

mixtures was tried, but the only successful method was that using the infrared spectrum. Cyclohexane was found to be the most satisfactory solvent, and 0.3 *M* solutions were used throughout. Curves of % ketone against the 5.93 μ carbonyl peak intensity and of % ether against the 8.88 μ band intensity were constructed using mixtures of known amounts of ketone and ether. The analysis for % ketone was very satisfactory since the base line near 6 μ was very stable from one reaction mixture to the next. The base line near 9 μ was not as stable and led to some uncertainty about the % ether in the reaction products. For this reason, all of the rate constants are given for the appearance of ketone. In all cases, the rate of disappearance of ether and the rate of appearance of ketone (presumably both the product ketone and that formed by the initiation step since they have the same carbonyl band) was the same within experimental error.

Analysis for β -Cyanoisovalerophenone.—The rearrangement of α -benzyloxystyrene was carried out under the conditions for run 8, using azo-bis-isobutyronitrile- C^{14} , for a period of 24 hr. The contents of the tube were transferred to a flask with benzene, and a weighed quantity of β -cyano-isovalerophenone (quantities given in Table III) was added. The benzene was evaporated, and concentrated hydrochloric acid (16.5 ml.) and water (20 ml.) were added. After heating to reflux for 24 hr., the solution was made basic and was extracted three times with ether. The aqueous solution was acidified and extracted with three 30-ml. portions of ether. Evaporation of this ether solution, followed by recrystallization from petroleum ether-benzene, gave the β -benzoyl- α,α -dimethylpropionic acid, m.p. 169.5–171°; 2,4-dinitrophenylhydrazone, m.p. 197.5–198.5°. ¹² The activity

of the sample was determined by liquid scintillation counting¹³ giving the data in Table III.

Analysis for Dibenzyl and Toluene.— α -Benzyl- C^{14} -oxystyrene was prepared by the procedure described above, except that benzyl- C^{14} alcohol was used. The rearrangement was carried out as above, and the contents of the tube were placed in a flask containing 25 ml. of toluene and a weighed quantity of dibenzyl. The mixture was warmed until the contents of the tube had dissolved, and was heated under reflux for 5 minutes. The toluene was separated by distillation, and a middle fraction was taken for C^{14} analysis. To the residue was added 15 ml. of pentane, and the precipitated β -phenylpropionophenone was removed by filtration. The pentane was added to an alumina-packed column, which was then eluted with pentane. The dibenzyl came through rapidly, and was shown to have less than 0.1% of the ketone by comparing the intensities of the ultraviolet absorption at 244 and 269 m μ . A very small amount of ketone will cause a noticeable change in the ratio of intensities at these two wave lengths. The dibenzyl was further purified by three (sample 1) or four (sample 2) recrystallizations from ethanol-water. The data for the C^{14} analyses are given in Table IV.

The thermal rearrangement was carried out at 174° for 18 hr. (about 10 half-lives) using 3.11 g. of the benzyloxystyrene. To this was added 3.11 g. of dibenzyl and the latter was isolated as described above.

(12) E. Rothstein and M. Saboor, *J. Chem. Soc.*, 425 (1943), reported acid m.p. 173°; 2,4-dinitrophenylhydrazone, m.p. 198–199°.

(13) The C^{14} analyses were performed by the New England Nuclear Assay Co., Boston, Mass.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO]

Polymerization of Benzene to *p*-Polyphenyl by Aluminum Chloride-Cupric Chloride¹

BY PETER KOVACIC AND ALEXANDER KYRIAKIS²

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Benzene is polymerized under remarkably mild conditions on treatment with aluminum chloride-cupric chloride-water to a solid possessing the properties of *p*-polyphenyl. Evidence for the structural assignment is based upon the C/H atomic ratio obtained from elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, oxidative degradation, insolubility, color and thermal stability. The polymer is very similar in its properties to the *p*-polyphenyl prepared previously by Marvel and Hartzell by another method. The reaction is believed to proceed by oxidative cationic polymerization of the aromatic nuclei.

Introduction

The literature appears to contain no reports on the use of benzene as a monomer in well-defined polymerizations leading to homopolymers. However, benzene is known to give resins, dark-colored solids, and other uncharacterized higher molecular weight products on treatment with aluminum chloride or aluminum bromide.³ Usually, rather drastic conditions were employed. More than sixty years ago, Thomas⁴ found that treatment of benzene with ferric chloride resulted in formation of a black solid. In a more recent investigation, Kovacic and Wu⁵ reported data indicating the presence of polynuclear structures in this product, apparently formed by oxidative cationic polymerization. In a related area concerned with benzene polymerization, evidence has been presented by Stockmayer and Peebles⁶ for the free radical copolymerization of benzene with vinyl acetate.

