tate, the semicarbazone (5.4 g.) obtained from a portion (21 g.) of these fractions melted at 225–227° dec.

*Anal.* Calcd. for $C_{11}H_{19}ON_3$: N, 20.07. Found: N, 19.99.

The ketone obtained from this semicarbazone by regeneration with sulfuric acid boiled at 222° without decomposition and had the physical constants: $n^{20}D$ 1.4760, $d^{20}_4$ 0.9617, $[\alpha]^{20}D$ −56.07° (1 dm. neat). Its infrared spectrum was identical with that of dihydroverbenone produced by hydrogenating verbenone with Adams catalyst. Schulz and Doll[17] list the material as isoverbanone with the constants: b.p. 84° (20 mm.), $d^{20}_4$ 0.9644, $n^{20}D$ 1.4779, $[\alpha]D$ −59°, semicarbazone, 227°.

*Anal.* Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.80; H, 10.47.

**α-Terpineol.**—The major component of fractions 44 to 54 was an alcohol. The residual infrared absorption spectra after correction for the isoverbanone were essentially identical with that of authentic α-terpineol.

The secondary alcohols present in fractions 55–58 were converted to the *p*-nitrobenzoates for purification. Exhaustive recrystallization from pentane yielded an ester, m.p. 84–85°, $[\alpha]D$ 29.5° (c 3.8, chloroform), 48° (c 3.34, benzene).

(17) L. Schulz and W. Doll, "Ber. Schimmel & Co. Akt.-Ges.," 1942–1943, p. 50.

*Anal.* Calcd. for $C_{17}H_{20}O_4N$: C, 67.30; H, 6.97. Found: C, 67.65; H, 7.00.

The 3,5-dinitrobenzoate, m.p. 90–91.5°, was prepared in a similar manner.

Saponification of a sample of the *p*-nitrobenzoate (m.p. 80–81°) gave an alcohol in 90% yield, b.p. 220–221°, $n^{20}D$ 1.4843, $d^{20}_4$ 0.9568, $[\alpha]D$ 2.8° (c 5.4, benzene). The alcohol on standing partially solidified in long needles. One recrystallization from pentane gave a solid which melted at 54–56°. The infrared spectrum of the solid alcohol was substantially equivalent to that of the mixture from which it was isolated. Attempts to prepare a solid phenylurethan were unsuccessful.

*Anal.* Calcd. for $C_{10}H_{18}O$; C, 77.87; H, 11.83. Found: C, 77.35; H, 11.66.

Samples of authentic isopinocampheol were prepared by reduction of hydroxypinocamphone by the procedure of Kuwata,[18] and by catalytic hydrogenation of *trans*-pinocarveol.[8] The starting materials available were not optically homogeneous; hence the products were semi-solid. Infrared spectra of the two reduction products and of the alcohol isolated from the decomposition mixture were all substantially identical.

(18) T. Kuwata, THIS JOURNAL, 59, 2509 (1937).
OLUSTEE, FLA.

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# Preparation and Aromatization of Poly-1,3-cyclohexadiene[1]

BY C. S. MARVEL AND GORDON E. HARTZELL[2]

The polymerization of 1,3-cyclohexadiene to a low molecular weight polymer utilizing a Ziegler catalyst composed of triisobutylaluminum and titanium tetrachloride is reported. Although attempted dehydrogenation of the poly-1,3-cyclohexadiene failed to give a completely aromatized *p*-polyphenyl which could be isolated, evidence obtained from infrared spectra, analyses and X-ray diffraction studies confirmed the presence of *p*-polyphenyl in the products of the dehydrogenation reactions.

The lower members of the *p*-polyphenyl series possess remarkably high melting points, with *p*-quinquiphenyl and *p*-sexiphenyl melting without decomposition at 380 and 460–465°, respectively.[3,4] Numerous attempts have been made to obtain high molecular weight *p*-polyphenyls. The Ullmann reaction has not been successful for the preparation of *p*-polyphenyls larger than *p*-sexiphenyl.[5] A polyphenyl having a molecular weight of 2700–2800 has been reported from the condensation of *p*-dichlorobenzene in the presence of a liquid potassium–sodium alloy.[6] However, the physical properties of the polymer indicate that it was probably not an all-*para* polyphenyl.

