313. *Poly*-p-*xylylene and Related Polymers.*

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Poly-*p*-xylylene and some related polymers have been prepared in good yields by the reaction of phenyl-lithium with di(halogenomethyl) aromatic compounds.

ALTHOUGH poly-*p*-xylylene has been extensively investigated on account of its high thermal stability, most of the work was done with polymers prepared by the pyrolysis of *p*-xylene. Such polymers are sparingly soluble in organic solvents, owing [1,2] to slight cross-linking of the essentially linear chains, and other syntheses [3,4] lead to more readily soluble products. The pyrolytic method is available [5] for the preparation of related polymers, but potential starting materials must be thermally stable and are restricted to those aromatic compounds containing two methyl groups *para* to each other. Accordingly, the formation of polymers by the coupling of di(bromomethyl) compounds, a less severe method of wider potential applicability, has been investigated. Coupling of *p*-di(bromomethyl)benzene by magnesium,[6] Grignard reagents,[7] or sodium [2,3,6,8] yields poly-*p*-xylylene and, since bromomethylarenes are readily coupled [9] by phenyl-lithium (*e.g.*, as in the preparation of aceanthrene,[10] acenaphthene,[11] and 2,3:6,7-dibenzophenanthrene,[12] etc.), the preparation of polymers by this route has been studied.

Reaction of *p*-xylylene dibromide with phenyl-lithium gave poly-*p*-xylylene (74%). Infrared examination of this material, and of specimens prepared by Wurtz–Fittig condensation of the dibromide with sodium–potassium alloy and by pyrolysis of *p*-xylene, revealed

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[1] Corley, Haas, Kane, and Livingston, *J. Polymer Sci.*, 1954, **13**, 137.
[2] Auspos, Burnam, Hall, Hubbard, Kirk, Schaefgen, and Speck, *J. Polymer Sci.*, 1955, **15**, 19.
[3] Vansheydt, Mel'nikova, Kukhareva, and Krakovyak, *Zhur. priklad. Khim.*, 1958, **31**, 1898.
[4] Schaefgen, *J. Polymer Sci.*, 1959, **41**, 133; du Pont de Nemours, B.P. 807,196.
[5] Errede and Swarc, *Quart. Rev.*, 1958, **12**, 302.
[6] Jacobson, *J. Amer. Chem. Soc.*, 1932, **54**, 1513.
[7] Carothers, *Chem. Rev.*, 1931, **8**, 353.
[8] Brown and Farthing, *J.*, 1953, 3270; Muller and Roscheisen, *Chem. Ber.*, 1957, **90**, 543.
[9] Wittig and Witt, *Ber.*, 1941, **74**, 1474.
[10] Bergmann and Ikan, *J. Org. Chem.*, 1958, **23**, 907.
[11] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1953, **75**, 2760.
[12] Bergmann and Ikan, *J. Amer. Chem. Soc.*, 1958, **80**, 208.

their identity, except that slight carbonyl absorption (1681 cm.$^{-1}$) was present only in the pyrolysis product. *X*-Ray powder photographs showed that the phenyl-lithium product was in the α-lin. form described by Brown and Farthing.[8] The molecular weight (M_N 8200) of the phenyl-lithium polymer was calculated from the bromine content, by assuming all end-groups to be bromine; this method is not completely reliable as the presence of some hydrogen end-groups is probable. The polymer was appreciably soluble in high-boiling aromatic solvents.

Poly-*p*-xylylene was also prepared by treating *p*-xylylene dibromide with lithium, but in lower yield, and the product had a lower softening point and smaller molecular weight than the product from the phenyl-lithium reaction.

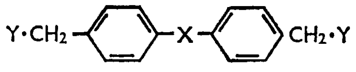
Poly(tetramethyl-*p*-phenylenedimethylene), similarly prepared from *p*-di(chloromethyl)-durene by Wurtz-Fittig reaction and by the action of phenyl-lithium on *p*-di(-iodomethyl)-durene was not appreciably soluble in organic solvents and softened above 400°.

Poly-(2,5-dimethoxy-1,4-phenylenedimethylene) was obtained by reaction of phenyl-lithium with 1,4-di(-iodomethyl)-2,5-dimethoxybenzene. The low softening point (238°) and ease of solubility in bromoform and aromatic solvents of this polymer, as compared with poly-*p*-xylylene, suggests that the substituent methoxy-groups have an internal plasticising effect. The dimethoxy-polymer readily underwent Zeisel cleavage to the corresponding dihydroxy-polymer but attempted oxidation of this by chromic oxide to the poly-quinone was unsuccessful.