Polymers containing polyphenyl structures have been synthesized by various procedures. Marvel and Hartzell⁷ prepared impure *p*-polyphenyl by chloranil oxidation of poly-1,3-cyclohexadiene which was obtained

by Ziegler polymerization. In general, use was made by other investigators of the Fittig and Ullmann methods.⁸ For example, treatment of *p*-dichlorobenzene with sodium-potassium alloy gave a polyphenyl which, however, possessed structural irregularities.^{8a} Polymerization is also reported to occur on heating *p*-dibromobenzene with activated copper.⁹ In studies involving catalytic hydrogenation of dibromobenzene in the presence of methanol, Busch and co-workers¹⁰ isolated polyphenyls through the septiphenyl homolog in the *para* series. It is claimed that oily or waxy polyphenyls are formed in high yield from a mixture of benzene and biphenyl in the presence of sulfur at 650–950°.¹¹ Organometallic compounds have also been used as precursors for this type of polymer, e.g., in the reaction of dilithium benzene with heavy metal halides.^{12a,b} Electrolysis of phenylmagnesium bromide gave small amounts of incompletely characterized polymer presumed to be polyphenyl.^{12c} Low molecular weight polyphenyls containing halogen or alkyl substituents have been prepared by the Fittig and Ullmann syntheses.¹³ As an outgrowth of their

(1) Paper II in the series, "Polymerization of Aromatic Nuclei"; an abstract of the M.S. thesis of Alexander Kyriakis, Case Institute of Technology, 1962; preliminary communication, *Tetrahedron Letters*, 467 (1962); presented at the 142nd National Meeting of the American Chemical Society.

(2) American Chemical Society-Petroleum Research Fund Fellow, 1961.

(3) C. H. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 716.

(4) V. Thomas, *Compt. rend.*, **126**, 1211 (1898).

(5) P. Kovacic and C. Wu, *J. Polymer Sci.*, **47**, 45 (1960).

(6) W. H. Stockmayer and L. H. Peebles, Jr., *J. Am. Chem. Soc.*, **75**, 2278 (1953).

(7) C. S. Marvel and G. E. Hartzell, *ibid.*, **81**, 448 (1959).

(8) (a) G. A. Edwards and G. Goldfinger, *J. Polymer Sci.*, **16**, 589 (1955); (b) G. Goldschmidt, *Monatsh.*, **7**, 40 (1886); (c) W. Fuchs and H. Metz, *Ber.*, **55**, 738 (1922).

(9) A. A. Berlin, *J. Polymer Sci.*, **55**, 621 (1961).

(10) M. Busch, W. Weber, *et al.*, *J. prakt. Chem.*, **146**, 1 (1936).

(11) W. H. Williams, U. S. Patent 1,976,468 (1934).

(12) (a) G. Wittig and F. Bickelhaupt, *Ber.*, **91**, 883 (1958); (b) V. Y. Bogomolny and B. A. Dolgoplosk, *Akad. Nauk SSSR Izv. Old., Khim. Nauk*, 1912 (1961); (c) W. V. Evans, R. Pearson and D. Braithwaite, *J. Am. Chem. Soc.*, **63**, 2574 (1941).

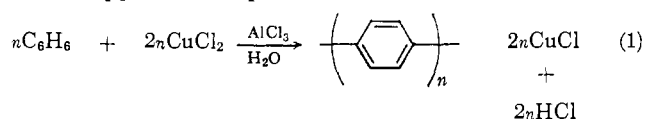
(13) (a) M. Hellmann, A. J. Bilbo and W. G. Pummer, *ibid.*, **77**, 3650 (1955); (b) W. Kern and O. H. Wirth, *Kunststoffe-Plastics*, **6**, 12 (1959).

interest in linear polyphenyls, Berlin and co-workers^{9,14} examined the reaction of bisdiazaromatics, e.g., 4,4'-bisdiazobiphenyl, with ammoniacal cuprous salt. Polymers were obtained having both polyphenyl units and azo linkages in the chains. The polyphenyl literature has been reviewed recently.¹⁵

The objective of the present work was to polymerize benzene in the system, Lewis acid catalyst-cocatalyst-oxidizing agent.