Research was undertaken to determine the feasibility of preparing a high molecular weight *p*-polyphenyl (III) by dehydrogenation of poly-1,3-cyclohexadiene (II).

(2) National Science Foundation Fellow, 1956–1958.
(3) A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, 1170 (1939).
(4) R. Pummerer and L. Seligsberger, *Ber.*, 64, 2477 (1931).
(5) P. E. Fanta, *Chem. Revs.*, 38, 139 (1946).
(6) G. A. Edwards and G. Goldfinger, *J. Polymer Sci.*, 16, 589 (1955).



Numerous preparations of 1,3-cyclohexadiene (I) have been reported, including dehydrobromination of 1,2-dibromocyclohexane either with quinoline[7] or with sodium ethoxide,[8] dehydrobromination of 3-bromocyclohexene with quinoline[9] and pyrolysis of 1,2-diacetoxycyclohexane.[10] The most convenient synthesis yielding the highest purity 1,3-cyclohexadiene was that involving dehydrobromination of 3-bromocyclohexene, which was obtained in 70–80% yield from the reaction of N-bromosuccinimide and cyclohexene. The bromocyclohexene was heated with quinoline at 190° to give 1,3-cyclohexadiene in 50–60% yield. Vapor phase chromatography analysis showed the product to contain a minimum of 99% 1,3-cyclohexadiene. The other preparations were judged less convenient and generally gave 1,3-cyclohexadiene contaminated with cyclohexene and benzene. Dehydrobromination of 1,2-dibromocyclohexane with quinoline gave a product containing only 45% 1,3-cyclohexadiene, with 40% cyclohexene and 15% benzene.

(7) J. Pirsch, *Ber.*, 67, 1303 (1926).
(8) M. Mousseron and F. Winternitz, *Bull. soc. chim.*, 13, 332 (1946).
(9) A. T. Blomquist and J. Kwiatek, THIS JOURNAL, 73, 2098 (1951).
(10) W. J. Bailey and W. B. Lawson, *ibid.*, 79, 1444 (1957).

Polymerization of 1,3-cyclohexadiene to a linear polymer containing recurring cyclohexene units was accomplished in conversions as high as 92% using a Ziegler catalyst composed of a mixture of triisobutylaluminum and titanium tetrachloride. Conditions for the polymerization included the use of 0.6–4.0% triisobutylaluminum and sufficient titanium tetrachloride to obtain a molar ratio of the aluminum alkyl to the titanium compound of from 0.9 to 10.0. Best results were obtained at temperatures of 25° or lower and using n-heptane or cyclohexane as the solvent. The polymers obtained under optimum conditions were low molecular weight, amorphous powders, possessing inherent viscosities in the range of 0.11 to 0.16. These values may correspond very roughly to a molecular weight of perhaps five thousand to ten thousand. Poly-1,3-cyclohexadiene is a white, somewhat waxy powder, which appears to soften at about 170–180°. The polymer is oxidized slowly by air at room temperature and is quite rapidly oxidized at elevated temperatures, turning from a white to a yellow-amber color. Various samples of poly-1,3-cyclohexadiene were from 75–100% soluble in benzene, toluene and carbon disulfide, but were insoluble in ether, acetone and methanol. A brittle transparent film is formed upon slow evaporation of a solution of the polymer.

Although 1,3-cyclohexadiene can be polymerized in the presence of titanium tetrachloride alone, it was observed that the monomer is polymerized at a visibly faster rate by the Ziegler catalyst. In general, the use of titanium tetrachloride as the sole catalyst gave lower conversions to polymers which were indicated by their inherent viscosities to possess lower molecular weights than the corresponding poly-1,3-cyclohexadienes produced from a Ziegler catalyst system under identical conditions. The polymers obtained from a titanium tetrachloride catalyst were also considerably less soluble than those obtained using a Ziegler catalyst.

Aromatization of poly-1,3-cyclohexadiene was attempted using both catalytic and chemical methods. Various procedures involved the use of palladium, chloranil, sulfur and N-bromosuccinimide. Although none of the attempted dehydrogenation procedures enabled isolation of a completely aromatized p-polyphenyl, all of the above reagents led to products which possessed nearly identical infrared spectra which indicated the presence of p-polyphenyl in the products of the dehydrogenation reactions.

