Deacetylation of VI and Conversion to D-*lyxo*-Hexose Phenylosazone.—*N*-Acetyl-penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (1 g.) was treated with 50 ml. of methanol nearly saturated with ammonia and left overnight at room temperature, then evaporated to dryness in a vacuum desiccator. The residue was dissolved in water (20 ml.) and heated with phenylhydrazine (0.5 g.) and acetic acid (0.5 ml.) on the water bath for 1 hr. On cooling, D-*lyxo*-hexose phenylosazone separated in its characteristic crystalline shape and was identified by mixture melting point and comparative infrared spectra.

Acknowledgment.—H. El Khadem is indebted to the Educational and Cultural Exchange Program of the United States State Department for a Fulbright Grant to visit The Ohio State University where part of this work was carried out, to Professor M. L. Wolfrom for his valued advice and counsel, and to The Ohio State University for the laboratory facilities provided.

Infrared Spectra and Synthesis of Some Polyphenyls

RICHARD C. DOSS AND PAUL W. SOLOMON

Phillips Petroleum Company, Bartlesville, Oklahoma

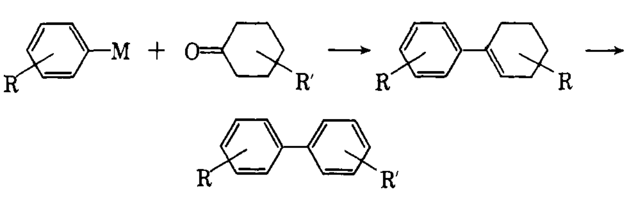
Received August 16, 1963

A general method of preparing polyphenyls by the addition of an aryl Grignard or an aryllithium to a substituted cyclic ketone followed by dehydration and aromatization was used to synthesize five polyphenyls heretofore unreported. These newly prepared polyphenyls are 3-bromo-*m*-terphenyl, 2,3'-di-(3-xenyl)biphenyl, 2,4-di(3-xenyl)biphenyl, 2,4-di(4-xenyl)biphenyl, and 3,5-diphenyl-4'-(3-xenyl)biphenyl. In addition, ten known polyphenyls were prepared, some by new routes. Infrared spectral correlations were developed which apply to *meta*- and *para*-type linkages in polyphenyls. These correlations are useful in indicating (a) the presence of single or consecutive *meta*- or *para*- and 1,3,5-substituted benzene rings in large polyphenyl molecules, and (b) the type of substitution present in the terminal groups of polyphenyls.

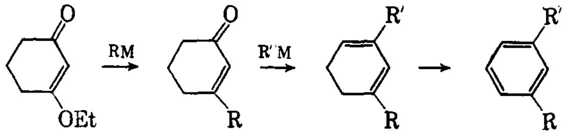
During a recent program under an Atomic Energy Commission Contract,[1] the need arose to prepare certain selected polyphenyls, particularly quaterphenyls and hexaphenyls. This was done for the most part by extending the methods of Woods and Scotti.[2] An examination of the infrared spectra of polyphenyls which are described in the literature and those obtained during the present study revealed certain characteristic shifts of assigned absorption bands in the 11.0- to 15.0-μ region. These band shifts were dependent upon the number and type of linkages involved.

Discussion

Syntheses.—The best general method found for the unambiguous synthesis of polyphenyls was that of the addition of an aryl Grignard or an aryllithium to an aryl cyclic ketone followed by dehydration and aromatization according to the following general scheme.

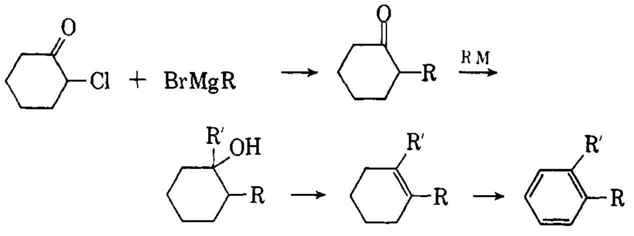


The introduction of internal *meta* linkages was accomplished by the method of Woods and Tucker,[3] whereby the monoethyl ether of dihydroresorcinol was treated (twice) with an aryl Grignard or an aryllithium followed by aromatization.



The compound 3-bromo-*m*-terphenyl was prepared by this method. 3-Ethoxycyclohex-2-en-1-one was added to 3-bromophenylmagnesium bromide, and the resulting 3-(3-bromophenyl)cyclohex-2-en-1-one added to phenylmagnesium bromide to give 3-bromodihydro-*m*-terphenyl. This was aromatized with bromine in chloroform to the desired 3-bromo-*m*-terphenyl.

The introduction of *ortho* linkages in positions other than terminal was brought about by the use of 2-chlorocyclohexanone.[2] An aryl Grignard was added to 2-chlorocyclohexanone, whereby rearrangement occurred giving the intermediate 2-aryl substituted cyclohexanone. This product was added to another aryl Grignard or aryllithium followed by hydrolysis, dehydration, and aromatization to the desired polyphenyl.



The Grignards of 3-xenyl bromide and 4-xenyl bromide were added to 2-chlorocyclohexanone to give the compounds 2-(3-xenyl)cyclohexane and 2-(4-xenyl)-cyclohexanone.[2] The butyllithium interchange products of 3-bromo-*m*-terphenyl and 4-bromo-*m*-terphenyl[4] were added to 2-(3-xenyl)cyclohexanone which after dehydration and aromatization gave, respectively, 2,3'-di(3-xenyl)biphenyl and 2,4'-di(4-xenyl)biphenyl. Lithio-*p*-terphenyl[5] was treated with 2-(4-xenyl)cyclohexanone in a similar manner to give 2,4'-di(4-xenyl)-biphenyl. Preparative details are given here only when the compounds were not found in the literature

---

[1] U. S. Atomic Energy Commission Contract AT(10-1)-1080, Phillips Petroleum Co., Bartlesville, Okla.