Results and Discussion

Benzene was found to polymerize smoothly in the system Lewis acid catalyst-cocatalyst-oxidizing agent to a solid product possessing the properties of *p*-polyphenyl. For example, in the presence of aluminum chloride, water and cupric chloride, benzene was converted under remarkably mild conditions (35–37° for fifteen minutes) to a brown solid in about 60% yield (Table I). At higher temperatures and longer reaction times, the yield was essentially unchanged, but the chlorine content of the polymer increased. The evidence supports the equation



Both acid gas and cuprous chloride¹⁶ were formed in the reaction

TABLE I
p-POLYPHENYL FROM BENZENE-ALUMINUM CHLORIDE-CUPRIC CHLORIDE-WATER^a

Time, hr.	Temp., °C.	Yield		%				C/H atomic ratio
		g.	% ^b	C	H	Cl	O	
0.25	35–37	11.0	58	93.38	5.36	0	0.62	1.45
0.50	35–37	12.0	63	92.87	5.25	0.73	.89	1.47
1 ^c	80	11.7	62	92.80	4.99	1.80	.80	1.55

^a Quantities are given in the general procedure. ^b Based on cupric chloride. ^c Initially at 35–40° for 0.5 hr.

Since the product prepared under the mildest conditions was closest to a hydrocarbon in composition, the characterization work was concentrated upon this material. Evidence for the *p*-polyphenyl structure is based upon the C/H atomic ratio obtained from elemental analyses, infrared spectrum, X-ray diffraction pattern, pyrolysis products, oxidative degradation, insolubility, color and thermal stability. The polymer is very similar (color, insolubility, thermal stability, infrared and X-ray data) to the *p*-polyphenyl synthesized by Marvel and Hartzell⁷ by another method.

The *p*-polyphenyl prepared from benzene under various conditions contained 92.80–93.38% carbon and 4.99–5.36% hydrogen (Calcd. for C₆H₄: C, 94.70; H, 5.30), less than 2% chlorine and less than 1% oxygen. The C/H atomic ratio varied from 1.45 to 1.55 with an average of 1.49. *p*-Polyphenyl possesses a limiting theoretical C/H atomic ratio of 1.5. The previous *p*-polyphenyl was estimated to contain 15% of reduced chloranil, and 30% unaromatized poly-1,3-cyclohexadiene.⁷ Although heating removed the tetrachlorohydroquinone and destroyed the unaromatized poly-1,3-cyclohexadiene, some carbonization occurred in the process.

The infrared spectrum of our polyphenyl gave good evidence for the *para* configuration, with phenyl end groups constituting a minor part of the structure.

(14) A. A. Berlin, V. I. Liogonkii and V. P. Parini, *J. Polymer Sci.*, **55**, 675 (1961).

(15) E. H. Smith, Polyphenyls: Literature Search, U. S. Atomic Energy Commission, ER-8098, 1956.

(16) J. Oziomek, unpublished work.

The spectrum was very similar to that of the Marvel and Hartzell polymer.⁷ In our case the principal absorption band occurred at 805–807 cm.⁻¹, characteristic of *para* substitution. The less intense absorption maxima at 765 and 695 cm.⁻¹ can be attributed to monosubstituted benzene rings. Additional bands of secondary intensity were situated at 1000, 1400 and 1480 cm.⁻¹. It is evident that the position of the *para* band shifts to longer wave lengths with increasing molecular weight in the *p*-polyphenyl series¹⁷: *p*-terphenyl, 837 cm.⁻¹; *p*-quaterphenyl, 826 cm.⁻¹; *p*-quinquephenyl, 818 cm.⁻¹. Since this band occurs at 811 cm.⁻¹ for the Marvel and Hartzell polymer,¹⁸ our *p*-polyphenyl probably possesses a higher molecular weight. The absence of fine structure in the spectrum may possibly result from a high degree of orientation involving the polymer chains.¹⁹ A comparison of the spectra of the lower *p*-polyphenyls reveals a decrease in intensity of the fine structure as one moves up the homologous series.¹⁷ The absence in our polymer of the 3035, 1603, 1575, 1190 and 890 cm.⁻¹ maxima reported by Marvel and Hartzell also supports a higher molecular weight for the benzene product. The intensities of the monosubstitution bands might also be used as an indication of relative molecular weights in the series.

Less than 0.2% of soluble material was obtained from the polymer by successive extractions with boiling ether, chloroform and *p*-xylene. There was no evidence for the presence of biphenyl or *p*-terphenyl in the extract. However, gas chromatography revealed that trace amounts of biphenyl, present in the benzene filtrate, were formed during the reaction.¹⁶ The almost complete absence of low molecular weight species is characteristic of addition polymerization.^{20a} The extreme insolubility of the polymer precludes molecular weight determination by the usual methods. Little assistance is provided by the average C/H atomic ratio (1.49) since the corresponding ratio for a low molecular weight polyphenyl containing 50 rings is 1.485 and the limiting ratio for polyphenyl is 1.5. Although the ultraviolet reflectance spectrum has not yet been obtained, the position of the absorption maximum for the polymer could theoretically provide information on the molecular weight. The plot of wave number versus 1/*a*² (*a* = number of benzene rings) shows a good straight line relationship for the *p*-polyphenyl series.^{17,21,22} However, only a very small segment of the line is available to the higher polyphenyls, thereby seriously decreasing the accuracy of this method. In the previous synthesis of *p*-polyphenyl, the poly-1,3-cyclohexadiene used as the precursor was assigned an approximate molecular weight of 5,000–10,000 (60–120 monomer units).⁷