Best results were obtained using chloranil, an especially convenient dehydrogenating agent where conditions of low temperatures are desirable.[11] Treatment of poly-1,3-cyclohexadiene with chloranil in refluxing xylene for 48 hours gave a 60% yield of a tan-brown insoluble powder. The infrared absorption spectrum of this material was almost identical to a spectrum of p-quaterphenyl.[12] The absorption maxima corresponding to aromatic C–H stretching (3035 cm.$^{-1}$) and C=C skeletal inplane vibrations (1603, 1575 and 1486 cm.$^{-1}$) were very nearly identical with those of p-quater-

phenyl.[13] The maximum at 1006 cm.$^{-1}$, characteristic of para aromatic substitution, also corresponded very closely. The most intense absorption maximum in the infrared spectrum of the p-polyphenyl was that occurring at 811 cm.$^{-1}$, which can be assigned to para aromatic substitution. Absorption maxima at 765 and 695 cm.$^{-1}$ in the spectra of the impure polyphenyl correspond to out-of-plane deformation vibrations of five adjacent carbon-hydrogen bonds. The presence of these monosubstituted aromatic absorption maxima could be explained only by the end rings of the polyphenyl molecule. The possibility of phenyl side groups in the polymer does not seem likely in view of X-ray diffraction studies. The spectrum of the crude polyphenyl also showed absorption maxima corresponding to O–H stretching (3500 cm.$^{-1}$) and –CH$_2$– stretching (2925 and 2860 cm.$^{-1}$), showing that although partial aromatization had occurred, some tetrachlorohydroquinone and unaromatized poly-1,3-cyclohexadiene were also present in the tan-brown material. Analysis of the material showed 80.32% carbon, 5.81% hydrogen and 8.90% chlorine.[14] The presence of chlorine was assumed to be due to the tetrachlorohydroquinone impurity, and appropriate correcting calculations were made to arrive at an empirical formula of $(C_6H_{5.4})_x$ for the polymer. Since poly-1,3-cyclohexadiene has the formula $(C_6H_8)_x$ and polyphenyl has the formula $(C_6H_4)_x$, it appeared that about 65% of the theoretical amount of hydrogen necessary for complete aromatization had been lost by the polymer. From the analysis it was estimated that the tan-brown product contained 15% tetrachlorohydroquinone, 30% unaromatized poly-1,3-cyclohexadiene and 55% polyphenyl.

Although heating the impure polyphenyl for several hours at 450° under nitrogen removed the tetrachlorohydroquinone and destroyed the unaromatized poly-1,3-cyclohexadiene, this treatment also caused some carbonization to occur. A black powder was obtained, the infrared spectrum of which was identical to that of the brown material before heating, except for the absence of maxima corresponding to the tetrachlorohydroquinone and unaromatized poly-1,3-cyclohexadiene impurities. The weight of the material lost during the heating experiment corresponded almost exactly to the quantities of tetrachlorohydroquinone and unaromatized polymer which had been calculated to be present in the impure polyphenyl. The black powder, which did not melt when heated to 530°, was indicated by analysis to be composed of about 90% polyphenyl and 10% carbon. Although the black material was very stable under a nitrogen atmosphere, it was destroyed slowly by heating in air at temperatures above 300°. This instability of the aromatized polymer at high temperatures may be attributed to oxidation of isolated unsaturation or unaromatized sections of

(11) H. Gilman and E. A. Weipert, THIS JOURNAL, 79, 2281 (1957).

(12) The infrared spectra were determined by Mr. Paul McMahon, Miss Mary DeMott and Mr. James Brader, University of Illinois.

(13) Assignments of infrared absorption maxima were made in accordance with L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 54–71.

(14) The microanalyses were performed by Mr. Jozsef Nemeth, Miss Claire Higham, Mrs. Maria Stingl and Mrs. Frederic Ju, University of Illinois.

the polymer. The polyphenyl appeared to be relatively stable in air at 230–240°, since heating the material at this temperature for 72 hours failed to cause a loss in weight. A 3% gain in weight over the 72-hour period was observed, due probably to oxidation. It appears that any polyphenyl prepared by dehydrogenation of poly-1,3-cyclohexadiene must be completely aromatized, since any isolated unsaturation or unaromatized sections of the polymer would be susceptible to oxidation at high temperatures.