[2] G. F. Woods and F. Scotti, *J. Org. Chem.*, **26**, 312 (1961).

[3] G.F. Woods and I. W. Tucker, *J. Am. Chem. Soc.*, **70**, 3340 (1948).

[4] G. F. Woods, J. P. Oppelt, and R. B. Isaacson, *ibid.*, **82**, 5227 (1960).

[5] J. A. Cade and A. Pilbeam, United Kingdom Atomic Energy Authority, AERE-R 3038, p. 3.

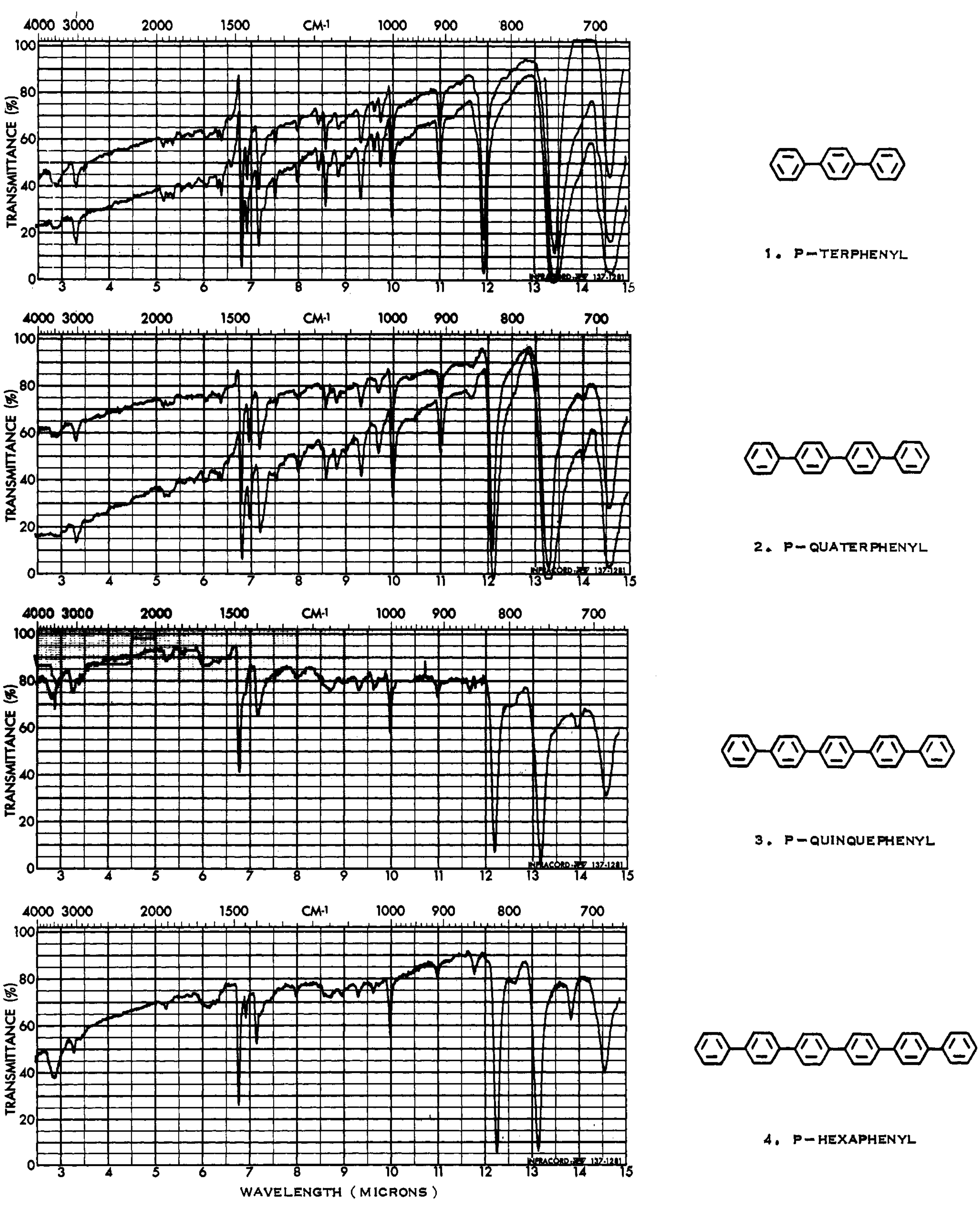


Fig. 1.—Infrared spectra of polyphenyls.

or when known compounds were prepared by a new method. Table I presents a list of these materials.

Infrared Correlations.—Bellamy[6] has noted the infrared correlations for CH out-of-plane deformations for variously substituted benzene rings found in Table II. These correlations have proved of considerable help in confirming the structure of the newly synthesized polyphenyls. With the availability of a number of spectra of these compounds, it was possible to refine and extend the correlations by limiting them to polyphenyl structures only (see Fig. 1–5).

A. ***para*-Type Substitution.**—The normal band at 11.6–12.5 μ due to two adjacent hydrogens was found to shift according to the number of consecutive *para*-

