[Contribution from the National Bureau of Standards, U. S. Department of Commerce]

The Synthesis and Infrared Absorption Spectra of Some *m*-Polyphenyls

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Received July 6, 1956

The syntheses of 1-amyl-3-(3-xenyl)benzene, *m*-sexaphenyl, and *m*-octaphenyl are described. Infrared absorption spectra are given for *m*-quatraphenyl, *m*-quinquaphenyl, *m*-sexaphenyl, and *m*-octaphenyl.

In connection with work carried on in this laboratory involving the synthesis of organic heat transfer liquids, certain *m*-polyphenyls have been prepared and the infrared spectra of these compounds have been determined.

The method of preparation in all cases was that of Woods and Reed[1] or a modification of their work. The results obtained in the synthesis of *m*-quatra- and *m*-quinqua-phenyl agree with those reported by Woods and Reed except for a disagreement on the melting point of *m*-quinquaphenyl.[2] 1-Amyl-3-(3-xenyl)benzene was prepared by dehydrogenating the intermediate diene [1-amyl-3-(3-xenyl)cyclohexadiene-1,3] prepared from the reaction of *n*-amylmagnesium bromide and 3-(3-xenyl)-Δ^2-cyclohexenone. *m*-Sexaphenyl and *m*-octaphenyl were synthesized by dehydrogenating the respective partially hydrogenated analogs obtained from the reaction of 3-phenyl-Δ^2-cyclohexenone with 3,3′-dilithiumbiphenyl in the case of *m*-sexaphenyl and from the reaction of 3-(3-xenyl)-Δ^2-cyclohexenone with 3,3′-dilithiumbiphenyl in the case of *m*-octaphenyl.

All the compounds prepared had a maximum absorption in the ultraviolet very close to 249 mμ. The extinction coefficients for *m*-quatraphenyl and *m*-quinquaphenyl are in good agreement with those reported by Woods, Van Artsdale, and Reed.[3] The values obtained for the other polyphenyls are given in Table I.

TABLE I

Melting Points and Extinction Coefficients of *m*-Polyphenyls

Compound	M.W.	M.P., °C.	ϵ
1-Amyl-3-(3-xenyl)benzene	300		35,500
m-Quatraphenyl	306	86.5–87.3	59,000
m-Quinquaphenyl	382	117–117.5	79,500
m-Sexaphenyl	458	147.2–147.8	102,000
m-Octaphenyl	610	129–131	146,000

A mass spectrometer analysis of the sexaphenyl and octaphenyl products showed the molecule ion of molecular weight 458 in the former analysis and the molecule ion of molecular weight 610 in the latter analysis to be the most abundant ion in the spectrum.

The melting point obtained on the material isolated from the synthesis of *m*-octaphenyl appears to be considerably lower than that which would be expected if one obtains progressively higher values with increase in molecular weight of the *m*-polyphenyls. In addition it should be noted that the melting range of this material was not easily defined due to the high viscosity and opacity of the resulting glass. The isolated product may possibly contain some partially hydrogenated rings which would effect an appreciable lowering of the melting point of pure *m*-octaphenyl.

The infrared absorption spectra shown in Fig. 1 are typical of those obtained from *m*-disubstituted benzenes. The strong band at 770–800 cm.$^{-1}$ and the medium band at 860–910 cm.$^{-1}$ are characteristic of this class of compounds and have been assigned[4,5] to motions involving the deformation of C—H bonds out of the plane of the 6-carbon nucleus. It is of interest to note the shift of the band at 770–800 cm.$^{-1}$ to a higher frequency, and the increase in complexity of this band with increase in molecular weight of the polyphenyls.

Acknowledgments. The author wishes to thank Mr. James E. Stewart who determined the infrared absorption spectra and assisted in their interpretation. Carbon-hydrogen analyses were performed by Mr. Lawrence A. Machlan and Miss Lorna J. Tregoning. The work was supported by a contract with the Atomic Energy Commission.

