s, CH_2N^+) and complex multiplet (including 7.27 and 7.62 as part of an AB system) 7.4 ppm (m, $-C_6H_4-$ and $-C_6H_5$).

Preparation of p-*methylbenzhydryltrimethylammonium bromide (12)*

Preparation of p-*methylbenzhydryl bromide (17)*. *p*-Methylbenzhydrol (**14**, Aldrich catalogue name, also *p*-methylphenyl phenyl methanol, 20 g, 0.1 mol) was treated with a solution of HBr in glacial acetic acid (120 g, 45 w/v%) and stirred at 40°C for 3 h. The excess acid was removed *in vacuo* (0.05 mmHg) and the crude product distilled (101–106°C/0.05 mmHg) to give a liquid (23 g) which g.c.-mass spectrometry showed was a mixture of *p*-methylbenzhydryl bromide (**17**, 94 parts by g.c.) and *p*-methylbenzhydrol (**14**)/α-phenyl-*p*-xylene (**19**) (6 parts). Found: C 66.01, H 5.13%. A mixture of 94% (**17**), 3% (**14**) and 3% (**19**) requires C 65.84, H 5.12%. For the major component (**17**), δ_H ($CDCl_3$) 2.25 (s, CH_3), 6.21 (s, CHBr), 7.05 and 7.39 (AB, $-C_6H_4-$) and 7.26 ppm (m, $-C_6H_5$).

The crude *p*-methylbenzhydryl bromide (**17**, 0.613 g, 2.34 mmol) was sent through a silica column slowly, using dichloromethane as elutant. The extremely viscous oil that was isolated was identified as di(*p*-methylbenzhydryl) ether (**18**, 0.42 g); m.p. 69–71°C (from methanol). Found: C 88.51, H 6.92%; $C_{28}H_{26}O$ requires C 88.85, H 6.92%. δ_H ($CDCl_3$) 2.08 (s, CH_3), 5.24 (s, CHOCH), 6.91 and 7.20 (AB, C_6H_4) and 7.04 ppm (m, $-C_6H_4-$ and $-C_6H_5$); ν_{max}(neat) 1055 cm^{-1} (ether stretch).

Distillation of the crude *p*-methylbenzhydryl bromide (**17**, 30 g, 0.115 mol) through a Fischer-Spahltrohr column gave only α-phenyl-*p*-xylene (**19**, 10 g, 0.06 mol); b.p. 112–132°C (1.0 mmHg). Found: C 92.05, H 7.54%; $C_{14}C_{14}$ requires C 92.26, H 7.74%. δ_H ($CDCl_3$) 2.27 (s, CH_3), 3.90 (s, CH_2), 7.05 (m, C_6H_5) and 7.15 and 7.21 ppm (AB, $-C_6H_4-$).

p-Methylbenzhydryl bromide (**17**), was converted into 1,2-di-(*p*-tolyl)-1,2-diphenylethane (**20**) as follows: the bromide (0.25 g, 0.96 mmol), zinc (0.5 g, 7.7 mmol) and ethyl acetate (5 ml) were stirred at room temperature for 18 h before the zinc was filtered off and washed with ethyl acetate. The filtrate was concentrated by rotary evaporation to a yellow solid, purified by recrystallization from ethanol (0.165 g, 95%); m.p. 212–214°C. Found: C 92.90, H 7.51%; $C_{28}H_{26}$ requires C 92.77, H 7.23%. δ_H ($CDCl_3$) 2.17 (s, CH_3), 4.72 (s, CH) and 6.89–7.18 ppm (m, $-C_6H_4-$ and $-C_6H_5$).

Reaction of p-*methylbenzhydryl bromide* (*17*) *with trimethylamine.* Crude *p*-methylbenzhydryl bromide (**17**, 0.685 g, 2.62 mmol) in dry diethyl ether (15 ml) and trimethylamine (1.07 g, 18 mmol) were left to stand under nitrogen for 6 days. The resulting white solid was washed by decantation under nitrogen with dry diethyl ether and dried *in vacuo* for 3 h to give *p*-methylbenzhydryltrimethylammonium bromide (**12**, 0.40 g, 48%). Found: C 63.82, H 7.13, N 4.10%; $C_{17}H_{22}BrN$ requires C 63.75, H 6.92, N 4.37%. δ_H ($CDCl_3$) 2.39 (s, CH_3), 3.50 (s, $N^+(CH_3)_3$), 6.99 (s, CHN^+) and four multiplets from 7.38–8.18 ppm ($-C_6H_5$ and $-C_6H_4-$).