---

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

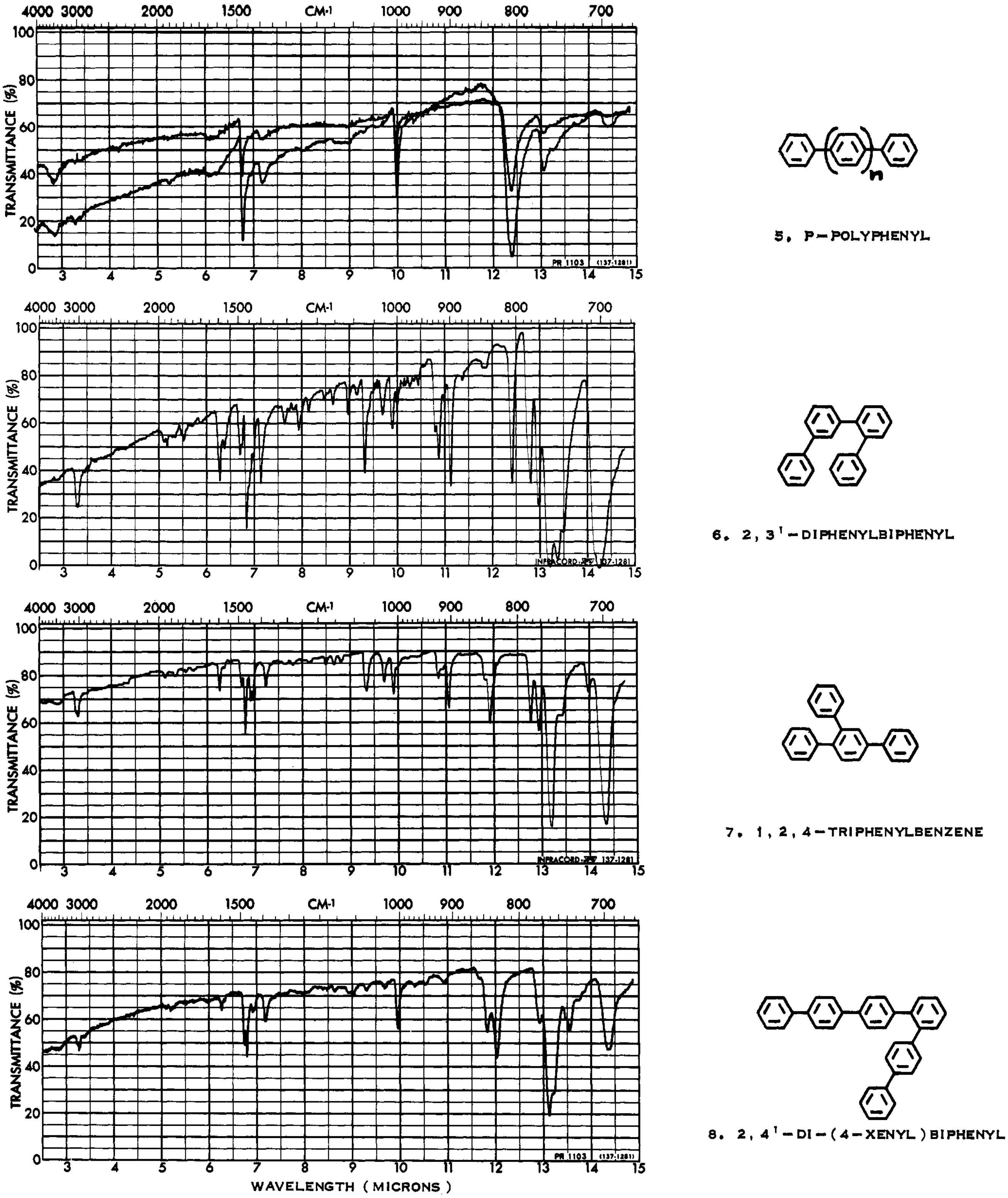


Fig. 2.—Infrared spectra of polyphenyls.

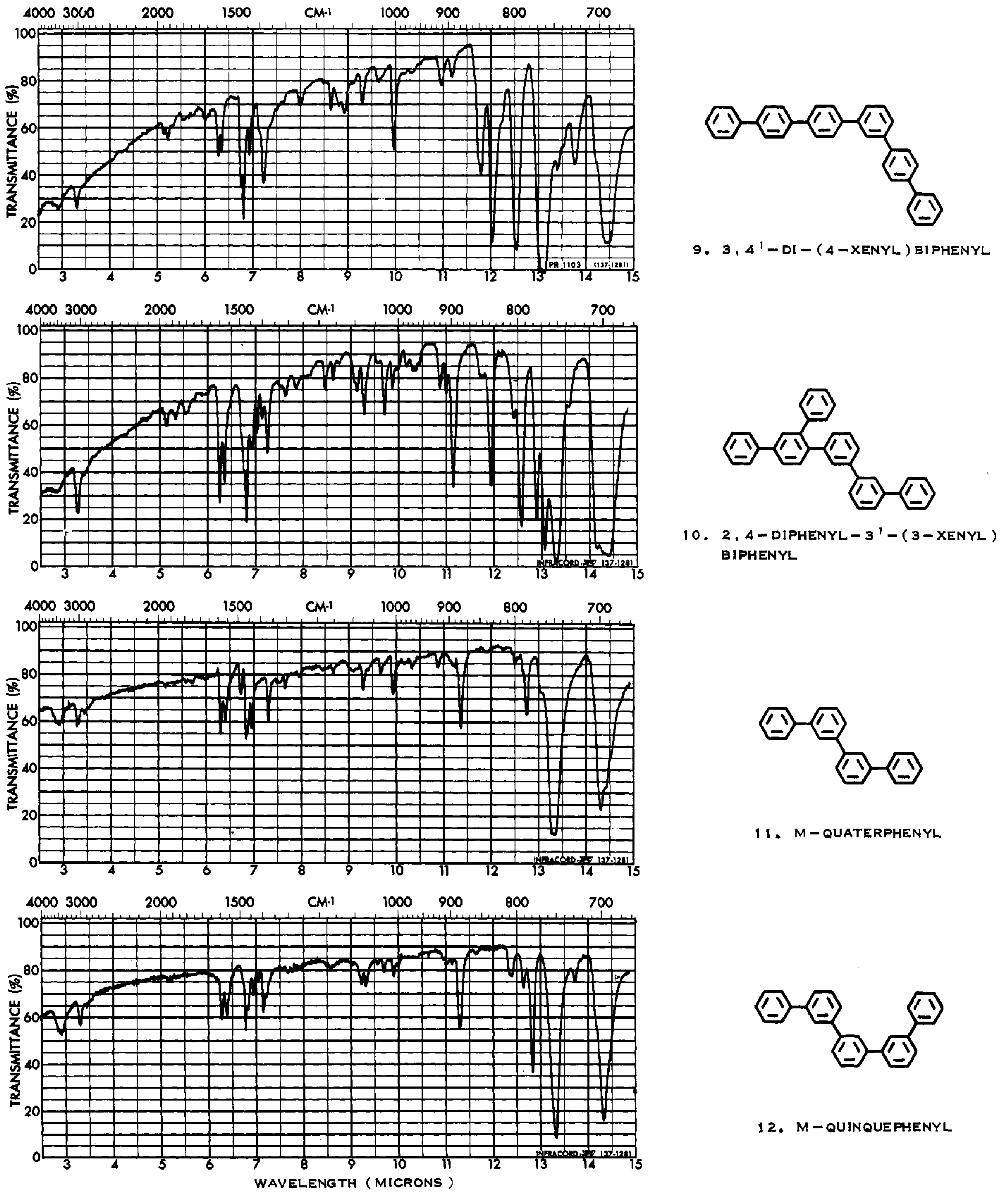
type linkages present (see Table III, also Fig. 6). When a single *para* linkage and two consecutive *para* linkages are present in the same molecule but separated by an *ortho*- or *meta*-linked phenylene group, both expected bands occur (see spectra 8 and 9). Two bands sometimes occur in the region where only one band would be expected (see spectra 16 and 19).