EXPERIMENTAL

1-Amyl-3-(3-xenyl)benzene. A solution of *n*-amylmagnesium bromide was prepared from 72.5 g. of *n*-amyl bromide (0.48 mole) and 11.8 g. of magnesium (0.48 g.-atom) in dry ether (500 ml.) in the usual manner. A solution of 99.2 g. of 3-(3-xenyl)-Δ^2-cyclohexenone (0.4 mole) in 300 ml. of an equal mixture of ether and benzene was added to the Grignard solution over a period of three hours with stirring. The resulting complex was hydrolyzed with cold 10% sulfuric acid (500 ml.) and the ether-benzene layer was washed with

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(1) Woods and Reed, *J. Am. Chem. Soc.*, **71**, 1348 (1949).

(2) Woods and Reed report a melting point of 97–98° for this compound, while the value found in this laboratory was 117–117.5°. An equal mixture of the latter material and a sample of the former, kindly provided by Dr. Woods, gave a melting range of 103–113°, indicating a higher degree of purity for the material reported in this paper.

(3) Woods, Van Artsdale, and Reed, *J. Am. Chem. Soc.*, **72**, 3221 (1950).

(4) Bailey, Ingold, Poole, and Wilson, *J. Chem. Soc.*, 222 (1946).

(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1954, p. 54.

dilute sodium carbonate followed by several water washes. After removal of the solvent the residue was distilled at reduced pressure. The crude 1-amyl-3-(3-xenyl)cyclohexadiene-1,3 (95.4 g.) was obtained as a yellowish-green liquid boiling at 190–204° (2 mm.). Removal of the unreacted 3-(3-xenyl)-Δ^2-cyclohexeneone from this intermediate was accomplished by refluxing the crude product (84.9 g.) with 19.8 g. of 2,4-dinitrophenylhydrazine in 95% ethanol (1.5 l.) containing 4 ml. of concentrated hydrochloric acid to form the red phenylhydrazone (m.p. 209–210.5°), 9 g. of which was obtained following cooling and filtration of the alcoholic solution. The oil which had settled out of the alcohol filtrate was dissolved in ether, washed with dilute hydrochloric acid, dilute sodium hydroxide, and several water washes. Distillation of the residue under reduced pressure following removal of the ether gave 59.3 g. of distillate boiling at 180–205° (2 mm.) which upon redistillation gave 44.5 g. of 1-amyl-3-(3-xenyl)cyclohexadiene-1,3, a yellowish-green liquid boiling at 196–203° (2 mm.). This intermediate (44.5 g.) was dehydrogenated with 4.5 g. of 5% palladium-on-charcoal at 300° for three hours. After cooling, the residue was dissolved in ether, filtered, and washed twice with dilute sodium hydroxide and several times with water. Distillation of the residue after removal of the ether yielded 40 g. of 1-amyl-3-(3-xenyl)benzene boiling at 200–205° (2 mm.).

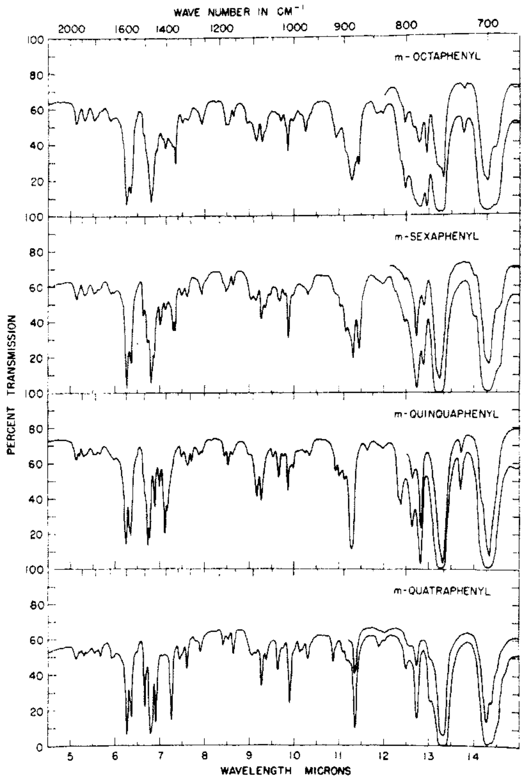

FIG. 1. INFRARED ABSORPTION SPECTRA OF *m*-POLYPHENYLS.

