# 647. lin-*Poly*-p-*xylylene. Part I. Intermediates and Polymers of Low Molecular Weight.*

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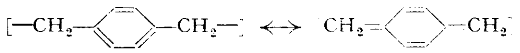
Preliminary work is described which was aimed at preparation of *lin*-poly-*p*-xylylene and examination of its structure. Polymer prepared by pyrolysis of *p*-xylene is shown to contain, *inter alia*, low polymers of *p*-xylene, namely, the linear dimer 4 : 4′-dimethyldibenzyl and the cyclic dimer di-*p*-xylylene. Co-distillation with ethylene glycol is used to purify some high-melting methylanthracenes.

SZWARC has described the pyrolysis of alkylated benzenes at low pressures (*J. Chem. Phys.*, 1948, **16**, 128; *Discuss. Faraday Soc.*, 1947, **2**, 39, 46). When *p*-xylene was so treated, the walls of the apparatus where the effluent gasses were cooled became coated with a film of a white substance of high melting point and low solubility. He concluded that the substance was polymeric and presumably had the structure $[\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot]_n$.

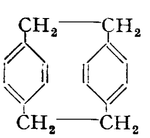
A pyrolysis apparatus similar to Szwarc's was set up and operated by F. Lord and J. S. F. Gill of these Laboratories. At the same time the authors of this series of papers set out to investigate the structure of the polymer and ways of making it other than by the pyrolysis of *p*-xylene. All polymer from the pyrolysis route used in this work was made by Lord and Gill, and their assistance is gratefully acknowledged. The polymer is now shown to be a linear polymer of the *p*-xylylene diradical, or of the labile quinodimethene molecule



and will be called *lin*-poly-*p*-xylylene.

As the most likely structure for the polymer appeared to be that given above, it was decided to examine the polymer obtained by the Wurtz condensation of *p*-xylylene dichloride, since this would be expected to have the same structure. This work is included in Part III (*J.*, 1953, 3270). *p*-Xylylene dichloride and 4-methylbenzyl chloride were made by chlorination of *p*-xylene in carbon tetrachloride, in the presence of traces of phosphoric oxide so as to inhibit the action of traces of metals which catalyse nuclear chlorination and Friedel–Crafts condensations. *p*-Di-2-chloroethylbenzene was made from *p*-xylylene dichloride through the dicyanide to provide an analogous dichloride for the Wurtz reaction.

On storage, crystals appeared on the surface of the films of *lin*-poly-*p*-xylylene made by pyrolysis. The material was extracted with hot chloroform (Soxhlet), the extract being separated by acetone into two fractions. The acetone-insoluble fraction was a very small proportion of the whole and appeared to be homogeneous, having m. p. 285° after recrystallisation from pyridine and acetic acid. In view of its high melting point this fraction was first thought to be an anthracene, possibly a methylated anthracene. 2 : 7-Dimethylanthracene was prepared by the Friedel–Crafts condensation of toluene and methylene dichloride. The purification was tedious but it was found that co-distillation in ethylene glycol provided a very simple technique. The same hydrocarbon is known to be formed by pyrolysis of *p*-xylene at atmospheric pressure (Meyer and Hofmann, *Monatsh.*, 1916, **37**, 681). Accordingly, this preparation was imitated, and 2 : 7-dimethylanthracene isolated readily from the crude product by co-distillation in ethylene glycol. The samples of 2 : 7-dimethylanthracene differed from the acetone-insoluble fraction in melting point and colour reaction with concentrated sulphuric acid. 2 : 3 : 6 : 7- and 1 : 4 : 5 : 8-Tetramethylanthracenes were also prepared and gave the same colour reaction with concentrated sulphuric acid as did the 2 : 7-dimethylanthracene. It was concluded that the acetone-insoluble fraction was probably not a methylated anthracene. Analysis and molecular-weight determination indicated the molecular formula to be $C_{16}H_{16}$, a dimer of the xylylene radical. Attempts to isolate terephthalic acid from oxidation products of the compound were unsuccessful. Eventually, the compound was shown by *X*-ray analysis to be the cyclic dimer, *tricyclo*[8 : 2 : 2 : $2^{4:7}$]hexadeca-4 : 6 : 10 : 12(1) : 13 : 15-hexaene (I), or di-*p*-xylylene (Brown and Farthing, *Nature*, 1949, **164**, 915; see also Part II, *J.*, 1953, 3265).