The X-ray diffraction patterns, which demonstrate that the polymer is quite crystalline, gave values of 4.53, 4.00 and 3.20 Å. for the *d*-spacings, in decreasing order of intensity. Essentially the same *d*-spacings, in the same order of intensity, were reported for the *p*-polyphenyl prepared from poly-1,3-cyclohexadiene.⁷ We did not observe weak bands corresponding to *d*-spacings of 9.07 and 6.39 Å. which were noted by

(17) A. Kyriakis, M.S. thesis, Case Institute of Technology, 1962.

(18) Comparison of the Marvel and Hartzell infrared data for *p*-quaterphenyl and *p*-polyphenyl with the published values [ref. 19; J. E. Stewart and M. Hellmann, *J. Res. Natl. Bur. Standards*, **60**, 125 (1958)], as well as with our own results involving a polystyrene standard for calibration, indicates that this figure should be corrected to 809 cm.⁻¹. See the Ph.D. thesis of G. E. Hartzell, University of Illinois, 1958, for the detailed infrared data.

(19) J. Dale, *Acta Chem. Scand.*, **11**, 640 (1957).

(20) F. W. Billmeyer, Jr., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1957; (a) pp. 172, 192; (b) p. 264.

(21) We are grateful to Dr. D. R. Whitman for valuable assistance.

(22) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).

Marvel and Hartzell. The d -spacing of 4.53 Å. corresponds to the length of a phenyl unit.^{7,23} It was postulated that the rings are nearly coplanar on the basis of the high intensity of the 4.53 Å. d -spacing, and that the structure is essentially all *para*, since the presence of other types of linkages would decrease the crystallinity and produce more complex transmission patterns.⁷

Further evidence bearing upon the polymer structure was obtained from pyrolysis studies. The major product identified from pyrolysis-gas chromatography was benzene. Thermal decomposition at 750–800° *in vacuo* yielded a sublimed product in addition to residual material. The sublimate proved to be a mixture containing biphenyl and lower molecular weight *p*-polyphenyls, including terphenyl, quaterphenyl and quinquephenyl. These hydrocarbons were characterized by comparison of their infrared and ultraviolet spectra, as well as melting points, with those of authentic materials. The sublimate also contained uncharacterized higher molecular weight materials whose infrared and ultraviolet spectra pointed to a *p*-polyphenyl structure. It is significant that, except for an unidentified band in the ultraviolet spectrum at 259 $m\mu$, there was no evidence for the presence of products other than *p*-polyphenyls. Moreover, the gas chromatogram of the *p*-terphenyl fraction demonstrated the essential absence of isomeric terphenyls. These data indicate that the polymer possesses a configuration which is predominantly, if not all, *para*, or else that any *ortho* or *meta* linkages present are preferentially cleaved during pyrolysis.

The thermal degradation very likely proceeds for the most part in a random fashion by homolytic scission of the bonds joining the benzene rings. Abstraction of a hydrogen atom from another polymer chain by the initially formed aryl radical would yield lower molecular weight *p*-polyphenyl. The polymer chain radicals generated by hydrogen abstraction could conceivably form cross-links by dimerization or substitutive attack on other chains, thus giving rise to the non-volatile, dark-colored, residual material. It is noteworthy that the infrared spectrum of the residue closely resembles that of lampblack.

Silverman and co-workers^{15,24} found that *p*-terphenyl, on pyrolysis for extended periods of time, gave degradation products, including biphenyl, and higher molecular weight polyphenyls, such as quater-, quinque- and sexiphenyls. Under these conditions, which differ substantially from our own, the generated polyphenyls appeared to contain both *meta* and *para* linkages.

Oxidation of *p*-polyphenyl with chromic acid yielded a mixture containing terephthalic acid and 4,4'-biphenyldicarboxylic acid. The acids were identified as their dimethyl ester derivatives. The terephthalic acid would be formed from *p*-terphenyl units in the polymer chain, and the 4,4'-biphenyldicarboxylic acid from *p*-quaterphenyl units. It is significant that the gas chromatogram and infrared spectrum of the unpurified dimethylterephthalate demonstrated the absence of the 1,2- and 1,3-isomers.