Additional proof of the existence of polyphenyl, as well as information concerning the structure of the polymer, was gained from X-ray diffraction studies.[15] X-Ray powder patterns showed that whereas the original poly-1,3-cyclohexadiene was amorphous, the polyphenyl is quite crystalline. The X-ray powder pattern of the polyphenyl was found to be identical to that obtained from p-quaterphenyl with respect to the positions and relative intensities of the three major rings. However, the patterns of the polyphenyl did show the presence of some amorphous material. Calculations made from the X-ray transmission patterns gave values of 9.07, 6.39, 4.54, 3.96 and 3.22 Å. for the d-spacings of the crystalline polyphenyl. The d-spacings corresponding to the most intense rings in the pattern were 4.54 Å. (most intense), 3.96 and 3.22 Å. The observation that the polymer gave an X-ray transmission pattern essentially identical with that of p-quaterphenyl lends additional support to the existence of p-polyphenyl. The d-spacing of 4.54 Å. found for the polymer is very close to the length of one phenyl unit of 4.4–4.5 Å. found by subtracting the length of the p-terphenyl molecule[16] from that of the p-quaterphenyl molecule.[17] The distance of 9.07 Å. corresponds to twice the length of one phenyl unit, and may be explained by postulating that two phenyls are required to comprise the true repeating unit, and that adjacent rings may be tilted slightly with respect to each other. However, since the d-spacing of greatest intensity is 4.54 Å., it is postulated that the rings are very nearly coplanar. The X-ray studies also indicated that the polyphenyl is essentially an all-para polymer, since the presence of ortho linkages (from 1–2 polymerization of 1,3-cyclohexadiene) would decrease the crystallinity of the polymer or lead to a more complex transmission pattern.

All attempts to isolate polyphenyl from the black mixture were unsuccessful due to the insolubility of the polymer, even in boiling biphenyl and hot p-terphenyl. However, the polymer did appear to dissolve slowly in hot sulfuric acid and in fuming sulfuric acid.

Partial dehydrogenation of poly-1,3-cyclohexadiene was accomplished using a palladium-on-charcoal catalyst at 350–370°. A low yield of a tan powder was obtained which was soluble in benzene, chloroform and carbon disulfide. The material melted at about 240–250°. The in-

frared spectrum of the tan powder was identical to that obtained from the product of the chloranil dehydrogenation reaction, with the absorption maximum at 811 cm.$^{-1}$ corresponding to para aromatic substitution being the most intense absorption in the spectrum. However, the spectrum also showed absorption corresponding to saturated carbon–hydrogen bond vibrations, indicating incomplete aromatization. Analysis of the material gave the empirical formula $(C_6H_{5.7})_x$. In view of the solubility of the product and its low melting point, it appeared likely that degradation as well as partial aromatization occurred. The low yield indicated that considerable quantities of the starting material and/or the reaction product could not be separated from the catalyst.

Attempted dehydrogenation of poly-1,3-cyclohexadiene with N-bromosuccinimide and also with sulfur gave products which possessed infrared spectra showing only very slight aromatization to have occurred.

Although a pure p-polyphenyl could not be isolated because of its insolubility, evidence obtained from infrared spectra, X-ray diffraction studies and analyses confirmed the existence of a p-polyphenyl obtained by dehydrogenation of poly-1,3-cyclohexadiene.

## Experimental

**1,3-Cyclohexadiene.**—According to the general method described by Pirsch,[18] 513 g. (2.12 moles) of 1,2-dibromocyclohexane[19] was added dropwise to 684 g. of quinoline heated to 190°. The crude 1,3-cyclohexadiene, which distilled from the reaction mixture, was washed with dilute sulfuric acid, dried over anhydrous calcium chloride and distilled to give 80.0 g. (47%) of product, b.p. 79–81°, $n^{20}$D 1.4630. Vapor phase chromatography analysis showed the product to contain 45% of 1,3-cyclohexadiene, 40% of cyclohexene and 15% of benzene.