The preparation of the di(halogenomethyl) compounds (I; Y = Cl, Br, and I) and their reaction with phenyl-lithium to give the polymers (II) was undertaken since these polymers are inaccessible by the pyrolytic route.

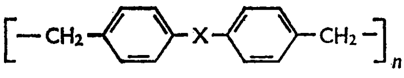
The ether (Ia; Y = H) with bromine in the presence of ultraviolet light gave a complex mixture from which a small quantity of di-*p*-(bromomethyl)phenyl ether was isolated; however, reaction with *N*-bromosuccinimide (cf. selective bromination of methyl-naphthalenes [13]) yielded the required product in good yield. The sulphone (Ib; Y = H) was brominated by *N*-bromosuccinimide (with difficulty) and by bromine,[14] both products after extensive fractional crystallisation yielding di-*p*-(bromomethyl)phenyl sulphone. The ketone (Ic; Y = Br) was also prepared by using *N*-bromosuccinimide, but difficulties were again encountered in the purification. The presence of polyhalogenomethyl contaminants among the products of both the bromine [14] and the *N*-bromo-succinimide [15] reaction is probable.

The iodomethyl compounds (Ia, b, c; Y = I) prepared by halogen exchange from the bromomethyl compounds (Ia, b, c; Y = Br), and di(iodomethyl)durene all showed a marked tendency to lose iodine and correct analytical figures were difficult to obtain. The acetoxy-compounds (Ia, b, c; Y = OAc) were prepared by the action of silver acetate on the bromo-compounds. The 4,4′-di(acetoxymethyl)benzophenone, m. p. 79°, was homogeneous and casts doubt on the purity of the 4,4′-di(chloromethyl)benzophenone prepared by Connerade [16] which, on treatment with silver acetate, yielded a mixture of oil and crystals, m. p. 42—48°, described as the acetoxy-compound (Ic; Y = OAc).



(Ia) X=O ; (Ib) X=SO$_2$

(Ic) X=CO



(IIa) X=O ; (IIb) X=SO$_2$

(IIc) X=CO

Treatment of the sulphone (Ib; Y = H) with sulphuryl chloride yielded the

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[13] Doukas, *J. Chem. Educ.*, 1954, **31**, 12; Ried and Bodem, *Chem. Ber.*, 1958, **91**, 1981.

[14] Horner and Medem, *Chem. Ber.*, 1952, **85**, 520.

[15] Horner and Winkelmann, *Angew. Chem.*, 1959, **71**, 356.

[16] Connerade, *Bull. Soc. chim. belges*, 1933, **42**, 311.

chloro-compound (Ib; $Y = Cl$), but similar reactions with the ether and ketone yielded complex mixtures which could not be completely separated.

The polymers (IIa, b) were prepared by the action of phenyl-lithium on the bromo-compounds (Ia, b; $Y = Br$). The poly-ether, softening point 185°, was readily soluble in halogenated solvents and aromatic hydrocarbons; its molecular weight was determined by end-group analysis (5070) and cryoscopy (6300). The poly-sulphone was almost insoluble in organic solvents and had a much higher softening point [>360° (decomp.)].

The product obtained by reaction of a mixture of *p*-xylylene dibromide and di-*p*-(bromomethyl)phenyl ether with phenyl-lithium gave elemental analyses and an infrared spectrum between those of the two homopolymers. The low solubility and high melting point suggest a copolymer rather than a mixture of two homopolymers, one of which should be readily extractable.

Treatment of 4,4′-di(bromomethyl)benzophenone with phenyl-lithium did not yield polymer, as a preferred reaction involved the carbonyl group; the microanalysis and infrared analysis of the product were consistent with the structure 4,4′-di(bromomethyl)-triphenylmethanol.

The infrared spectra of all the polymers prepared by phenyl-lithium reactions closely resembled those of the respective simple dimethyl compounds, apart from the aliphatic vibrations, and this, together with the other physical properties examined, suggests an essentially linear structure for these polymers.

The ether (Ia; $Y = H$) was oxidised to the corresponding di-acid which was converted (cf. Conix [17]) into its poly-anhydride, softening point 315—320°, sparingly soluble in high-boiling aromatic solvents.