In summary of the data relative to the polymer configuration, evidence from the infrared spectrum, X-ray diffraction pattern, pyrolysis studies and oxidative degradation indicates essentially an all-*para* structure. Allen and Pingert,²⁵ in an investigation of *o*-terphenyl rearrangement induced by aluminum chloride, found

(23) L. W. Pickett, *Proc. Roy. Soc. (London)*, **A142**, 333 (1933); *J. Am. Chem. Soc.*, **58**, 2299 (1936).

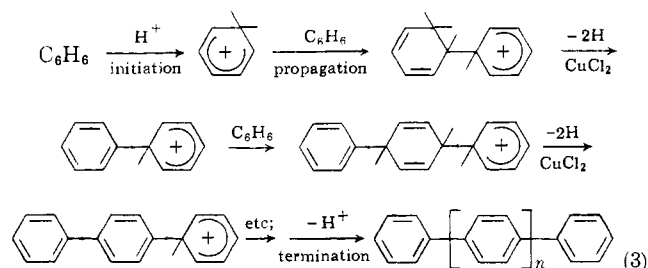
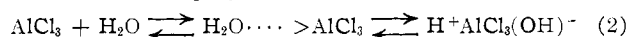
(24) L. Silverman, *et al.*, NAA-SR-1203, North American Aviation, Inc., 1955.

(25) C. F. H. Allen and F. P. Pingert, *J. Am. Chem. Soc.*, **64**, 1365 (1942).

that first *m*-terphenyl and then the *para* isomer were formed. It is unlikely that the *p*-polyphenyl obtained in our work is a rearranged product, since the conditions are very mild and the polymer is highly insoluble.

Other properties of the main product were also studied. At temperatures up to 500–525° the polymer demonstrated good resistance to thermal degradation and air oxidation. The high thermal stability of polyphenyls is well known and has attracted much attention.^{7,14} *p*-Polyphenyl is very insoluble in organic solvents including boiling chlorobenzene, *p*-xylene, chloroform, acetone, and alcohol. The low solubility, in accord with previous observations,⁷ is probably due to close-packing of the long, linear chains. The color of our polymer, similar to that of the previously prepared *p*-polyphenyl,⁷ can be attributed to the long conjugated system of benzene rings, perhaps to minor segments of polynuclear structures produced by cross-linking, or to impurities.

The following reaction sequence is suggested for oxidative cationic polymerization of aromatic nuclei.



The critical importance of the Lewis acid catalyst is indicated by the failure of reaction to occur when aluminum chloride is omitted. This suggests a cationic polymerization mechanism.^{5,26} By analogy with the olefin-catalyst,²⁶ and benzene-ferric chloride systems,⁵ a cocatalyst is presumably involved. The effect of variation in water content is currently under investigation. Initiation would entail formation of a sigma complex (benzenonium ion) which then undergoes propagation as illustrated. It is significant that, whereas the cationic polymerization of olefins^{26b} can occur at -100° within a few seconds, temperatures in the vicinity of room temperature are required in order for the benzene polymerization to take place at an appreciable rate.

In another control experiment, no solid product resulted when the oxidant was omitted. Although the stage at which dehydrogenation takes place is unknown, as well as the mechanism, the proposed transformation (cyclohexadiene structure \rightarrow benzene structure) would certainly occur with ease. Dehydrogenation by the oxidizing agent would, by restoring aromaticity, prevent reversibility of the propagation step.

The small amount of chlorine in the polymer prepared under more drastic conditions could result from a termination reaction involving chloride ion or from nuclear chlorination effected by the metal halide. Cupric chloride is known to halogenate aromatic compounds, but does so only with the more active types at elevated temperatures.²⁷

The oxygen present (<1%) in the *p*-polyphenyl might conceivably arise from chain termination involving water, or air oxidation during the work-up procedure.

At this early state of the investigation, it would be prudent to consider alternative mechanisms, *e.g.*,

(26) D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954); P. H. Plesch, Ed., "Cationic Polymerization and Related Complexes," Heffer, Cambridge, England, 1953.

(27) J. C. Ware and E. E. Borchert, *J. Org. Chem.*, **26**, 2263, 2267 (1961).

the operation of surface effects in the heterogeneous reaction mixture.

From the present study and previous results⁵ there is no evidence for the polymerization of benzene by aluminum chloride alone under our standard conditions. However, with more severe treatment uncharacterized polymers were obtained, in addition to biphenyl, phenylcyclohexane, phenylmethylcyclopentane and diphenylcyclohexane.^{3,28} Apparently, in the absence of an added oxidant, the intermediates undergo disproportionation, as well as rearrangement, when appropriate conditions are used. With these modifications in interpretation, application of the proposed polymerization mechanism to the aluminum chloride-benzene reactions appears reasonable.