A shift can be noted in the 13.0–13.7-μ band due to monosubstituted phenyl structures when increasing consecutive *para* linkages are present. The band shifts from 13.45 μ for *p*-terphenyl to 13.05 μ for *p*-polyphenyl (see spectra 1–5). This correlation is only useful for all *para*-linked polyphenyls, however.

B. ***meta*-Type Substitution.**—The normal band at 12.3–13.3 μ was found to shift according to the number of consecutive *meta* linkages present (Table IV, Fig. 6). This has been noted by Alexander[7] also. As with

---

[7] R. L. Alexander, Jr., *J. Org. Chem.*, **21**, 1464 (1956).



9. 3,4'-DI-(4-XENYL)BIPHENYL

10. 2,4-DIPHENYL-3'-(3-XENYL)BIPHENYL

11. M-QUATERPHENYL

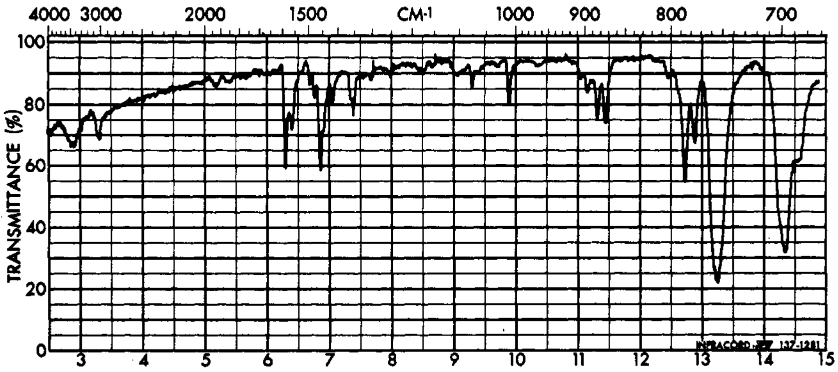
12. M-QUINQUEPHENYL

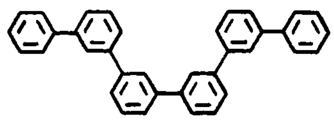
Fig. 3.—Infrared spectra of polyphenyls.

para linkages, these bands sometimes become multiple bands either when both mono- and poly-*meta* linkages are present (see spectra 16, 17) or when only a single type is present (see spectra 10, 12, 13).

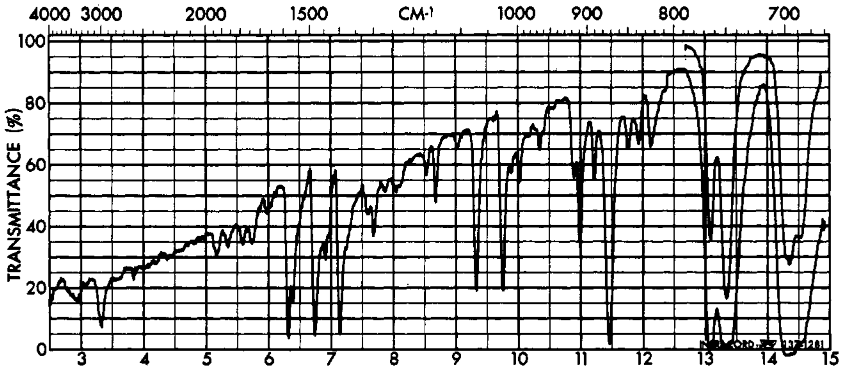
The band at 11.1–11.6 μ due to the single hydrogen present in this structure is displaced to longer wave length when it occurs in the special "*meta*" case of a 1,3,5-trisubstituted benzene ring (see Table V, Fig. 6). The latter correlation is not well established, as only two spectra of the 1,3,5-substitution type are available. Both types of bands are sometimes rather weak.