POLYMERIZATION REACTIONS

Using p-*benzylbenzyltrimethylammonium bromide* (*11*)

A solution of *p*-benzylbenzyltrimethylammonium bromide (**11**, 6.39 g, 0.02 mol) in water (100 ml) was treated with silver(I) oxide (6.8 g, 0.03 mol; from reaction of silver nitrate with sodium hydroxide) and mechanically stirred at room temperature for 2.5 h. The silver(I) bromide and excess silver(I) oxide were filtered off and washed with water (20 ml) to leave a solution of *p*-benzylbenzyltrimethyl ammonium hydroxide (120 ml, 0.167 M). This solution was mixed with toluene (250 ml) and phenothiazine (0.25 g, 1.26 mmol) before removing water under reflux using a Dean–Stark apparatus. After 2.5 h no more water or trimethylamine were evolved and the toluene solution was filtered hot to remove the very small amount of insoluble impurities. The filtrate was concentrated by rotary evaporation to leave crude product (4.32 g) which was extracted for 18 h in a Soxhlet apparatus using light petroleum (b.p. 80–100°C). The remaining material (2.19 g) was dissolved in tetrahydrofuran and reprecipitated in methanol to give poly(α-phenyl-*p*-xylylene) (**36**, 1.17 g, 32%). $M_n = 1.83 \times 10^4$; $M_w = 4.12 \times 10^4$; $M_w/M_n = 2.26$. Found: C 91.34, H 6.75%; $(C_{14}H_{12})_n$ requires C 93.29, H 6.71%. δ_H ($CDCl_3$) 2.7 (CH_2, tt), 3.19 (CH_2, ht), 4.05 (CH, ht), 4.64 (CH, hh) and 6.74–7.25 ppm (m, $-C_6H_4-$ and C_6H_5-) (see *Figure 5*).

The Soxhlet extracts (1.45 g) were separated by chromatography on alumina using ethyl acetate in hexane (10 v/v%) as elutant and the fastest moving components (1.1 g) were further separated on alumina using diethyl ether in light petroleum (b.p. 40–60°C) (5 v/v%) as elutant. Two products were isolated in chromatographically pure states. The faster moving component was a cyclic trimer of α-phenyl-*p*-xylylene (the 'major' trimer) and was purified by recrystallization from toluene and dried *in vacuo* at 100°C (1.3 g, 36%); m.p. 269–272°C. Found: C 93.67, H 6.68%, M^+ 540; $C_{42}H_{36}$ requires C 93.29, H 6.71%, M^+ 540). δ_H ($CDCl_3$), see *Figures 1* and *2*.

The slower moving component was another cyclic trimer of α-phenyl-*p*-xylylene and was purified by recrystallization from ethanol (0.43 g, 11%); m.p. 97–100°C. Found: M^+ 540.2977; $C_{42}H_{36}$ requires M^+ 540.2817. δ_H ($CDCl_3$), see *Figure 4*.

Using p-*methylbenzhydryltrimethylammonium bromide* (*12*)

A solution of *p*-methylbenzhydryltrimethylammonium bromide (**12**, 4.29 g, 0.013 mol) in water (70 ml) was treated with freshly prepared silver(I) oxide (3.44 g, 0.015 mol; from reaction of silver nitrate with sodium hydroxide) and mechanically stirred at room temperature for 1 h. The silver bromide and excess silver oxide were filtered off and washed with water to leave a solution of *p*-methylbenzhydryltrimethylammonium hydroxide (100 ml, 0.13 M). This solution was mixed with toluene (150 ml) and phenothiazine (0.18 g, 0.90 mmol) and water removed under reflux using a Dean–Stark apparatus. After 3 h no more water or trimethylamine were evolved. The hot toluene solution was filtered to remove the small amount of insoluble impurities and concentrated by rotary evaporation to leave crude product (2.67 g). Extraction of this product for 24 h in a Soxhlet apparatus using light petroleum (b.p. 80–100°C) left polymeric material (0.305 g) further purified by dissolving in tetrahydrofuran and reprecipitating into methanol. The polymer was identified by ^1H n.m.r. as poly(α-phenyl-*p*-xylylene) and was less pure than the previous sample (**36**, 0.30 g, 12%). $M_w = 6.37 \times 10^4$; $M_n = 2.88 \times 10^4$; $M_w/M_n = 2.22$. Found: C 88.27, H 6.32%; $(C_{14}H_{12})_n$ requires C 93.29, H 6.71%.

The composition of the Soxhlet extracts (2.3 g) was very complex by t.l.c. Partial separation of components was achieved by column chromatography on alumina using diethyl ether in light petroleum (b.p. 40–60°C, 5% v/v) as elutant. Further column chromatography on alumina using diethyl ether in light petroleum (b.p. 40–60°C, 1% v/v) as elutant enabled three components to be isolated. One component, obtained as a liquid, was further purified by distillation (60°C/0.05 mmHg) and identified by ^{1}H n.m.r. as an equimolar mixture of 2-benzyl-5-methyl-*N*,*N*-dimethylbenzylamine (**23**) and 2-(4-methylbenzyl)-*N*,*N*-dimethylbenzylamine (**24**, 0.25 g, 8%). Found: C 85.10, H 9.08, N 5.88%, M^+ 239; $C_{17}H_{21}N$ requires C 85.30, H 8.84, N 5.85%, M^+ 239. δ_H ($CDCl_3$) 2.24 (s, $N(CH_3)_2$), 2.34 (s, CH_3), 2.37 (s, CH_3), 3.37 (s, CH_2N), 3.40 (s, CH_2N), 4.20 (s, $C_6H_5\underline{CH_2}C_6H_4-$) and 7.29 ppm (m, C_6H_5, C_6H_3 and C_6H_4, $\overline{C}_6H_4$). The second product, a solid, was recrystallized from toluene, and identified as the 'major' cyclic tri(α-phenyl-*p*-xylylene) described above, by i.r. spectroscopy (0.40 g, 17%); m.p. 270–273°C. The third component was not identified.

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