1,3-Cyclohexadiene was prepared in greater purity utilizing a procedure based on that reported by Blomquist and Kwiatek.[9] A mixture of 500 g. (6.10 moles) of cyclohexene and 900 ml. of carbon tetrachloride was heated to reflux temperature and 253 g. (1.42 moles) of N-bromosuccinimide was added in small portions over a period of 40 minutes. Heating was continued at reflux temperature for five hours and the mixture was then allowed to stand overnight. The insoluble succinimide was removed by filtration and all distillate boiling below 85° was removed at atmospheric pressure. 3-Bromocyclohexene was distilled under reduced pressure, b.p. 64–70° (18 mm.). Redistillation gave 167 g. (73%) of 3-bromocyclohexene, b.p. 63–65° (16 mm.).

While maintaining continuous stirring under a nitrogen atmosphere, 353 g. (2.07 moles) of 3-bromocyclohexene was added dropwise to one liter of quinoline heated to 190°. Crude 1,3-cyclohexadiene was collected as it distilled. The crude product was washed with 3 N hydrochloric acid, dried over anhydrous magnesium sulfate, and distilled from sodium under nitrogen to give 84 g. (51%) of 1,3-cyclohexadiene, b.p. 79–80°, $n^{20}$D 1.4750. Vapor phase chromatography analysis showed the product to contain a minimum of 99% of 1,3-cyclohexadiene, with only a trace of cyclohexene.

*Anal.* Calcd. for $C_6H_8$: C, 90.00; H, 10.00. Found: C, 90.03; H, 10.35.

**Poly-1,3-cyclohexadiene (II).**—Polymerization of 1,3-cyclohexadiene was effected utilizing a catalyst composed of triisobutylaluminum[20] and titanium tetrachloride.[21] Sol-

(15) We are indebted to Dr. G. L. Clark and Mr. Ray Hunt, University of Illinois, for determination and interpretation of the X-ray transmission patterns.

(16) L. W. Pickett, *Proc. Roy. Soc. (London)*, **142A**, 333 (1933).

(17) L. W. Pickett, THIS JOURNAL, **58**, 2299 (1936).

(18) J. Pirsch, *Ber.*, **67**, 1303 (1926).

(19) A. H. Blatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1943, Coll. Vol. II, pp. 171–173.

(20) The triisobutylaluminum was obtained from the Hercules Powder Company.

(21) The titanium tetrachloride was purified as described by W. S. Clabaugh, R. T. Leslie and R. Gilchrist, *J. Research Natl. Bur. Standards*, **55**, 261 (1955).

Table I

POLYMERIZATION OF 1,3-CYCLOHEXADIENE

| Sample | Solvent | Parts by weight per 100 parts monomer | | | Moles Al(iBu)₃ moles TiCl₄ | Temp., °C. | Time, hr. | Conversion, % | Viscosity data | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Solvent | Al(iBu)₃ | TiCl₄ | $Al(iBu)_3$ moles TiCl$_4$ | | | | Concn. in g./100 ml. toluene | $\eta_{inh.}$ |
| 1 | n-Heptane | 1085 | 1.20 | 0.95 | 1.21 | 50 | 24 | 24 | 0.250 | 0.05 |
| 2 | n-Heptane | 546 | 1.00 | .80 | 1.21 | 4 | 96 | 36 | .257 | .08 |
| 3 | n-Heptane | 36 | 0.58 | .48 | 1.16 | 25 | 144 | 54 | .238 | .13 |
| 4 | n-Heptane | 36 | .58 | .48 | 1.16 | −20 | 144 | 70 | .104 | .13 |
| 5 | n-Heptane | 36 | .58 | .48 | 1.16 | −75 | 144 | 88 | .101 | .16 |
| 6 | n-Heptane | 29 | 1.16 | .96 | 1.16 | −75 | 144 | 92 | .100 | .14 |
| 7 | n-Heptane | 50 | .. | 1.22 | .. | −20 | 24 | 14 | .132ᵃ | .08ᵃ |
| 8 | n-Heptane | 29 | 1.16 | 1.28 | 0.87 | −20 | 144 | 86 | .153 | .14 |
| 9 | n-Heptane | 29 | 1.16 | 0.55 | 2.01 | −20 | 144 | 44 | .095 | .11 |
| 10 | n-Heptane | 144 | 2.48 | .80 | 3.00 | 25 | 48 | 54 | .214 | .12 |
| 11 | n-Heptane | 72 | 0.94 | .18 | 5.10 | 25 | 66 | 44 | .204 | .16 |
| 12 | n-Heptane | 100 | 4.00 | .38 | 10.00 | 25 | 24 | 54 | .193ᵃ | .13ᵃ |
| 13 | Toluene | 346 | 0.60 | .48 | 1.21 | 50 | 48 | 90 | .228 | .05 |
| 14 | Benzene | 209 | 1.12 | 1.07 | 1.00 | 4 | 48 | 83 | .213ᵃ | .12ᵃ |
| 15 | Benzene | 50 | .. | 1.11 | .. | 4 | 24 | 16 | .227ᵃ | .03ᵃ |
| 16 | Cyclohexane | 400 | 2.48 | 2.40 | 1.00 | 25 | 120 | 76 | .504 | .08 |
| 17 | Cyclohexane | 100 | 2.48 | 0.80 | 3.00 | 25 | 120 | 72 | .505 | .14 |