Anal. Calc'd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.60; H, 8.20.

m-Sexaphenyl. A solution of 75 g. of 3,3'-dibromobiphenyl[6] (0.24 mole) in 250 ml. of dry ether was added over a period of one hour to a solution of *n*-butyllithium prepared from 68.5 g. of *n*-butyl bromide (0.5 mole) and 8.3 g. of lithium (1.2 g.-atoms) in 250 ml. of dry ether. The mixture was kept at 0–5° during the addition and was maintained under an atmosphere of nitrogen. Following the addition the reaction mixture was stirred for four hours at 0–10°.

The partially saturated analog of *m*-sexaphenyl was prepared by the addition of a solution of 86 g. of 3-phenyl-Δ^2-cyclohexenone (0.5 mole) in 300 ml. of an equal mixture of benzene and ether to the solution of 3,3'-dilithiumbiphenyl. The addition, which was complete in about 1$^1/_2$ hours, caused gentle refluxing. The mixture was stirred for three hours and allowed to stand overnight. Hydrolysis of the complex was effected with cold 12% sulfuric acid (500 ml.). The ether-benzene layer was washed with dilute sodium carbonate followed by several water washes. After removal of solvent, the residue was distilled at reduced pressure. The fraction (50.8 g.) boiling at 300–335° (2 mm.) was collected as the product and had the appearance of a yellowish-orange glass. Attempts to crystallize this material were unsuccessful.

This product (25 g.) was dehydrogenated by treatment with 2.5 g. of 5% Pd-C at 280–310° for three hours. The resulting glass was extracted with successive portions (250 ml.) of 95% ethanol which after filtration of the hot solution and cooling gave 16.9 g. of a white powdery solid. Several recrystallizations from 95% ethanol gave *m*-sexaphenyl, a white crystalline solid melting at 147.2–147.8°.

Anal. Calc'd for $C_{36}H_{26}$: C, 94.28; H, 5.72. Found: C, 94.15; H, 5.56.

m-Octaphenyl. The procedure employed was essentially the same as that described for *m*-sexaphenyl with the substitution of 3-(3-xenyl)-Δ^2-cyclohexenone instead of the 3-phenyl-Δ^2-cyclohexenone. The 3-(3-xenyl)-Δ^2-cyclohexenone obtained by the procedure of Woods and Reed[1] was purified by several crystallizations from ether to give a yellowish-white crystalline solid melting at 82.5–84.0°. Distillation of the ether-benzene extract of the reaction mixture left 120 g. of residue which was originally prepared from 49.3 g. of *n*-butyl bromide (0.36 mole), 5.5 g. of lithium (0.8 g.-atom), 56 g. of 3,3'-dibromobiphenyl (0.18 mole), and 90 g. of 3-(3-xenyl)-Δ^2-cyclohexenone (0.36 mole). Part of the residue boiling at 112–227° (2 mm.) was separated by distillation and the remainder (105.5 g.) was fractionated in a molecular still which had a slightly modified design from that reported by Madorsky, Bradt, and Straus.[7] By means of a multiple receiver, five fractions were obtained, two of which were investigated. Fraction 3 (18 g.) distilled at a pot temperature of approximately 320–370° and condensed to a brownish-orange glass. A portion of fraction 3 was dehydrogenated with 5% Pd-C. This reaction was accompanied by the evolution of hydrogen bromide. Extraction of the dehydrogenated residue with hot 95% ethanol followed by filtration and cooling gave a solid which upon recrystallization from ethanol yielded a white crystalline solid which was identified as *m*-quinquaphenyl by a mixture melting-point determination. From this evidence it is reasonable to assume that fraction 3 may be the partially saturated analog of the bromoquinquaphenyl occurring as an unreacted intermediate. Fraction 5 (30 g.) distilled at a pot temperature of approximately 415–421° and condensed as a yellowish-orange glass. Attempts to crystallize this material were unsuccessful.