It is interesting that there are fundamental similarities between the theoretical concepts advanced for oxidative cationic polymerization of aromatics and the mechanisms proposed for (1) coke formation in catalytic cracking²⁹ and (2) the Scholl reaction.³⁰

Experimental³¹

Materials.—Reagent grade chemicals were obtained from the indicated sources: benzene, thiophene-free, Mallinckrodt Chemical Works; aluminum chloride, anhydrous powder, Mallinckrodt Chemical Works or Matheson Coleman and Bell; biphenyl, *p*-terphenyl and terephthalic acid, Eastman Kodak Co.; *p*-quaterphenyl, K and K; 4,4'-biphenyldicarboxylic acid, Aldrich Chemical Co. *p*-Quinquephenyl (K and K) was crystallized from pyridine. Anhydrous cupric chloride (Fisher Scientific Co.) and cupric chloride hydrate (Mallinckrodt Chemical Works or Baker Chemical Co.) were dried by heating overnight at 120°.

Apparatus.—X-Ray diffraction apparatus (copper K α radiation, $\lambda = 1.539 \text{ \AA}$.) was equipped with a camera, or a "Norelco" automatic recording X-ray diffraction unit; Beckman DK-2 ultraviolet spectrophotometer (chloroform solvent); Beckman IR-5 infrared spectrophotometer, 0.25 or 0.5% in potassium bromide; F and M Model 500 gas chromatograph, 6-ft. Chromosorb column containing 15% silicone grease.

***p*-Polyphenyl from Benzene-Aluminum Chloride-Cupric Chloride-Water. General Procedure.**—The reaction was carried out under nitrogen in a 3-necked flask equipped with a paddle stirrer. After the dropwise addition of water (1 ml.) to a mixture of benzene (1 mole) and aluminum chloride (0.5 mole), cupric chloride (0.5 mole) was introduced. The temperature was increased to 35–37° and the reaction allowed to proceed for 30 min. at these temperatures. Acid gas was evolved. The reaction mixture was then added to water and filtered. After treatment with 18% hydrochloric acid, the product was triturated repeatedly with boiling concentrated hydrochloric acid, and washed with water until the washings were colorless. After two triturations with boiling 2 *M* sodium hydroxide solution, water washings were continued until the filtrate was colorless. Then the polymer was washed repeatedly with distilled water until the filtrate gave a negative test for chloride ion (silver nitrate method). After being dried at 120° for 5 hr. the product was in the form of a finely divided, light brown solid. Great care was taken to avoid contamination.

Data for the various runs are shown in Table I. The identification work was performed on the polymer prepared at 35–37° for 15 min. Values of 4.53, 4.00 and 3.20 \AA . for the *d*-spacings, in decreasing order of intensity, were obtained from the X-ray diffraction powder patterns.^{32,33} The infrared spectrum³⁴ possessed absorption bands at 695, 765, 805, 1000, 1400, 1480 and 1650 (diffuse) cm^{-1} . With the Beckman IR-7 spectrophotometer,³² the principal *para* band was situated at 807 cm^{-1} . A polystyrene standard was used for calibration in both cases.

Pyrolysis of *p*-Polyphenyl.—Apparatus A consisted of an 8-ml. quartz flask attached to a tube 150 mm. in length which was bent in the middle at a 90° angle and connected to two U-tubes immersed in Dry Ice. After extraction with boiling ether, chloroform and *p*-xylene, the polymer was pyrolyzed in 0.3-g. portions

at 750–800° (Labasco gas burner) at 1–2 mm. for 30 min. The dark brown residue, which was removed after each decomposition, possessed an infrared spectrum very similar to that of lamp-black (essentially no fine structure except for a weak band at 805 cm^{-1}). The solid which collected in the U-tube proved to be essentially biphenyl on the basis of the melting point (68°), infrared spectrum, ultraviolet spectrum and gas chromatogram.

The extracted polymer was also decomposed thermally under similar conditions in a horizontal Vycor pyrolysis tube (apparatus B) in 0.6-g. portions. The sublimed products from both methods, about 0.5 g. from 10 g. of *p*-polyphenyl, were combined and extracted repeatedly with boiling ether. After removal of the ether by distillation, the very small quantity of residue was dissolved in chloroform and subjected to gas chromatography. Biphenyl and *p*-terphenyl were separated and characterized by their infrared and ultraviolet spectra, gas chromatograms and melting points; m.p. 68° for the biphenyl product, lit.¹⁵ m.p. 70°; m.p. 206° for the *p*-terphenyl product, lit.¹⁵ m.p. 210°. The gas chromatograms for the unpurified *p*-terphenyl product revealed either no other peaks or a very small one immediately preceding the main peak.

