Anal. Calcd. for $C_{28}H_{18}Cl_2O_2$: C, 73.53; H, 3.97. Found: C, 73.78; H, 3.96.

2,5-Di-*p*-chlorophenyl-2,5-diethoxydihydrofuran (Vbd)[28] was prepared from tetraphenylfuran (I) as described above (F): **higher melting isomer**, crystallized from absolute ethanol, m.p. 210–213°; ultraviolet maximum: 260 mμ, ε 14,160. *Anal.* Calcd. for $C_{32}H_{28}Cl_2O_3$: C, 72.31; H, 5.31. Found: C, 72.44; H, 4.92. **Lower melting isomer**,[28] m.p. 176–178.5°; ultraviolet maximum: 260 mμ, ε 15,570. *Anal.* Calcd. for $C_{32}H_{28}Cl_2O_3$: C, 72.31; H, 5.31. Found: C, 72.58; H, 5.00.

Isomerization of *cis*-di-(*p*-chlorobenzoyl)-stilbene (IV) to the *trans* isomer was effected by refluxing for 24 hr. a mixture of 0.3 g. of IV, 0.2 g. of potassium hydroxide and 6 ml. of ethanol. The insoluble *trans* isomer precipitated during the course of the reaction; 0.1 g. (33%), m.p. 231–233°, identified by mixture m.p. with a sample prepared from di-*p*-chlorobenzoylacetylene.[29]

Phosphorus Trichloride Reduction of *cis*-Di-*p*-chlorobenzoylstilbene (IV).—A solution of 0.5 g. of IV and 0.6 g. of phosphorus trichloride in 20 ml. of phosphorus oxychloride was shaken at room temperature for 30 min. The solvent was evaporated under reduced pressure and the residue was hydrolyzed with water and crystallized from glacial acetic acid; 0.4 g. (83%), identified as the furan III by m.p. 171–173° and mixture m.p.

Action of Bromine on Tetraphenylfuran (I). (**A**).—In moist ether in an experiment similar to that carried out by Dickerson,[38] a solution of 1.0 g. of I in 100 ml. of ether was shaken with a solution of 1.4 g. (3.2 molecular equivalents) of bromine in 100 ml. of water (20 min). The precipitate which separated together with a second crop obtained upon evaporation of the ether was recrystallized from glacial acetic acid; 0.95 g. (91%, identified as *cis*-dibenzoylstilbene (II)).

(**B**) **In Ether–Ethanol.**—A solution of 1.5 g. of bromine (3.5 molecular equivalents) in 20 ml. of absolute ethanol was added to a solution of 1.0 g. of the furan I in 75 ml. of ether. After periodic shaking over 75 min. at room temperature and evaporation under reduced pressure, fractional crystallization of the residue gave *ca.* 0.4 g. of unchanged furan I, and 0.65 g. of the higher-melting cyclic ketal Vbc (*ca.* 90% calculated from the furan actually used up in the reaction).

(**C**) **In Dry Ether.**—A mixture of 1.0 g. of I, 2 g. (4.6 molecular equivalents) of bromine and 50 ml. of absolute ether was allowed to react for 3 hr. at room temperature. Evaporation under reduced pressure and crystallization of the residue from petroleum hexane and then from glacial acetic acid gave 0.8 g. (56%) of the 2,5-di-*p*-bromo furan XXIV, m.p. 193.5–195° (identified).[40]

(**D**) **In Chloroform.**—A solution of 0.5 g. of I and 1.0 g. (4.6 molecular equivalents) of bromine in 15 ml. of chloroform after 30 min. at room temperature was evaporated under reduced pressure. The residue was treated with aqueous sodium thiosulfate and then crystallized from glacial acetic acid; yield 0.28 g. (40%), identified as the dibromo furan XXIV. The filtrate was evaporated and the residue was crystallized from absolute ethanol; 0.2 g. (27%), identified as *cis*-di-*p*-bromobenzoylstilbene (XXV).