The reported reaction [18] of 4-bromobenzyl bromide with butyl-lithium to give 4-*p*-bromobenzylbenzyl bromide, m. p. 112—113°, was re-investigated, as extension of this reaction would provide a route to the unknown poly-*p*-benzylene:

$$\mathrm{Br{\cdot}C_6H_4{\cdot}CH_2Br} \longrightarrow \mathrm{Br{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2Br} \longrightarrow \mathrm{[C_6H_4{\cdot}CH_2]_n}$$

In the present case only 1-bromo-4-pentylbenzene (24%) and 4,4′-dibromobibenzyl (49%), m. p. 114—116°, were isolated. It appears that the reported [28] compound of m. p. 112—113° was in fact the bibenzyl so that the reaction is analogous to the coupling of *o*-bromobenzyl bromide.[19]

EXPERIMENTAL

Yields of polymers are based on the theoretical structures, end-groups etc. being neglected. Softening points given for polymers are the temperatures at which viscous melts were obtained on a Kofler hot-stage.

*Poly-*p*-xylylene.*—(a) *Lithium coupling.* *p*-Xylylene dibromide (26·4 g.) in ether (200 ml.) was added dropwise to a stirred suspension of finely divided lithium (5·6 g.) in ether (100 ml.) during 1 hr. The solution was refluxed for 24 hr., stirred at room temperature for 3 days, treated with methanol (100 ml.), and poured into 5% acetic acid (1 l.). Filtration yielded a solid (7·2 g.) which was exhaustively extracted with ether, leaving a white powder (6·7 g., 64%). Extraction of a sample with 4 : 1 ethanol–concentrated hydrochloric acid and organic solvents gave poly-*p*-xylylene [Found: C, 89·2; H, 7·7; Br, 2·9. Calc. for $(C_8H_8)_{51}Br_2$: C, 89·7; H, 7·4; Br, 2·9%], softening pt. 230—233°, soluble in high-boiling solvents, *e.g.*, nitrobenzene, biphenyl, diphenyl ether.

(b) *Phenyl-lithium coupling.* An ether solution of phenyl-lithium (7·64 g. in 250 ml.) was added dropwise to a stirred solution of *p*-xylylene dibromide (24 g.) in ether (400 ml.) during 45 min. The white suspension was refluxed for 30 min. and then decomposed with 10% acetic acid (200 ml.). After filtration and separation *p*-xylylene dibromide (2·3 g.) was recovered from the ether layer. The white precipitate was extracted (Soxhlet) with ether, leaving poly-*p*-xylylene (6·3 g., 74%), almost insoluble in high-boiling solvents. Extraction of a sample as in (a) caused no loss in weight. The polymer [Found: C, 90·7; H, 7·5; Br, 1·95. Calc. for

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[17] Conix, *Makromol. Chem.*. 1957, **24**, 76; *J. Polymer Sci.*, 1958, **29**, 343.

[18] Rosenberg, *J. Amer. Chem. Soc.*, 1954, **76**, 4389.

[19] Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 5176.

$(C_8H_8)_{77}Br_2$: C, 90·4; H, 7·6; Br, 2·0%] had a softening pt. >370° and *X*-ray powder pattern: 5·38s, 4·00s, 3·50vw, 3·06vw, 2·81vw Å (compare α-lin form [8]).

Di(chloromethyl)durene.—Hydrogen chloride was passed into a stirred mixture of durene (100 g.), paraformaldehyde (92 g.), and anhydrous zinc chloride (200 g.) in glacial acetic acid (2 l.) at 70—80° during 24 hr. The cooled solution was filtered from grey crystals (122 g.), m. p. 185°, and the liquors were treated with water to yield a second crop of crystals. Recrystallisation of the combined crops from benzene gave di(chloromethyl)durene (112 g., 65%), m. p. 196° (Rhoad and Flory [20] give m. p. 193—194°).

Di(iodomethyl)durene.—Sodium iodide (80 g.) in acetone (200 ml.) was added to a solution of di(chloromethyl)durene (46 g.) in refluxing acetone. After refluxing for 4 hr. the mixture was poured into water (4 l.). The washed precipitate (78·5 g.), m. p. 213° (decomp.), recrystallised from chloroform as pale yellow needles (70 g., 85%), m. p. 213° (decomp.). Further recrystallisation (from benzene) gave pure *di(iodomethyl)durene* (Found: C, 35·1; H, 3·8; I, 61·6. $C_{12}H_{16}I_2$ requires C, 34·8; H, 3·9; I, 61·3%), m. p. 214° (decomp.).