The residue from ether extraction was placed in apparatus A and sublimed at 550–600° (1–2 mm.) during 30 min., leaving only a small amount of residue. The sublimate deposited in various bands in the cooler part of the apparatus. The solid nearest the flask was yellow-green, whereas that at greater distances was cream colored. Repeated sublimations of the material in the several bands yielded *p*-quaterphenyl and *p*-quinquephenyl, which were characterized by their infrared and ultraviolet spectra and melting points; m.p. 313°, softening at 306°, for the *p*-quaterphenyl product, lit.¹⁶ m.p. 320°, authentic material m.p. 313°, softening at 307°; m.p. 395°, softening at 384°, for the *p*-quinquephenyl product, lit.¹⁶ m.p. 395°, authentic material m.p. 400°, softening at 387°. The infrared spectrum of *p*-quinquephenyl possessed absorption maxima at 818, 757 and 688 cm^{-1} . The unidentified higher molecular weight portion of the sublimate, presumably a mixture, possessed absorption bands in the infrared region at 810, 762 and 690 cm^{-1} ; ultraviolet spectrum (chloroform soluble portion), λ_{max} 317 $\text{m}\mu$, minor absorption band at about 259 $\text{m}\mu$; lit.²¹ ultraviolet spectrum for *p*-sexiphenyl, λ_{max} 317 $\text{m}\mu$.

Pyrolysis-gas chromatography yielded three peaks, the major one being benzene (1.9% yield).³⁵

Oxidation of *p*-Polyphenyl.³⁶—A mixture of *p*-polyphenyl (10 g.), chromic anhydride (100 g.), glacial acetic acid (610 ml.) and water (60 ml.) was heated at reflux with stirring for 10 hr. The cooled mixture was stirred with dilute hydrochloric acid and filtered. The solid was washed thoroughly with 5% hydrochloric acid and dried; wt. 7 g. The combined filtrate contained no ligroin-soluble material.

A mixture of the cream-colored oxidation product (3 g.), 100 ml. of methanol saturated with hydrogen chloride and concentrated sulfuric acid (6 ml.) was refluxed for 7 hr. The mixture was diluted with water (50 ml.) and filtered. Extraction of the solid with ether yielded soluble and insoluble fractions. After extraction of the ether solution with 5% sodium hydroxide solution and distillation of the ether, 2 g. of residue was obtained. Steam distillation separated the volatile dimethylterephthalate, wt. 1.8 g., m.p. 141° from aqueous ethanol; authentic material, m.p. 141°, mixture m.p. 140°. The infrared spectrum of the product was identical with that of the authentic ester. The unpurified volatile ester contained no *ortho* isomer on the basis of the gas chromatogram (20-ft. column, 15% silicone grease-0.5% Carbowax on Chromosorb P 35/80 mesh, 200°, flow rate 70 ml./min.), and contained no *meta* isomer (no absorption at 988 cm^{-1} in the infrared region).

The non-volatile material was found to be dimethyl 4,4'-biphenyldicarboxylate, 20 mg., m.p. 213° from aqueous ethanol; authentic material, m.p. 212°, lit.³⁷ m.p. 212–213°, mixture m.p. 211°. The infrared spectrum of this product corresponded to that of the authentic material.

Solubility of *p*-Polyphenyl.—The polymer was extremely insoluble in boiling ethanol, ethyl ether, petroleum ether, chloroform, benzene, *p*-xylene, chlorobenzene, acetone, hexane and carbon tetrachloride.

Thermal and Oxidative Stability of *p*-Polyphenyl.—The polymer was placed in a muffle furnace for 30 min. at each temperature level and the weight loss determined; temp., % wt. loss; 400°, 1.8; 450°, 3.2; 500°, 5.0; 550°, 78.0; 600°, 99.4.

Differential thermal analysis³⁴ (Deltatherm apparatus) of a mixture of *p*-polyphenyl (0.2 g.) and Alundum aluminum oxide (0.3 g.) revealed a peak starting at 525°.

(35) Pyrolyzed at 1150° for 20 sec., Aerograph A-600B, 5-ft. column, 15% Halcomid M-18 on Chromosorb W 60/80, 75°, flow rate 25 ml./min. We are grateful to Wilkens Instrument & Research, Inc., for this analysis.

(36) This oxidation procedure was developed by Mr. R. M. Lange.

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(31) Elemental analyses were performed by Drs. Weiler and Strauss, Oxford, England, and by Geller Laboratories, Bardonia, N. Y. Melting points are uncorrected.