The dehydrogenation of fraction 5 and treatment of the resulting glass were carried out by two methods.

(*A*). In the first method fraction 5 (5 g.) was dehydrogenated with 0.5 g. of 5% Pd-C by heating at 230–250° for three hours. Extraction of the residue with hot 95% ethanol (250 ml.) followed by filtration and cooling yielded a grayish-white amorphous solid (50 mg.) melting at 75–93°. Continued alcoholic extractions gave the same amorphous solid. The dehydrogenated residue (5 g.) then was dissolved in ether, filtered to remove catalyst, and distilled until all the solvent had been removed. A portion (2 g.) of the glass obtained was dissolved in 200 ml. of ligroin (b.p. 90–120°) and adsorbed on a chromatographic column containing adsorption alumina (80–200 mesh). Solutions of increasing concentrations of ether in ligroin were used as eluents. Evaporation of solvent from twenty 50-ml. fractions of 30%

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(6) Snyder, Weaver, and Marshall, *J. Am. Chem. Soc.*, **71**, 289 (1949).

(7) Madorsky, Bradt, and Straus, *J. Research Natl. Bur. Standards*, **41**, 205 (1948).

ether in ligroin by volume gave white powdery solids of increasing melting ranges starting at 55–75° for early fractions, 70–90° for intermediate fractions, and 115–123° for the last seven fractions. Recrystallization of the higher-melting material from ether gave a white powdery solid melting at 129–131°.

(*B*). In the second method dehydrogenation of 5.5 g. of fraction 5 was effected by the method of Woods and Tucker.[8] The glossy residue obtained following the removal of the *p*-cymene was extracted with hot 95% alcohol from which an amorphous solid (m.p. 75–110°) precipitated upon cooling. The residue then was dissolved in dry ether (200 ml.), passed through a short column of adsorption alumina to remove colored impurities, and the resulting solution was concentrated to a volume of approximately 70 ml. After standing overnight a white crystalline solid (3 g.) formed which melted at 115–123°. Several recrystallizations of this material from ether gave a white crystalline solid (m.p. 129–131°) which showed no depression in melting point when mixed with an equal portion of the product obtained in procedure (*A*). A portion (0.4496 g.) or the solid obtained in procedure (*B*) was placed in a drying pistol under vacuum for 64 hours at 118°. The loss of weight at the end of this period was insignificant (0.03%) with no change in melting point.

Anal. Calc'd for $C_{48}H_{34}$: C, 94.39; H, 5.61. Found: C, 94.25; H, 5.60.

Infrared and ultraviolet absorption spectra. The infrared absorption spectra were determined with a Perkin Elmer Model 21 spectrophotometer using potassium iodide pellets of 1-cm. diameter and containing approximately 2 mg. of polyphenyl in 100 mg. of potassium iodide. For higher resolution in the region of 12–15 μ an additional pellet concentration of approximately 0.25 mg. in 100 mg. of potassium iodide was employed.

The ultraviolet absorption spectra were obtained with a Beckman D U spectrophotometer. Spectro grade cyclohexane was used as a solvent. Spectra were obtained at concentrations of approximately 2 and 4 mg./l. for each polyphenyl. Extinction coefficients in Table I were calculated from the optical densities of the dilute concentrations. The values calculated from the more concentrated solutions differed from those of the dilute solutions by 1% or less.

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[8] Woods and Tucker, *J. Am. Chem. Soc.*, **70**, 2174 (1948).