(I)

The acetone-soluble fraction was shown to contain at least five fractions by chromatography on alumina. One compound, m. p. 82°, separated by fractional precipitation, was shown (mixed m. p.) to be the linear dimer of *p*-xylene, *viz.*, 4 : 4′-dimethyldibenzyl. As interest was largely centred on the polymer, no more work was done on the acetone-soluble fraction. It may have contained other polymers of the xylenes, such as di-*m*-xylylene or tri-*p*-xylylene which are being examined by Baker *et al.* (*J.*, 1945, 27; *Chem. and Ind.*, 1950, 77). When kept, the acetone-soluble fraction partly sublimed in the form of platy crystals, shown (mixed m. p.) to be 4 : 4′-dimethyldibenzyl. They provided single crystals for *X*-ray examination (Part III, *loc. cit.*). The compound was too soluble to allow the easy growth of suitable crystals from solution.

Authentic samples of 4 : 4′-dimethyldibenzyl were made by the Wurtz condensation of 4-methylbenzyl chloride and by persulphate oxidation of *p*-xylene to see whether higher polymers could be formed by this method, but yields of linear dimer formed in the latter process were low and there was an abundance of oxidation products which were not examined. The former preparation provided a close analogy to the Wurtz condensation of *p*-xylylene dichloride (Part III).

## EXPERIMENTAL

*Preparation of Intermediates.*—*p*-Xylene (setting point 13·1°, 99·6% pure) was purified by filtration, drying ($CaCl_2$), boiling over sodium for 2 hr., and then distillation from the same sodium. It was then stored over " Drierite " (anhydrous $CaSO_4$) until used.

p-*Xylylene dichloride.* Equal weights of *p*-xylene and carbon tetrachloride were placed in a flask fitted with a gas lead and two double-surface reflux condensers in series with a calcium chloride tube and illuminated with a 100-w lamp. A trace of phosphoric oxide was added. Dry chlorine was passed into initially cold *p*-xylene, the flask being heated with a free flame when the heat of reaction was not sufficient to keep the solution gently boiling. Reaction was continued until the mixture solidified completely on standing overnight (approx. 30 hr.' chlorination for 1000 g. of *p*-xylene). This gave appreciable amounts of *p*-methylbenzyl chloride, but reduced the yield of trichloro-derivatives. The reaction mixture was fractionated at 12 mm. with a 6″ × 0·75″ column packed with glass helices, lagged and electrically heated. The first fraction, b. p. 50—95°/11 mm., was liquid, the second, b. p. 98—118°/10 mm., was a mixture of liquid and solid and was rejected, and finally *p*-xylylene dichloride came over at 135°/12 mm. (m. p. 90°). It was recrystallised from xylene, to yield free-flowing crystals, m. p. 98°, not raised by further recrystallisation. The crude product, m. p. 90°, was used for preparation of *p*-xylylene dicyanide. Both the crude and the pure product were mildly dermatitic and lachrymatory.

4-*Methylbenzyl chloride.* The fraction of b. p. 50—95°/11 mm. (above) was redistilled through the same short column in presence of a trace of phosphoric oxide. The bulk passed over at 78°/11 mm. as a colourless liquid. It was stored over a trace of phosphoric oxide.

p-*Di*-2-*chloroethylbenzene.* This was prepared in the usual manner from *p*-xylylene dichloride, through the cyanide (Ruggli and Theilheimer, *Helv. Chim. Acta*, 1941, **24**, 899). The crude product did not crystallise so it was purified by distillation (b. p. 92°/0·25 mm.) and then had m. p. 44°. Attempts to convert *p*-di-2-hydroxyethylbenzene into the dichloride by use of thionyl chloride were unsuccessful.

2 : 7-*Dimethylanthracene.* This was prepared by Morgan and Coulson's method (*J.*, 1929, 2203). The crude tarry product was warmed with water and a little wetting agent (sulphated long-chain alcohol), filtered through sintered glass, and washed with a little cold acetone. This product (1 g.) and pure ethylene glycol (150 c.c.) were distilled. When 100 c.c. had been collected and cooled to room temperature the distillate was filtered and put back to distillation. Three further lots of 50 c.c. were similarly treated. The residue from the filtrations comprised pale cream-coloured plates (0·9 g., 90%), m. p. 235°. Two recrystallisations from acetone gave a solid of constant m. p., 239°. The crystals dissolved in concentrated sulphuric acid to give an intense yellow colour which was discharged on addition to water and became red with a trace of concentrated nitric acid.

2 : 3 : 6 : 7- *and* 1 : 4 : 5 : 8-*Tetramethylanthracene.* These were made by Hey's method (*J.*, 1935, 72; 1938, 1847). They were readily purified by co-distillation with ethylene glycol. Both compounds gave the same yellow colour with concentrated sulphuric acid as did the 2 : 7-dimethylanthracene.