ᵃ Viscosity was determined in benzene.

Vents used included n-heptane, cyclohexane, benzene and toluene, which were dried by heating under reflux over sodium, followed by distillation from sodium. The solvents were stored under a nitrogen atmosphere over sodium wire or calcium hydride.

Preparation of polymerization mixtures and all transfers of catalysts were made under a dry nitrogen atmosphere, using appropriate hypodermic syringes. The polymerization mixtures were prepared by adding the desired amount of a 10% solution of triisobutylaluminum to the polymerization solvent contained in two-ounce screw-cap bottles. Measured amounts of titanium tetrachloride then were added to the mixtures, causing the immediate formation of a dark brown precipitate. The bottles were sealed with rubber gaskets and the catalyst mixtures were allowed to age for 15–30 minutes, after which the monomer was injected into the bottles by means of a hypodermic syringe and needle, which was pushed through holes in the bottle caps and through the gaskets. Polymer formation generally was observed shortly after addition of the monomer. At the end of the polymerization period, the contents of the bottles were emptied into methanol to decompose the catalyst. The polymers were shaken in benzene and reprecipitated by addition to methanol as many times as was necessary to remove the color of the catalyst and obtain white polymers. The soluble portions of the polymers were freeze-dried from benzene solutions. Table I gives typical polymerization conditions and results. All polymerizations were made on a scale using 5 g. of monomer. Infrared spectra of films of poly-1,3-cyclohexadiene showed absorption maxima corresponding to =C–H stretching at 3010 cm.⁻¹, –CH₂– stretching at 2925 and 2850 cm.⁻¹, C=C stretching at 1647 cm.⁻¹ and –CH₂– deformation at 1450 cm.⁻¹.

Anal. Calcd. for (C₆H₈)ₓ: C, 90.00; H, 10.00. Found: C, 89.85; H, 10.00.

p-Polyphenyl (III).—A mixture of 30.8 g. of chloranil and 125 ml. of xylene was placed in a 500-ml., three-necked flask, equipped with a stirrer and a reflux condenser. After the mixture had been heated to reflux temperature, a mixture of 5.0 g. of poly-1,3-cyclohexadiene in 250 ml. of hot xylene was added. The reaction mixture was heated at reflux temperature with continuous stirring for 48 hours. The mixture, after cooling to room temperature, was filtered to obtain a brown solid. The brown material was placed in a Soxhlet apparatus and extracted with ethanol for 24 hours, ether for 8 hours, toluene for 24 hours, and finally with ethanol for an additional 8 hours. The remaining undissolved material was air-dried at room temperature, giving 2.9 g. of a tan-brown powder. Infrared spectra of this material were obtained on mulls in Nujol, Kel-F fluorocarbon grease and hexachlorobutadiene in order to examine all regions of the spectrum. The spectra showed absorption maxima corresponding to O–H stretching at 3500 cm.⁻¹, –CH₂– stretching

at 2925 and 2860 cm.⁻¹, aromatic C–H stretching at 3035 cm.⁻¹, C=C skeletal in-plane vibrations at 1603, 1575 and 1486 cm.⁻¹ and several maxima characteristic of aromatic substitution (1006, 811, 765 and 695 cm.⁻¹). Analysis of the material showed 80.32% carbon, 5.81% hydrogen and 8.90% chlorine. The chlorine analysis was assumed to be due to tetrachlorohydroquinone which was not removed by the extraction processes and would correspond to 15.6% of this impurity in the product mixture. Appropriate calculations, correcting for this quantity of tetrachlorohydroquinone, led to an empirical formula of (C₆H₅.₄)ₓ for the polymer. The tan-brown powder did not melt upon heating to 530°, but slowly turned black during the heating process.