*Poly(tetramethyl-*p*-phenylenedimethylene).*—(a) *Coupling by sodium–potassium alloy.* Sodium–potassium alloy (1·5 g.) was added dropwise to a stirred solution of di(chloromethyl)-durene (5 g.) in dioxan (125 ml.) at 60° during 1 hr. The temperature was raised during 1 hr. and the solution then refluxed for 10 hr. Ethanol–light petroleum (b. p. 60—80°) (1 : 10) was added and the sludge filtered off, washed with ethanol and water, and dried. The *polymer* [Found: C, 87·5, 88·3; H, 9·1, 9·6; Cl, 0·34, 0·33. $(C_{12}H_{16})_n$ requires C, 90·0; H, 10·0%] (2·7 g., 78%) was obtained as a cream powder softening at >400°, having negligible solubility in organic solvents. The combined liquors were treated with benzene and water; the benzene layer yielded a cream solid (1 g.), softening pt. 165—180°. (b) *Phenyl-lithium coupling.* Phenyl-lithium (10·3 g.) in ether (250 ml.) was added to a refluxing solution of di(iodomethyl)-durene (25·3 g.) in benzene (500 ml.) during 1·5 hr., the ether being removed by distillation. The solution was refluxed for a further 1 hr., kept overnight, decomposed with methanol (50 ml.), and poured into 10% hydrochloric acid (1 l.). The white solid was filtered off, washed thoroughly, dried, and then refluxed with ethanol–concentrated hydrochloric acid (1 : 1). The washed, dried *polymer* [Found: C, 86·5; H, 9·3; I, 4·3. $(C_{12}H_{16})_{35}I_2$ requires C, 86·0; H, 9·6; I, 4·3%] (9·6 g., 98%) had softening pt. >400°. The polymer was almost insoluble in high-boiling solvents but was swollen by 1-chloronaphthalene and benzyl benzoate. The *X*-ray powder pattern was 5·72m, 4·07w, 3·87w, 3·29vw Å.

2,5-Di(iodomethyl)-1,4-dimethoxybenzene.—2,5-Di(chloromethyl)-1,4-dimethoxybenzene [21] underwent halogen exchange with sodium iodide in acetone, to give *2,5-di(iodomethyl)-1,4-dimethoxybenzene* (96%), as pale yellow needles (from acetone or benzene) (Found: C, 28·5; H, 3·3; I, 61·0. $C_{10}H_{12}I_2O_2$ requires C, 28·7; H, 2·9; I, 60·7%), decomp. 136°. The iodo-compound lost iodine when heated alone or in, *e.g.*, toluene.

*Poly-(2,5-dimethoxy-*p*-phenylenedimethylene).*—Phenyl-lithium (8·4 g.) in ether (250 ml.) was added to a stirred refluxing solution of 2,5-di(iodomethyl)-1,4-dimethoxybenzene (20·9 g.) in benzene (300 ml.) during 1 hr., the ether being removed continuously. After a further hour the brown reaction mixture was decomposed with water (500 ml.), just acidified, and filtered. The precipitated polymer was washed with methanol and water and dried (7·1 g.). The product was purified by precipitation from bromoform into methanol, refluxed with ethanol–concentrated hydrochloric acid (1 : 1) for 8 hr., washed with water and ethanol, and dried (6·6 g., 80%). *Poly-(2,5-dimethoxy-*p*-phenylenedimethylene)* [Found: C, 73·0; H, 7·6; I, 2·6. $(C_{10}H_{12}O_2)_n$ requires C, 73·15; H, 7·3%] was obtained as a white powder, softening pt. 238°, soluble in bromoform and aromatic solvents.

*Poly-(2,5-dihydroxy-*p*-phenylenedimethylene).*—Poly-(2,5-dimethoxy-*p*-phenylenedimethylene) [Found: MeO, 34·5. $(C_{10}H_{12}O_2)_n$ requires MeO, 37·8%] underwent Zeisel cleavage to give the infusible *2,5-dihydroxy-polymer* [Found: C, 71·0; H, 5·2; I, 2·9. $(C_8H_8O_2)_n$ requires C, 70·6; H, 5·9%] as a chocolate-brown powder, insoluble in organic solvents and aqueous potassium hydroxide.

*Di-*p*-(bromomethyl)phenyl Ether.*—(a) *Use of* N*-bromosuccinimide.* A mixture of *N*-bromosuccinimide (80 g.) and benzoyl peroxide (1 g.) was added in portions during 20 min. to a refluxing solution of di-*p*-tolyl ether [22] (40 g.) and benzoyl peroxide (0·5 g.) in benzene (120 ml.). The

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[20] Rhoad and Flory, *J. Amer. Chem. Soc.*, 1950, **72**, 2216.

[21] Shimizu and Maki, *J. Pharm. Soc. Japan*, 1951, **71**, 958.