(32) We are grateful to Mr. R. M. Lange for obtaining these data.

(33) We appreciate the assistance in interpretation by Dr. C. S. Smith.

(34) We wish to thank the Master Builders Co., Division of Martin Marietta Corp., for the use of facilities and assistance from its personnel.

Low Molecular Weight Products in *p*-Polyphenyl.—Less than 0.2% of soluble material (brown tar) was obtained by successive extractions of the polymer with boiling ether, chloroform and *p*-xylene. There was no biphenyl or terphenyl in the extract on the basis of gas chromatographic analysis.

Benzene–Aluminum Chloride–Water.—A mixture of benzene (1 mole), aluminum chloride (0.5 mole) and water (1 ml.) was stirred at reflux under nitrogen for 1 hr. No *p*-polyphenyl was obtained.

Benzene–Cupric Chloride–Water.—A mixture of benzene (1 mole), cupric chloride (0.5 mole) and water (1 ml.) was stirred at reflux under nitrogen for 1 hr. No *p*-polyphenyl was obtained.

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[CONTRIBUTION FROM THE INSTITUTE FOR ENZYME RESEARCH, UNIVERSITY OF WISCONSIN, MADISON, WISC.]

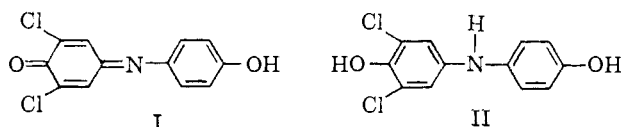
The Conjugation of Cysteine during its Oxidation by 2,6-Dichloroindophenol^{1a}

BY HERBERT I. HADLER,^{1b} MARY JANE ERWIN AND HENRY A. LARDY

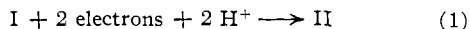
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When cysteine is oxidized by 2,6-dichloroindophenol not only is the reduced dye produced, as hitherto accepted, but also a conjugate between cysteine and the dye is formed. The nature of the conjugate and the relative amount of reduced dye are determined by the initial molar ratio of dye to cysteine. Contrary to expectation, polyconjugation of the dye with cysteine was favored by an excess of dye. The term *oxidative addition* or *oxidative substitution* has been proposed to emphasize the role of oxidation in fostering addition or substitution.

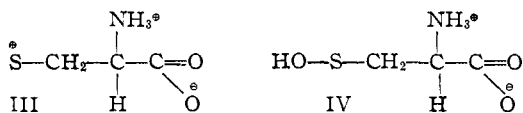
The reduction of an oxidation–reduction indicator, such as 2,6-dichloroindophenol (I), has frequently been used to follow the course of many biochemical oxida-



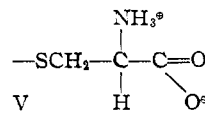
tion–reduction processes.² The stoichiometry has been represented by eq. 1 and the dye classed as a two-electron oxidant. The loss of color in the visible spectrum has been used as a convenient measure of the conversion of I to II.



Toderick and Walker³ found that one mole of I was decolorized by one mole of cysteine. This observation became of interest when Basford and Huennekens⁴ raised the question of the oxidation level of the altered thiol group. If cysteine had yielded the disulfide, cystine, two moles of cysteine would have reduced one mole of dye.⁵ These authors observed that the rate of decolorization was first order with respect to the hydrogen ion concentration. Thus in order to comply with the stoichiometry of eq. 1 they concluded that the medium yielded one proton, while one proton and two electrons were derived from cysteine. Consequently they proposed that cysteine had been converted to the sulfenium ion III, which is the cation derived from cysteinesulfenic acid (IV).



Benesch and Benesch⁶ studied the disulfide interchange between cystine and bis-(2,4-dinitrophenyl)-cystine in a strongly acidic medium (9.5 *N* hydrochloric acid). They believed the sulfenium ion III to



would be colorless in the visible, absorb in the ultraviolet, and likely be non-extractable by ether.

Evidence which suggested adduct formation was obtained by reducing the dye with a series of graded amounts of cysteine (two cases are shown in Fig. 1) and with an excess of potassium borohydride (Fig. 1). Although partial re-oxidation occurred during the spectral scanning of the mixture reduced with potassium borohydride, this curve (tube 3) intersected the curve of the original dye at three points (256.5, 279.5 and 291.5 μ). One of these points should be an isos-

(1) (a) Supported by a grant from the National Science Foundation and by a grant from the National Institutes of Health (H-2677). Presented at 142nd Natl. Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962. (b) Supported by a Special Fellowship, Division of Medical Sciences, National Institutes of Health.

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