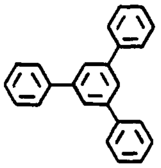
C. *ortho*-Type Substitution.—The band due to *ortho* substitution has not proved reliable as it tends to be hidden by the strong 13.0–13.6-μ band due to monosubstituted benzene. In some cases weak bands



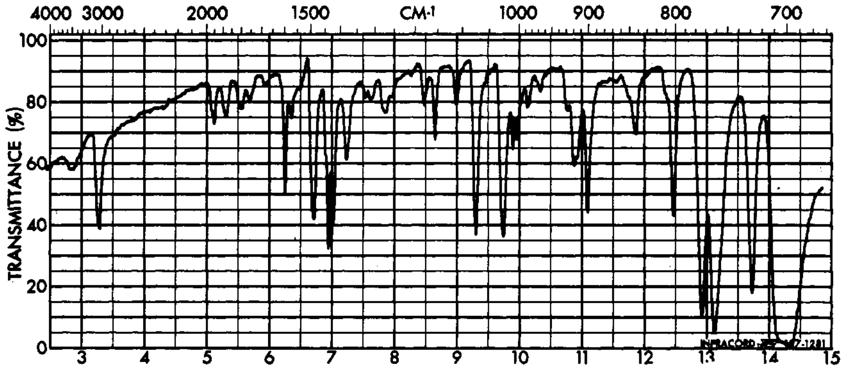


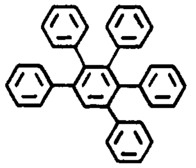
13. M—HEXAPHENYL



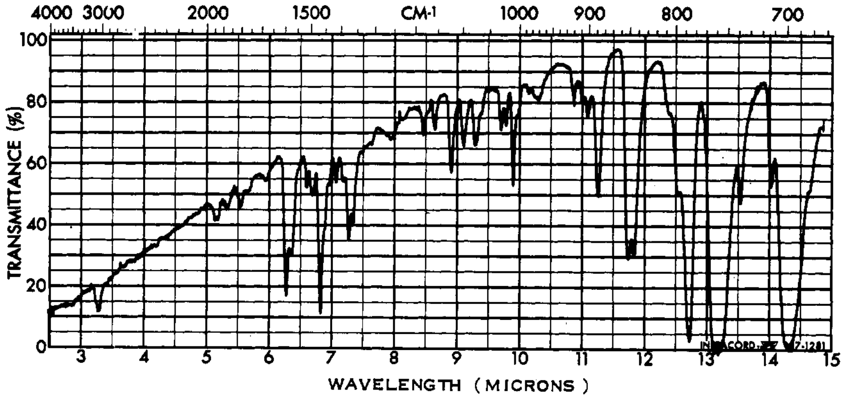


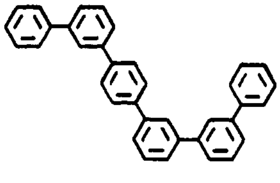
14. 1, 3, 5—TRIPHENYLBENZENE





15. PENTAPHENYLBENZENE





16. 3, 4'—DI—(3—XENYL)BIPHENYL

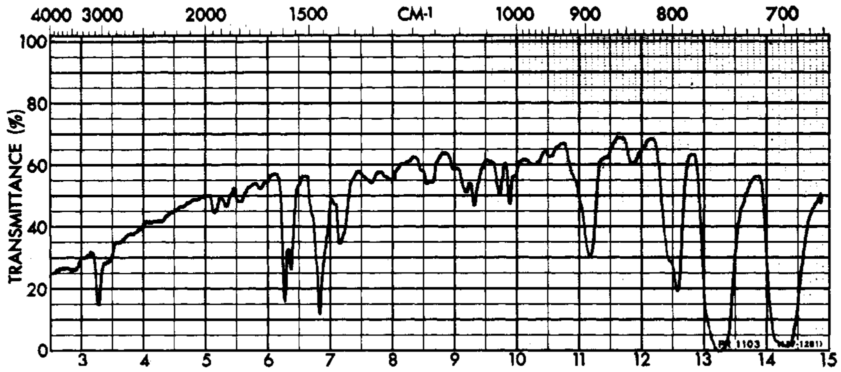
Fig. 4.—Infrared spectra of polyphenyls.

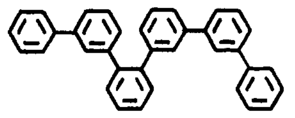
occur at 12.8–13.0 μ which may be due to this linkage. In a number of cases bands also occur in this last region when *ortho* linkages are absent.

D. Terminal Linkages.—The band at 14.1–14.5 μ due to monophenyl substitution is shifted in polyphenyls according to the type of terminal linkages present (see Table VI).

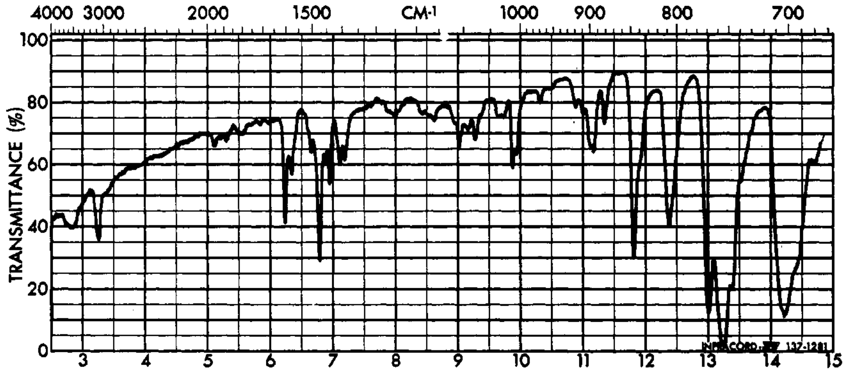
Experimental

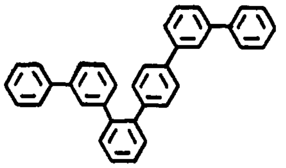
An F & M Model 500 programmed temperature gas chromatograph was used to analyze the samples for purity. Unless otherwise noted, the indicated purity was 98.5% or better. Potassium bromide wafers were prepared with the polyphenyl samples and a Perkin-Elmer Corporation Model 137 Infracord spectrophotometer was used for recording infrared spectra. The completeness of aromatization was determined from these spectra.