[22] Barrett, Drumm, and Reilly, *J.*, 1927, 67.

cooled solution was filtered from succinimide (44·4 g.; m. p. 127°), washed with aqueous sodium hydroxide and water, dried (Na_2SO_4; charcoal), filtered, and concentrated. The solid residue (75·2 g.), recrystallised from cyclohexanol, had m. p. 92° (43·9 g., 61%). Extractive recrystallisation from light petroleum (b. p. 60—80°) yielded the *dibromo-ether* (Found: C, 47·3; H, 3·7; Br, 44·9. $C_{14}H_{12}Br_2O$ requires C, 47·2; H, 3·4; Br, 44·9%) as colourless flakes, m. p. 98°.

(b) *Use of bromine.* Di-*p*-tolyl ether (19·8 g.) at 200—220° was irradiated with ultraviolet light and treated dropwise with bromine (32 g.) during 30 min. Working up yielded a neutral oil (44·2 g.) which on distillation (accompanied by considerable decomposition) yielded a fraction (4·1 g.), b. p. 231—240°/0·5 mm., n_D^{22} 1·6192, m. p. 87° alone or mixed with material prepared as under (a).

(c) *Reduction.* Di-*p*-(bromomethyl)phenyl ether (0·76 g.) and zinc dust (3 g.), suspended in acetic acid (20 ml.), were treated with a few drops of aqueous cupric sulphate and refluxed for 6 hr. Working up of the product gave di-*p*-tolyl ether (0·35 g.), m. p. and mixed m. p. 48—49° (from light petroleum).

(d) *Hydrolysis.* Di-*p*-(bromomethyl)phenyl ether (10 g.) was refluxed with 15% aqueous potassium hydroxide (100 ml.) for 32 hr. Working up yielded a glassy *diphenol* (6·2 g.) (Found: C, 77·3; H, 5·7%. $H\cdot[C_{14}H_{12}O_2]_3\cdot OH$ requires C, 77·0; H, 5·85%), m. p. 87—88°, soluble in aromatic hydrocarbons, dioxan, and chloroform, insoluble in light petroleum, alcohols, and esters.

*Di-*p*-(bromomethyl)phenyl Sulphone.*—(a) *Use of bromine.* Di-*p*-tolyl sulphone [23] (85 g.) at 160—180° was irradiated with ultraviolet light and treated dropwise with bromine (35·4 ml.) during 1 hr. After a further 2 hr. at 160° the mixture was poured into chloroform (1 l.) and was washed with aqueous sodium carbonate and water and dried (Na_2SO_4; charcoal). The filtrate was evaporated. The residue (140 g.), m. p. 90—95°, was fractionally crystallised (8 stages) from methanol–chloroform and benzene–cyclohexane alternately, yielding colourless plates of di-*p*-(bromomethyl)phenyl sulphone (Found: C, 41·6; H, 3·0; Br, 40·0; S, 8·35. Calc. for $C_{14}H_{12}Br_2O_2S$: C, 41·6; H, 3·0; Br, 39·55; S, 7·9%), m. p. 148—149° (Horner and Medem [14] give m. p. 148°). Di-*p*-tolyl sulphone was recovered after being refluxed for 6 hr. with bromine in carbon tetrachloride under ultraviolet irradiation. (b) *Use of* N-*bromosuccinimide.* A solution of di-*p*-tolyl sulphone (41 g.), *N*-bromosuccinimide (69 g.), and benzoyl peroxide (1·5 g.) in carbon tetrachloride (120 ml.) was refluxed for 32 hr. Working up as described for the ether gave a brown oil (63 g.) which on extensive fractional crystallisation, as in (a), yielded the dibromo-sulphone (2·5 g.), m. p. 143—146°. No reaction occurred when di-*p*-tolyl sulphone was treated with *N*-bromosuccinimide under the conditions described for the corresponding ether.

4,4′-Dimethylbenzophenone.—Condensation of toluene and carbon tetrachloride was carried out according to Gomberg and Todd's directions,[24] but distillation of the crude oily product led to polymerisation. However, addition of light petroleum (b. p. 40—60°) to the oil at 0° yielded the ketone which, recrystallised from light petroleum (b. p. 60—80°), had m. p. 90—91° (30% yield).

4,4′-Di(bromomethyl)benzophenone.—Di-*p*-tolyl ketone (84 g.) with *N*-bromosuccinimide (160 g., 10% excess) gave a product (194 g.) that, crystallised by extraction (Soxhlet) with cyclohexane, had m. p. 120—123° (65 g.). This was difficult to purify but extensive fractional crystallisation from chloroform–ethanol and cyclohexane yielded needles (12 g.) of *4,4′-di(bromomethyl)benzophenone* (Found: C, 48·9; H, 3·1; Br, 43·8. $C_{15}H_{12}Br_2O$ requires C, 49·0; H, 3·3; Br, 43·4%), m. p. 138—139°.