(**E**) **In Phosphorus Oxychloride.**—A solution of 1.0 g. of I and 1.0 g. (2.3 molecular equivalents) of bromine in 20 ml. of phosphorus oxychloride, after standing for 30 min. at room temperature, was hydrolyzed in water. The product was crystallized from glacial acetic acid; yield 1.25 g. (89%), m.p. 195–196°, identified as the di-*p*-bromofuran XIV.

(**F**) **In phosphorus oxychloride**, carried out exactly as above in (E) but using 2 g. of bromine (4.6 molecular equivalents). The yield of *cis*-di-*p*-bromobenzoylstilbene (XXV) was 1.3 g. (89%), m.p. 223–224° (identified).

Action of Phenyl Grignard Reagent on Di-*p*-bromobenzoylacetylene (XXVI).—To a stirred solution of phenyl Grignard reagent made in the usual way from 10 g. of magnesium and 7 g. of bromobenzene in 50 ml. of absolute ether and cooled in an ice–salt-bath was added portionwise 5 g. of di-*p*-bromobenzoylacetylene[46] (*cf.* ref. 29) with further stirring for 20 min. Hydrolysis and fractional crystallizations of the mixture of products first from glacial acetic acid, and then the alcohol–benzene mixture and from petroleum hexane, gave two pure compounds: 0.50 g. (20%) of the unsaturated 1,4-diketone XXV (from air oxidation of the di-enolate of reaction) and 0.15 g. (3%) of the furan XXIV.

***cis*-Di-(*p*-bromobenzoyl)-stilbene** (1,4-di-*p*-bromophenyl-2,3-diphenyl-2-butene-1,4-dione) (XXV), m.p. 223.5–225°; absorption maxima: 6.01, 6.07 μ (carbonyl groups); 268 mμ, ε 23,100.

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 61.56; H, 3.32. Found: C, 61.85; H, 3.33.

2,5-Di-*p*-bromophenyl-3,4-diphenylfuran (**XXIV**), m.p. 194–196°; ultraviolet maxima: 236.5, 265, 335 mμ, ε 20,200, 16,000, 24,300.

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 63.42; H, 3.40: Found: C, 63.26; H, 3.54.

Action of Bromine Water on the Furan XXIV.—A mixture of 0.20 g. of XXIV, 3 g. of bromine, 20 ml. of ether and 10 ml. of water was shaken for 15 min. The excess bromine was reduced by sodium thiosulfate and the ether solution was evaporated. Crystallization of the residue from glacial acetic acid gave 0.15 g. (75%) of the unsaturated diketone XXV, m.p. 224–226° (identified).

Acknowledgment.—We are indebted to Millard G. Reese[28] and David W. Boykin, Jr.,[25,36] for carrying out certain of the experiments included or referred to above.

[46] R. E. Lutz and W. R. Smithey, Jr., *J. Org. Chem.*, **16**, 51 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

Reactions of 3,5-Dimethylbenzene-1,4-diazoöxide

BY TOYOKI KUNITAKE[1] AND CHARLES C. PRICE

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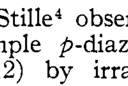
When 3,5-dimethylbenzene-1,4-diazoöxide was heated or irradiated with ultraviolet light in chlorinated hydrocarbons, the corresponding diazonium salt was obtained. When heated in chlorobenzene, the diazoöxide formed a mixture of hydroxybiphenyls and the diazonium salt. These results suggest the formation of an intermediate with free radical character. With boron trifluoride, a hydrated complex was obtained. The decomposition of the diazoöxide in tetrahydrofuran, thermally or photochemically, gave a one-to-one copolymer with the solvent. The product was crystalline under certain conditions. A cationic mechanism for this copolymerization is suggested.