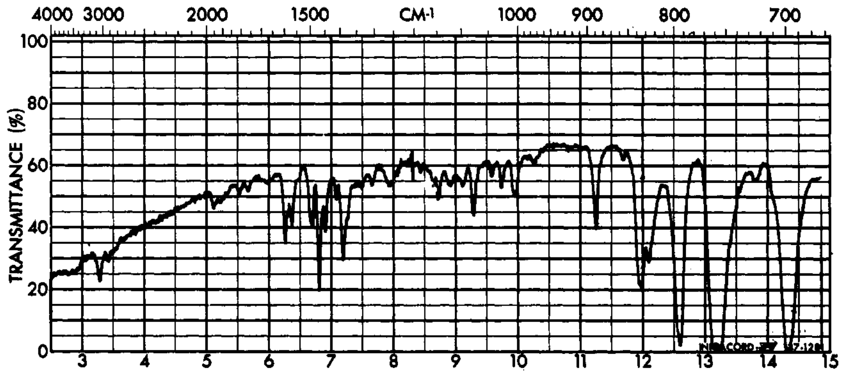


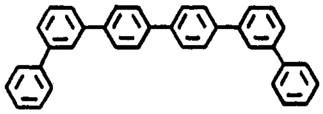
17. 2,3'-DI-(3-XENYL)BIPHENYL



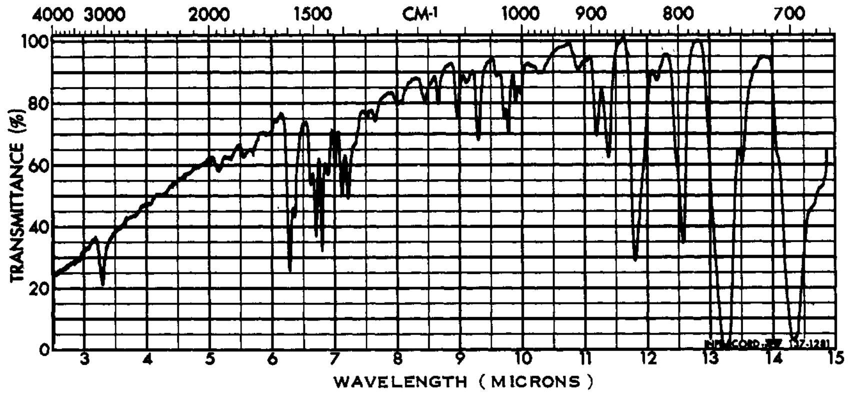


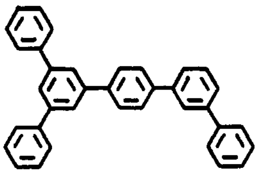
18. 2,4'-DI-(3-XENYL)BIPHENYL





19. 4,4'-DI-(3-XENYL)BIPHENYL





20. 3,5-DIPHENYL-4'-(3-XENYL) BIPHENYL

Fig. 5.—Infrared spectra of polyphenyls.

The succeeding polyphenyls were prepared by methods described in the literature: *p*-polyphenyl,[8] 3,3'-diphenylbiphenyl,[9] 2,3'-diphenylbiphenyl,[9] pentaphenylbenzene,[10] and 4,4'-di(3-xenyl)biphenyl.[11] Additional compounds were made available for this study: *p*-terphenyl and *p*-quaterphenyl (Eastman), *m*- and *p*-quinquephenyl (Monsanto), 1,3,5-triphenylbenzene (Aldrich), and *m*-hexaphenyl (National Bureau of Standards). The following descriptions given are of the synthesis of various polyphenyls in their pure state.

3-Bromo-*m*-terphenyl.—Phenylmagnesium bromide prepared from 30 g. of bromobenzene and 3.6 g. of magnesium turnings in 150 ml. of ether was stirred and cooled to 15°. A solution was slowly added which contained 25.1 g. of 3-(3-bromophenyl)cyclohex-2-en-1-one[12] dissolved in 100 ml. of ether. The mixture was refluxed for 1 hr., hydrolyzed with cold dilute sulfuric acid, and steam distilled. The residue was dissolved in 100 ml. of ether and washed with dilute, aqueous sodium hydroxide and with water.

---

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

[9] G. F. Woods and F. Reed, *J. Am. Chem. Soc.*, **71**, 1348 (1949).

[10] W. Dilthey and G. Hurtig, *Chem. Ber.*, **67**, 2004 (1934).

[11] G. F. Woods, Wright Air Development Center, Technical Report 59-496, p. 112.

[12] G. F. Woods, Aeronautical Research Laboratory, Report 62-306.