*Di-*p*-(iodomethyl)phenyl Ether.*—A solution of di-*p*-(bromomethyl)phenyl ether (5 g.) and sodium iodide (10 g.) in acetone (200 ml.) was refluxed for 1 hr. and poured into water (1·5 l.). Filtration gave a pale yellow solid (5·5 g., 88%), m. p. 104—105°. Recrystallisation from acetone–methanol and light petroleum (b. p. 60—80°) yielded *di-*p*-(iodomethyl)phenyl ether* (Found: C, 37·75; H, 2·8; I, 56·45. $C_{14}H_{12}I_2O$ requires C, 37·4; H, 2·7; I, 56·4%) as pale yellow needles, m. p. 107—108°.

*Di-*p*-(iodomethyl)phenyl Sulphone.*—Di-*p*-(bromomethyl)phenyl sulphone was converted, as was the corresponding ether, into the *iodo-compound* (90%), needles (from methanol–acetone and chloroform–light petroleum) (Found: C, 34·2; H, 2·5; I, 50·4; S, 6·4. $C_{14}H_{12}I_2O_2S$ requires C, 33·8; H, 2·4; I, 51·0; S, 6·4%), m. p. 169°.

*4,4′-Di-*p*-(iodomethyl)benzophenone.*—The dibromo-ketone was converted, as was the ether,

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[23] Meyer, *Annalen*, 1923, **433**, 327.

into the *iodo-compound* (95%, yellow needles (from acetone–methanol and cyclohexane) (Found: C, 39·4; H, 2·8; I, 54·3. $C_{15}H_{12}I_2O$ requires C, 39·0; H, 2·6; I, 54·9%), m. p. 141°.

*Di-*p*-(acetoxymethyl)phenyl Ether.*—Di-*p*-(bromomethyl)phenyl ether (3 g.) in acetic acid (50 ml.) at 75° was treated with a solution from silver oxide (4 g.) in acetic acid (25 ml.). The mixture was refluxed for 15 min., cooled, and filtered (kieselguhr) from silver bromide into water (1·5 l.). Extraction with ether and working up of the extract gave a sticky solid (2·3 g.), m. p. 44°, very soluble in organic solvents. Recrystallisation from light petroleum (b. p. 30—40°) yielded *di-*p*-(acetoxymethyl)phenyl ether* (Found: C, 68·8; H, 6·0. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·8%) as colourless leaflets, m. p. 50°. The acetoxy-compound was not obtained by the action of lead tetra-acetate on di-*p*-tolyl ether in acetic acid.

*Di-*p*-(acetoxymethyl)phenyl Sulphone.*—Di-*p*-(bromomethyl)phenyl sulphone was converted, as described for the ether, into the *acetoxy-compound* (83%) needles from benzene–light petroleum (b. p. 60—80°) (Found: C, 59·4; H, 5·1; S, 9·15. $C_{18}H_{18}O_6S$ requires C, 59·65; H, 5·0; S, 8·8%, m. p. 107°.

*4,4'-Di-*p*-(acetoxymethyl)benzophenone.*—Di-*p*-(bromomethyl)benzophenone was converted, as described for the ether, into the acetoxy-compound (96%), needles from light petroleum (b. p. 40—60°) (Found: C, 70·1; H, 5·2. Calc. for $C_{19}H_{18}O_5$: C, 69·9; H, 5·6%), m. p. 79° (Connerade [16] gives m. p. 42—48°).

*Di-*p*-(chloromethyl)phenyl Sulphone.*—Benzoyl peroxide (0·75 g.) and sulphuryl chloride (18 ml.) in carbon tetrachloride (40 ml.) were added to a refluxing solution of di-*p*-tolyl sulphone (24·6 g.) and benzoyl peroxide (0·25 g.) in carbon tetrachloride (150 ml.) during 1 hr. The mixture was refluxed for a further 16 hr., cooled, diluted to 500 ml. with carbon tetrachloride, washed with aqueous sodium hydrogen carbonate and water, dried (K_2CO_3), filtered, and concentrated to an oil (32·4 g.). When diluted with cyclohexane and kept for several weeks at 0° this afforded a solid (7·6 g.), m. p. 114—118°, whence recrystallisation from light petroleum (b. p. 60—80°) (yield 6·2 g.) and then from methanol gave *di-*p*-(chloromethyl)phenyl sulphone* (Found: C, 55·0; H, 3·85; Cl, 22·9; S, 10·4. $C_{14}H_{12}Cl_2O_2S$ requires C, 53·35; H, 3·8; Cl, 22·5; S, 10·2%) as colourless rods, m. p. 139°. Treatment of this compound with sodium iodide in acetone gave the iodo-compound, m. p. and mixed m. p. 169°. No halogen interchange occurred on treatment of the chloro-compound with sodium or potassium bromide in acetone.