A small quantity (203 mg.) of the crude, incompletely aromatized polymer was heated under a nitrogen atmosphere at 445–450° for five hours. Rather pungent smelling, white vapors were evolved when the temperature reached 250° and continued to be evolved for the first two hours of heating. A black powder was recovered which weighed 118 mg. (58% recovery). This black residue, which did not contain chlorine, gave an analysis corresponding to the empirical formula (C₆H₄.₄)ₓ. X-Ray diffraction patterns of the black material showed it to be highly crystalline. An 800-mg. sample of the brown product of the chloranil dehydrogenation reaction was heated under nitrogen at 450° for 20 hours to determine whether further heating would cause a greater loss in weight of the material than was obtained by heating for five hours. A maximum weight loss of 39% was attained after ten hours of heating. Analysis of the black residue gave an empirical formula of (C₆.₇H₄)ₓ. Assuming the polymeric material to be completely aromatized, this analysis would indicate about 10% excess carbon. Infrared spectra of the black powder, obtained on mulls in Nujol, Kel-F grease and hexachlorobutadiene, were identical to those obtained from the brown material before heating, except for the absence of maxima corresponding to tetrachlorohydroquinone and unaromatized poly-1,3-cyclohexadiene. The black material obtained from these experiments was insoluble in all solvents, including dimethyl sulfoxide, boiling biphenyl and hot p-terphenyl. However, the polyphenyl did appear to be dissolved slowly by concentrated sulfuric acid and by fuming sulfuric acid. In order to determine whether the original poly-1,3-cyclohexadiene could survive under the conditions of the preceding experiments, a 440-mg. sample of the unaromatized polymer was heated under nitrogen at 450° for five hours. The same white fumes were evolved at temperatures above 250° and only 45 mg. of the sample was recovered as a dark brown to black film deposit (10% recovery).

To 500 mg. of poly-1,3-cyclohexadiene in a 20-ml. flask equipped with a side-arm was added 700 mg. of pure anthracene and 500 mg. of 10% palladium-on-charcoal. The flask was fitted with an outlet tube, and the contents were heated

slowly to 350° by a Woods metal-bath, while a stream of dry nitrogen was swept through the flask. The temperature of the bath was kept at 350–370° for 5 hours. At the end of 5 hours, the anthracene was removed by sublimation. The residue was extracted in a Soxhlet apparatus with hot benzene for 40 hours. The benzene solution was freeze-dried for 48 hours at 0.1 to 0.05 mm. pressure. A 110 mg. yield of a fluffy, tan powder was obtained, which was very soluble in benzene, chloroform and carbon disulfide and partially soluble in carbon tetrachloride. It was insoluble in methanol and acetone. The material appeared to melt at 240–250°. The infrared spectrum of the tan powder was almost identical to the spectra obtained from the product of the chloranil dehydrogenation reaction. All absorption maxima characteristic of $p$-polyphenyls were present, with the maximum at 811 cm.$^{-1}$ corresponding to 1–4 aromatic substitu-

tion being the most intense absorption. The spectrum also showed maxima corresponding to saturated carbon–hydrogen bond vibrations at 2930 and 2850 cm.$^{-1}$, indicating incomplete aromatization. Analysis of the product gave the empirical formula $(C_6H_{5.7})_x$.

*Anal.* Calcd. for $(C_6H_4)_x$: C, 94.74; H, 5.26. Found: C, 91.59; H, 7.21.

Some autoxidation apparently occurred after the attempted dehydrogenation.

Attempted dehydrogenation of poly-1,3-cyclohexadiene using N-bromosuccinimide in the presence of benzoyl peroxide and also using sulfur in boiling dimethylformamide gave products which were indicated by their infrared spectra to possess some aromatic character.

Urbana, Ill.