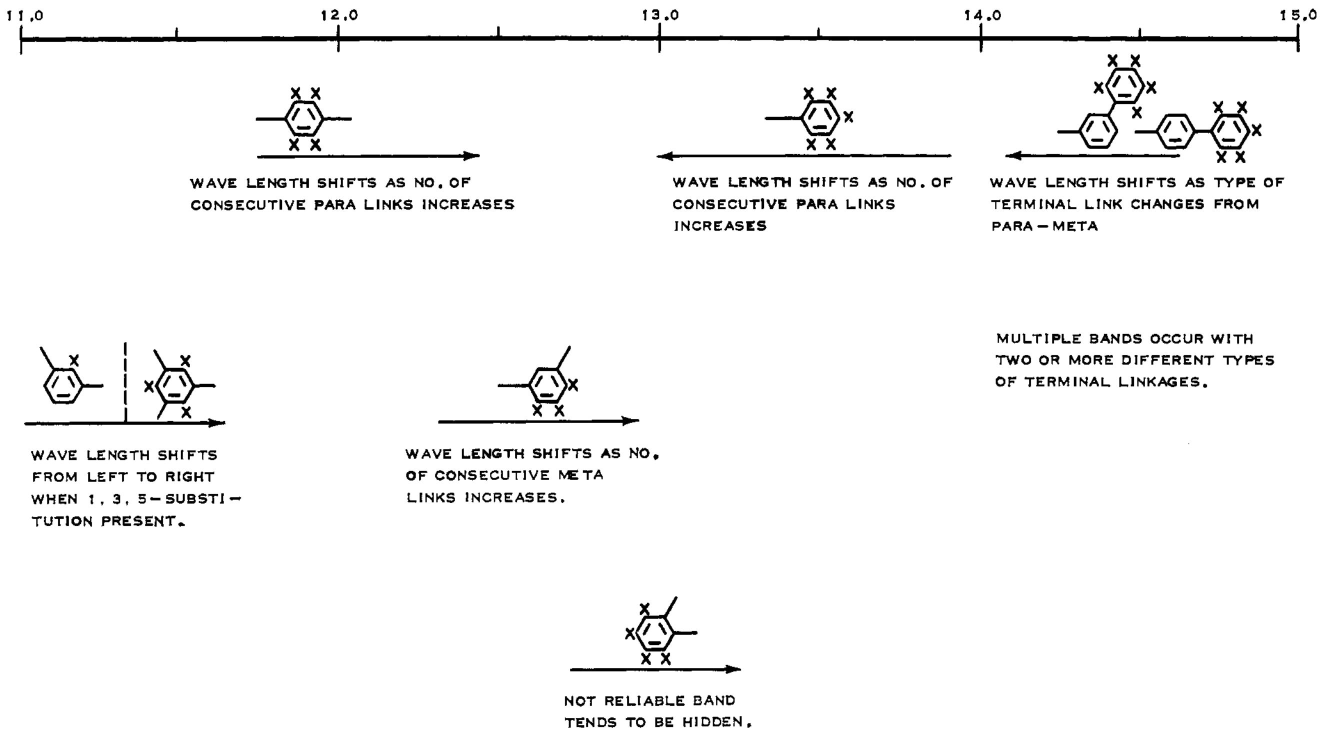


Figure 6.

TABLE I

POLYPHENYLS, NEW OR PREPARED BY A NEW ROUTE

Compound	Lit. m.p., °C.	Exptl. m.p., °C.
3-Bromo-*m*-terphenyl		200–205 (1.5 mm.)[a]
p-Hexaphenyl	465[b]	439–445
1,2,4-Triphenylbenzene	99–100[c]	96–97
3,4′-Di(3-xenyl)biphenyl	186–188[c]	192–195
2,4-Diphenyl-3′-(3-xenyl)biphenyl	145–146[c]	145–146
3,4′-Di(4-xenyl)biphenyl	312–314[b]	321–322
2,3′-Di(3-xenyl)biphenyl		58–60
2,4′-Di(3-xenyl)biphenyl		128–130
2,4′-Di(4-xenyl)biphenyl		231–232
3,5-Diphenyl-4′-(3-xenyl)biphenyl		155

[a] B.p., °C. [b] Ref. 5. [c] Ref. 11.

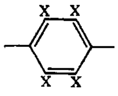
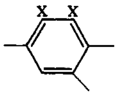
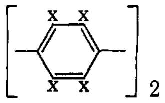
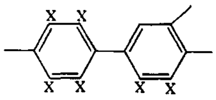
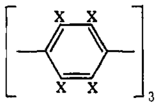
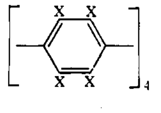
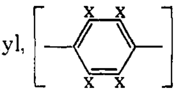
TABLE II

INFRARED CORRELATIONS

Number of adjacent hydrogen atoms on benzene ring	Band(s), μ
5	13.0–13.7 and 14.1–14.5
4	13.0–13.6
3	12.3–13.3
2	11.6–12.5
1	11.1–11.6

TABLE III

CONSECUTIVE *para*-TYPE LINKAGES[a]

	Wave length of band, μ	Spectral examples (Fig. 1–5)
 or 	11.7–12.0	1, 7, 8, 9, 10 16, 18, 20
 or 	12.0–12.1	2, 8, 9, 19
	12.2	3
	12.25	4
p-polyphenyl, 	12.4	5

[a] x = C–H bonds giving adsorption bands.

After drying the ether layer over magnesium sulfate, filtering, and evaporating the ether, 30 g. of a sirupy residue was obtained.

A solution which contained 30 g. of this sirupy residue and 20 g. of bromine dissolved in 200 ml. of chloroform was gently heated for 30 min. Upon distillation there was obtained 14.6 g. (45% yield) of a light yellow, viscous material boiling at 233–237° (4 mm.). The material was redistilled to obtain the product boiling at 200–205° (1.5 mm.) with a refractive index ($n^{20}D$) of 1.6786.

Anal. Calcd. for $C_{18}H_{13}Br$: C, 69.9; H, 4.2; Br, 25.8. Found: C, 69.5; H, 4.2; Br, 26.2.

***p*-Hexaphenyl.**—*p*-Hexaphenyl was prepared by subjecting 9 g. of *p*-terphenyl to electron irradiation at 316° for 14 hr. at approximately 10^9 rads dosage. Repeated extractions of the irradiation product with boiling benzene gave 0.1 g. of an insoluble material which was analyzed by infrared as *p*-hexaphenyl.

1,2,4-Triphenylbenzene.—To a solution of 4′-lithio-*m*-terphenyl prepared from 25 g. of 4′-bromo-*m*-terphenyl[13] and 66.4 ml. of a 1.2 *M* solution of butyllithium in *n*-heptane was added 4 g. of cyclohexanone, and the solution was stirred for 2 hr. at 10°. The solution was hydrolyzed with aqueous ammonium chloride and extracted with ether. The ether layer was dried over anhydrous magnesium sulfate, filtered, and distilled to give 7.8 g.

---

[13] J. J. E. Schmidt, J. A. Krimmel, and T. J. Farrell, Jr., Wright Air Development Center, Technical Report-207, part III.