*Reaction of Di-*p*-tolyl Ether with Sulphuryl Chloride.*—Chlorination of the ether (19·8 g.), as described for the sulphone, gave an oil which on repeated distillation yielded a fraction (0·89 g.), b. p. 233—234°/17 mm., n_D^{24} 1·5942 (Found: C, 61·8; H, 4·8; Cl, 27·2. Calc. for $C_{14}H_{12}Cl_2O$: C, 62·9; H, 4·5; Cl, 26·5%), which partly crystallised (m. p. 59°) (Plieninger, Horn, and Lutz [25] give m. p. 68°).

Reaction of 4,4'-Dimethylbenzophenone with Sulphuryl Chloride.—Chlorination of the ketone (21 g.), as described for the sulphone, gave a sticky solid (32·5 g.), recrystallisation of which from cyclohexane and light petroleum yielded needles (16·8 g.), m. p. 103° (Found: C, 64·7; H, 4·4; Cl, 25·25. Calc. for $C_{15}H_{12}Cl_2O$: C, 64·5; H, 4·3; Cl, 25·4%). Connerade [16] gives m. p. 110·5° for di-*p*-(chloromethyl)phenyl ketone. Attempted conversion of the chloro- into the acetoxy-derivative yielded an intractable mixture.

Poly-[p,p'*-oxidodi(phenylmethylene)*] (IIa).—(a) *Homopolymer.* Phenyl-lithium (9·44 g.) in ether (250 ml.) was added dropwise to a stirred solution of di-*p*-(bromomethyl)phenyl ether (20 g.) in ether–benzene (500 ml.; 10 : 1) during 1 hr. The solution was stirred for a further 15 min., decomposed with water (200 ml.), and filtered. The white precipitate was washed with 2N-hydrochloric acid, water, and ethanol, and dried (9·9 g.). Addition of a filtered benzene solution of the solid to ether, and repetition of this procedure, yielded the *poly-oxide* [Found: C, 82·9; H, 6·1; Br, 3·2%; *M*, cryoscopic in naphthalene, 6300. $(C_{14}H_{12}O)_{25}Br_2$ requires C, 82·95; H, 6·0; Br, 3·15%; *M*, 5066] as a white powder (6·9 g., 63%), softening pt. 185° The polymer was soluble in aromatic hydrocarbons, chloroform, and bromoform, but insoluble in acids, alcohols, and light petroleum, and swollen by cyclohexanol and carbon tetrachloride. On *X*-ray powder analysis it gave lines at 4·68s, 4·37w, 4·27m, 4·14s, 3·26m Å, and it had $\nu_{max.}$ 1241s, 1259s (aromatic ether), 2855, 2920 cm.$^{-1}$ (CH stretch). Di-*p*-tolyl ether had $\nu_{max.}$ 1242s, 2859, 2872, 2919 cm.$^{-1}$.

(b) *Copolymer with poly-*(p*-phenylenedimethylene*). A refluxing solution of di-*p*-(bromomethyl)phenyl ether (18 g., 1·1 mol.) and *p*-xylylene dibromide (12·35 g., 1 mol.) in benzene

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[24] Gomberg and Todd, *J. Amer. Chem. Soc.*, 1917, **39**, 2392.
[25] Plieninger, Horn, and Lutz, *Arch. Pharm.*, 1953, **286**, 285.

(350 ml.) was treated dropwise with phenyl-lithium (4·32 g.) in ether (140 ml.) during 45 min., ether being removed throughout. After a further 15 min. the mixture was worked up as in (a), to yield a white powder (5·7 g.) which closely resembled poly-*p*-xylylene in solubility. Extraction with alcohols and ether left the *copolymer* (5·6 g.) (Found: C, 86·2; H, 7·1; Br, 5·6%. Analysis intermediate between those of the homopolymers), m. p. >400°, $\nu_{max.}$ 1232 cm.$^{-1}$ (aromatic ether).