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# Anthracene Photodimers. I. Elimination and Substitution Reactions of the Photodimer of 9-Bromoanthracene[1]

By Douglas E. Applequist, Robert L. Litle, Edwin C. Friedrich and Robert E. Wall
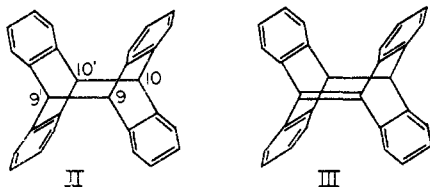
Chemical evidence for the head-to-tail structure of the photodimer of 9-bromoanthracene has been obtained. The dimer has been found to undergo transannular elimination of bromine with zinc, lithium aluminum hydride or organolithiums to give a new tetracyclododecane ring system. Products from halogen–metal exchange and from possible elimination–addition reactions have also been characterized. *t*-Butoxide ion has been found to dehydrobrominate the dimer with simultaneous ring opening to a 9,9'-dianthryl. Some examples of photoadducts of anthracene with substituted anthracenes have been discovered.

An olefin possessing a unique variety of strain is tricyclo[4.2.2.2$^{2,5}$]dodecene-1 (I), since the $\sigma$-



I
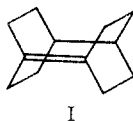
bonds around the double bond must be distorted out of the nodal plane of the $\pi$-bond, and yet as a result of the symmetry of the molecule, the coplanarity of the $p$-orbitals of the $\pi$-bond is undisturbed. Thus although I formally violates Bredt's rule,[2] it may be expected to have appreciable stability, and might be isolable in pure form. Compound I would be of interest as a tool for observing the chemical consequences of the $\sigma$–$\pi$-interference strain mentioned above and for a study of the stereochemistry of addition and elimination reactions in the same sense that bridgehead substituted compounds have been used to expose stereochemical requirements of substitutions reactions.[3] The only known examples of the tricyclododecane skeleton of I are anthracene photodimer II and the dimers of substitutued anthracenes.[4]



II        III

9-Anthraldehyde, methyl 9-anthroate and 9-hydroxymethylanthracene have been shown to give the head-to-head dimers (9,9'-disubstituted dianthracenes),[4] and it was anticipated that 9-bromoanthracene would dimerize in the same manner to give a compound which could be debrominated to 9,9'-dehydrodianthracene (III), a simple derivative of I.

9-Bromoanthracene did in fact dimerize readily in benzene solution in sunlight, but the only dimer isolated was 9,10'-dibromodianthracene (IV), the head-to-tail product, as shown by its zero dipole moment[5] and by the debromination to 9,10'-dehydrodianthracene (V) with zinc, lithium aluminum hydride or organolithiums, as discussed below. The simple free radical mechanism suggested by Greene[4] for the dimerization does not appear to account for the structure of the 9-bromoanthracene dimer. It is hoped that further work in progress will clarify the nature of the product-determining transition state.

The reaction of IV with zinc in acetone or with lithium aluminum hydride in tetrahydrofuran gave mainly dianthracene (II), but also small amounts of V, a thermostable, colorless, crystalline solid, subliming at about 320° and melting at 369–370°. It showed absorption maxima at 212 m$\mu$ (pseudomax., log $\epsilon$ 4.82) and 290 m$\mu$ (log $\epsilon$ 3.35), in satisfactory agreement with a structure containing four $o$-xylene chromophores.[6] The saturated character of V was demonstrated by its failure to react with

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(1) Presented at the 131st Meeting of the American Chemical Society at Miami, Fla., in April, 1957.

(2) F. S. Fawcett, *Chem. Revs.*, **47**, 219 (1950).

(3) D. E. Applequist and J. D. Roberts, *ibid.*, **54**, 1065 (1954).

(4) F. D. Greene, S. L. Misrock and J. R. Wolfe, Jr., This Journal, **77**, 3852 (1955).

(5) D. E. Applequist, E. C. Friedrich and M. T. Rogers, *ibid.*, **81**, 457 (1959).

(6) Compare with the spectra of 9,10-dihydroanthracene (R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectrum 114), triptycene (P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950)) and dianthracene (C. A. Coulson, L. E. Orgel, W. Taylor and J. Weiss, *J. Chem. Soc.*, 2961 (1955)).