TABLE IV

CONSECUTIVE *meta*-TYPE LINKAGES

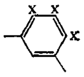
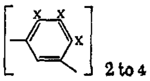
	Wave length of band, μ	Spectral examples (Fig. 1-5)
	12.4–12.7	6, 9, 16, 17, 18, 19, 20
	12.6–12.9	10, 11, 12, 13, 16, 17

TABLE V

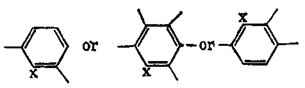
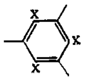
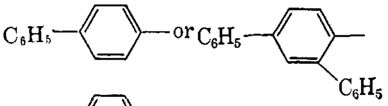
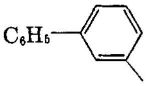
	Wave length of band, μ	Spectral examples (Fig. 1-5)
	11.0–11.35	6, 7, 9, 10, 11, 12, 13, 15, 16, 17, 18, 19, 20
	11.35–11.5	14, 20

TABLE VI

TERMINAL LINKAGES

	Wave length of bands(s), μ	Spectral examples (Fig. 1-5)
	14.35–14.6	1, 2, 3, 4, 5, 7, 8, 9
	14.2–14.35[a]	6, 11, 12, 13, 16, 17, 18, 19, 20

[a] Excluding *m*-Terphenyl.

of a viscous liquid which boiled at 225° (1.2 mm.). A small amount of this material was heated with 10% palladium–charcoal at 300° for 1 hr. The mixture was extracted with boiling *n*-hexane which, after evaporation of the solvent and recrystallization from *n*-hexane, gave the white crystalline product.

3,4′-Di(3-xenyl)biphenyl.—To a solution which contained 4-lithio-*m*-terphenyl in 100 ml. of ether prepared from 2.6 g. of 4-bromo-*m*-terphenyl[4] and 9.2 ml. of a 1.2 *M* solution of butyllithium-*n*-heptane was added 1.8 g. of 3(3-xenyl)cyclohex-2-en-1-one[9] dissolved in 30 ml. of ether. The mixture was stirred for 1.5 hr. at 10–20° and hydrolyzed with aqueous ammonium chloride; the ether layer was dried with magnesium sulfate and concentrated. The sirupy residue was heated at 260° for 30 min. with 10% palladium–charcoal. The mixture was extracted with hot *o*-xylene and after recrystallization from *o*-xylene gave 1.4 g. of the product.

2,4-Diphenyl-3′-(3-xenyl)biphenyl.—2,4-Diphenyl-3′-(3-xenyl)-biphenyl was prepared in a manner similar to the preceding procedure from 7.7 g. of 4′-bromo-*m*-terphenyl and 5.7 g. of 3-(3-xenyl)cyclohex-2-en-1-one followed by aromatization with 10% palladium–charcoal to give 1.5 g. of the desired polyphenyl.

3,4′-Di(4-xenyl)biphenyl.—3,4′-Di(4-xenyl)biphenyl was prepared in the same manner as that described for the preparation of 3,4′-di(3-xenyl)biphenyl, except that 4-bromo-*p*-terphenyl[5] and 3-(4-xenyl)cyclohex-2-en-1-one[3] were the reactants. Final purification was by sublimation at 360° (0.05 mm.).

Anal. Calcd. for $C_{36}H_{26}$: C, 94.3; H, 5.7. Found: C, 94.2; H, 5.7.

2,3′-Di(3-xenyl)biphenyl.—3-Lithio-*m*-terphenyl was prepared from 3.09 g. of 3-bromo-*m*-terphenyl dissolved in 100 ml. of ether and 10 ml. of a 1.2 *M* solution of butyllithium-*n*-heptane. After slowly adding at 10° with stirring a solution which contained 2.5 g. of 2-(3-xenyl)cyclohexanone dissolved in 50 ml. of ether, the mixture was stirred for 1 hr. and hydrolyzed with cold, dilute sulfuric acid. The ether layer was washed with aqueous sodium carbonate, dried over anhydrous magnesium sulfate, and concentrated to give 5.1 g. of a sirupy residue. The sirupy material was heated at 300° for 3 hr. with red phosphorus. The mixture was extracted with benzene and filtered; the filtrate was evaporated to dryness. This residue was dissolved in a 90:10 mixture of *n*-hexane and benzene and passed through a 12 × 700 mm. glass tube packed half full with F-20 activated alumina. Several fractions were obtained by eluting the column with graded concentrations of benzene–*n*-hexane. The desired material was eluted when the column was washed with a 60:40 mixture of *n*-hexane–benzene. The eluate was evaporated and the product was recrystallized from an ethanol–benzene mixture.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.3; H, 5.7. Found: C, 94.4; H, 5.8.

2,4′-Di(3-xenyl)biphenyl.—A solution of 3.5 g. of 2-(3-xenyl)-cyclohexanone[2] in 50 ml. of ether was added to 4-lithio-*m*-terphenyl prepared from 4.0 g. of 4-bromo-*m*-terphenyl and 12 ml. of a 1.2 *M* solution of butyllithium-*n*-heptane, and the total mixture was stirred for 3 hr. at 25°. The mixture was hydrolyzed and the sirupy precursor was separated in the usual manner. A solution which contained 3.0 g. of the precursor dissolved in a chloroform–bromine mixture was gently heated on a steam bath for 1 hr. and then concentrated. The resulting residue was digested with *n*-hexane to give 0.8 g. of a white crystalline product.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.3; H, 5.7. Found: C, 93.9; H, 5.8.

2,4′-Di(4-xenyl)biphenyl.—2,4′-Di(4-xenyl)biphenyl was prepared in the usual manner from 4-bromo-*p*-terphenyl and 2-(4-xenyl)cyclohexanone. Aromatization was effected with 10% palladium–charcoal.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.3; H, 5.7. Found: C, 94.3; H, 5.7.

3,5-Diphenyl-4′-(3-xenyl)biphenyl.—The addition of the aryllithium prepared from 2.1 g. of 1,3-diphenyl-5-(4-bromophenyl)-benzene[11] to 0.86 g. of 3-phenylcyclohex-2-en-1-one[11] was carried out in the usual manner. The precursor (1.7 g.) was aromatized with bromine–chloroform, and the residue was purified by passing through an activated alumina column to give 0.5 g. of the product after recrystallization from ethanol–benzene.

Anal. Calcd. for $C_{36}H_{26}$: C, 94.3; H, 5.7. Found: C, 94.2; H, 5.8.