4 : 4′-*Dimethyldibenzyl.* 4-Methylbenzyl chloride (70 g.) and sodium (23 g., 100% excess) in *p*-xylene (redistilled from sodium) were heated under reflux for 2 hr. with stirring. When cold, the mixture was added to ethanol (500 c.c.). Water was added to dissolve the solid, and the ethanol removed by distillation. The residue was diluted with water and extracted with benzene. The extract was dried, and benzene and *p*-xylene were removed *in vacuo.* On cooling, the residual 4 : 4′-dimethyldibenzyl crystallised; it had m. p. 82° from ethanol. No other products were detected. Similarly addition of 4-methylbenzyl chloride (141 g.) during 1 hr. to a boiling suspension of sodium (23 g.) in dioxan (pure, dry, 500 c.c.) gave only 4 : 4′-dimethyldibenzyl.

*Dimerisation of* p-*Xylene by Aqueous Potassium Persulphate* (cf. Moritz and Wolffenstein, *Ber.*, 1899, **32**, 432, 2531).—*p*-Xylene (21·2 g.), potassium persulphate (54 g.), and water (600 c.c.) were stirred at 60—70° for 5 hr. When cold, the mixture was extracted with benzene, and the benzene removed on the steam-bath. There was obtained an oil which partly crystallised. Only 4 : 4′-dimethyldibenzyl could be isolated; aldehydes were present, as shown by formation of 2 : 4-dinitrophenylhydrazones. In view of the by-products, this method did not appear suitable for polymerisation.

*Low-molecular-weight Substances in* lin-*Poly*-p-*xylylene formed by Pyrolysis.*—Several small samples of this *lin*-poly-*p*-xylylene were found to contain varying amounts of chloroform-soluble bodies. In general, polymer prepared with high rates of flow through the pyrolysis apparatus contained the greatest proportion. The following is a typical experiment. *lin*-Poly-*p*-xylylene (3·673 g.) was extracted with redistilled chloroform (150 c.c.) for 4 hr. The chloroform was evaporated to ~3 c.c., and the concentrate washed into a weighed dish with chloroform. Solvent was removed *in vacuo* at room temperature over concentrated sulphuric acid and paraffin wax. There remained 0·923 g. of yellow solid. The extract was made into a slurry with pure dry acetone (5 c.c.), and the bulk dissolved. The residue was collected and washed with a little acetone. The filtrate and washings were kept over concentrated sulphuric acid *in vacuo* until the solvent was removed. There was obtained 0·0247 g. of acetone-insoluble matter.

*Properties of the Acetone-soluble Fraction.*—The fraction was generally a yellow solid; one sample was a mixture of oil and solid. It had the characteristic odour of 4 : 4′-dimethyldibenzyl. In all samples the solid started to melt below 55°, but never had a sharp m. p. It was chromatographed in benzene down a ½″ × 8″ column of alumina type O and developed with light petroleum (b. p. 60—80°). Examination in ultra-violet and visible light showed the following zones, starting from the top, purple (u.v.), brown (visible), yellow (visible), purple (u.v.), yellow (u.v.), and then a large purple (u.v.) zone. On storage, small amounts of sublimate were formed. One sample, in a shallow covered dish, yielded pale yellow plates and after 6 months these were scraped off. They were 4 : 4′-dimethyldibenzyl, shown by m. p. and mixed m. p. 82° (hot-stage microscope) to be identical with the sample prepared as above. The *X*-ray diffraction pattern of the powdered crystals was identical with that of the earlier sample. 4 : 4′-Dimethyldibenzyl was very soluble in all the common organic solvents, and good crystals for *X*-ray analysis could not be grown from solution. The sublimate gave suitable single crystals for an *X*-ray examination (see Part III, *loc. cit.*). The acetone-soluble fraction was fractionally precipitated from ethanol solution by water. A trace of a white solid, m. p. 100—120°, was isolated first, and from the later fractions, after recrystallisation from methanol, there was obtained 4 : 4′-dimethyldibenzyl, m. p. and mixed m. p. 82°. There were also traces of a solid more soluble than 4 : 4′-dimethyldibenzyl.

*Properties of the Acetone-insoluble Fraction.*—The crude product was obviously crystalline, melting range 248—280° (slight decomp.). It could be recrystallised from glacial acetic acid, anhydrous *NN*-dimethylformamide, and pyridine. After three recrystallisations from the last, it had m. p. 285°, unchanged by a further crystallisation from glacial acetic acid (Found : C, 92·1; H, 7·8. $C_{16}H_{16}$ requires C, 92·3; H, 7·7%). The *substance* became red in concentrated sulphuric acid but did not dissolve. Attempts to oxidise it failed. Heating 4 : 4′-dimethyldibenzyl with sulphur at 200° for 12 hr. gave no di-*p*-xylylene, the product being a mixture of sulphur and a black resin. Another attempted synthesis, by the Wurtz condensation of *p*-xylylene dichloride at high dilution, is described in Part III (*loc cit.*).

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