Poly-[p,p′-*sulphonyldi(phenylmethylene)*] (IIb).—Phenyl-lithium (5·0 g.) in ether (250 ml.) was added dropwise to a refluxing solution of di-*p*-(bromomethyl)phenyl sulphone (12 g.) in ether (500 ml.) during 1 hr. The dark red-brown suspension was stirred for a further 15 min., decomposed by water (100 ml.), and just acidified. Filtration yielded a white solid which was washed with solvents and water (yield 7·4 g.), refluxed with 1 : 1 ethanol–concentrated hydrochloric acid (250 ml.) for 8 hr., washed with water and solvents, and dried, to give the *poly-sulphone* [Found: C, 68·2; H, 4·9; S, 13·2; Br, 0. $(C_{14}H_{12}O_2S)_n$ requires C, 68·8; H, 4·95; S, 13·1%] as a white powder (6·6 g., 90%), m. p. >360° (decomp.). This was almost completely insoluble, even in high-boiling aromatic solvents and had $\nu_{max.}$ 1151s, 1300s, 1318s (SO_2), 2857, 2926 (CH stretch). Di-*p*-tolyl sulphone had $\nu_{max.}$ 1148s, 1153s, 1294s, 1304s, 1319s, 2862, 2871, 2923, 2954.

Reaction of 4,4′-*Di(bromomethyl)benzophenone with Phenyl-lithium.*—Phenyl-lithium (2·77 g.) in ether (250 ml.) was added dropwise during 1 hr. to the bromo-compound (6 g.) in 1 : 1 benzene–ether (600 ml.) at 40°. The mixture was then decomposed by 10% acetic acid (150 ml.) and filtered (<0·1 g. of infusible solid). The organic layer was washed, dried, and concentrated to give a pale yellow oil (6·5 g.); the aqueous layer yielded no organic products. Repeated treatment of the oil with light petroleum (b. p. 60—80°) yielded a white solid (4·5 g.), m. p. 108—113°; recrystallisation (cyclohexane) of this 4,4′-*di(bromomethyl)triphenylmethanol* gave colourless rhombs (Found: C. 56·6; H, 3·9; Br, 32·7. $C_{21}H_{18}Br_2O$ requires C, 56·5; H, 4·0; Br, 35·8%), m. p. 121°; infrared analysis indicates the presence of OH (1153 and 3460 cm.$^{-1}$) and *p*-disubstituted benzene (1650—2000 cm.$^{-1}$), and absence of C=O. No reaction was effected between the starting material and lithium shavings in ether.

*Di-*p*-carboxyphenyl Ether.*—The method of Barrett *et al.*[22] led, in our hands, to impure mixtures of mono- and di-acid; instead, di-*p*-tolyl ether (17·1 g.), potassium permanganate (60 g.), and water (2 l.) were stirred and refluxed for 6 hr. The hot solution was filtered, cooled, and extracted with chloroform to remove unchanged ether (6·1 g.). The aqueous layer was concentrated to 1·5 l. and strongly acidified. The precipitate was filtered off and washed with water to give di-*p*-carboxyphenyl ether (8·5 g., 59%), m. p. 335—336° (equiv., 122·2. Calc., 129); the dimethyl ester formed needles (from benzene), m. p. 157° (Tomita[26] gives m. p. 153°).

The di-acid (5·148 g.) was dissolved in acetic anhydride (10 ml.) and heated at 280°/11 mm. for 2 hr. The residue (4·877 g.) was heated for 1 day at 280° and for 3 days at 280°/10^{-3} mm. The *poly-anhydride* [Found: C, 69·3; H, 3·6. $(C_{14}H_8O_4)_n$ requires C, 70·0; H, 3·4%], obtained as a tan powder (4·741 g.), softening pt. 320—322°, was soluble in benzyl benzoate but not in low-boiling solvents and was decomposed by sulphuric acid.

Reaction of 4-Bromobenzyl Bromide with Butyl-lithium.—Butyl-lithium (7·74 g.) in ether (250 ml.) was added dropwise during 20 min. to a stirred solution of 4-bromobenzyl bromide[27] (33 g.) in ether (200 ml.) at −30°. The solution was allowed to warm to room temperature and then refluxed for 8 hr. Treatment with methanol (20 ml.) and 5% hydrochloric acid (600 ml.) gave a clear solution. Extraction with ether gave a yellow oil (28 g.). Distillation of the oil yielded 1-bromo-4-pentylbenzene (7·1 g., 24%), b. p. 147—148°/19 mm., $n_D^{20·5}$ 1·5302, and 4,4′-dibromobibenzyl (11·1 g., 49%), b. p. 200—300°/19 mm., needles (from ethanol), m. p. 114—116°, undepressed on admixture with a specimen prepared by bromination of bibenzyl.[28]

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[26] Tomita, *J. Pharm. Soc. Japan*, 1937, **57**, 609.
[27] Shoesmith and Slater, *J.*, 1926, 214.
[28] Stelling and Fittig, *Annalen*, 1866, **137**, 267.