The photochemical decomposition of benzene-*p*-diazoöxide has been studied in various solvents. Süs and co-workers[2] irradiated a methanolic solution of the diazoöxide with ultraviolet light and obtained *p*-methoxyphenol. In aromatic solvents, *p*-arylphenols were obtained. However, Wang[3] obtained a solid (m.p. 300°) having characteristics of a phenol along with a trace amount of *p*-phenylphenol, when a benzene solution was irradiated at room temperature. Irradiation of a toluene solution gave a mixture including *p*-benzylphenol, and in boiling ethanol, quantitative conversion to 4,4′-dihydroxyazobenzene occurred. A carbene (I) or its electromers (II or III) were assumed to be the intermediate.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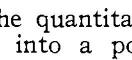
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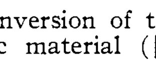
III

Stille[4] observed the quantitative conversion of the simple *p*-diazoöxide into a polymeric material ([η] 0.12) by irradiation in tetrahydrofuran. However, the rather low melting point reported for the polymer (120–130°) indicated it was not the expected poly-1,4-phenylene oxide.

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[1] Taken in part from the doctoral dissertation of T. Kunitake, Univ. of Pennsylvania, 1962.

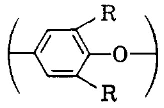
[2] O. Süs, K. Möller and H. Heiss, *Ann.*, **598**, 123 (1956).

[3] C. Wang, *Proc. Chem. Soc.*, 309 (1961).

[4] J. K. Stille, C. S. Marvel Symposium, Univ. of Arizona, Dec. 27, 1961.

Dewar and James[5] obtained a polymer by decomposing 3,5-dibromobenzene-1,4-diazoöxide (IV) at 72° in chlorobenzene. Analysis showed that the polymer (sintering at 200–220°, mol. wt. 1600–3600) contained both bromine and chlorine, indicating that some solvent molecules had been incorporated. The formation of free bromine, the considerable chlorine content (4–11%) in the polymer, and the isolation of several phenols suggested to these authors the occurrence of a diradical analogous to II as an active intermediate. When IV was irradiated in benzene at room temperature,[2] 3,5-dibromo-4-hydroxybiphenyl was the product.

Poly-(2,6-disubstituted phenylene oxides) (V) have been prepared by several workers.[6–8]



V. R = CH_3, C_2H_5, allyl, etc.

The purpose of our investigation was to obtain further information on the variety of courses for the decomposition of benzene-*p*-diazoöxides. 3,5-Dimethylbenzene-1,4-diazoöxide (VI) was selected for study since it has not been extensively investigated and since our experience in the preparation of poly-(xylenol)[6,7] indicated that two *ortho*-methyl groups markedly favored formation of linear high polymer.

Experimental

3,5-Dimethylbenzenediazoöxide (**VI**) was prepared either by a procedure based on the method by Hantzsch and Davidson (m.p. 113–114°,)[9] or by the method of Ried and Dietrich[10]; m.p. 121° (lit.[10] 121°). Strong infrared bands were noted at 2060 and 1600 cm.$^{-1}$ and ultraviolet absorption maxima in dioxane occurred at 349 mμ (log ε 4.27), 268 mμ (log ε 3.60) and 212 mμ (log ε 3.56).

Anal. Calcd. for $C_8H_8ON_2$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.64; H, 5.63; N, 18.66.

Thermal Decomposition in Dichloroethane.—Compound VI (5 mmoles, 750 mg.) was dissolved in 25 ml. of 1,2-dichloroethane (which had been distilled over phosphorus pentoxide) and heated at 50° under nitrogen for 7 days. A dark brown solution and a transparent precipitate were obtained. The filtered precipitate (0.18 g.) decomposed with bubbling at 118°. When treated with a warm mixture (4:1) of dioxane and ethanol, the precipitate lost its brown color without dissolution to give a grayish white powder and the decomposition point rose to 127°. The infrared spectrum of the substance showed a peak at 2220 cm.$^{-1}$ which is characteristic of diazonium salts. Thus the product is 3,5-dimethyl-4-hydroxybenzenediazonium chloride monohydrate (VII).

Anal. Calcd. for $C_8H_{11}N_2ClO_2$: C, 47.43; H, 5.48; N, 13.83; Cl, 17.52. Found: C, 47.76; H, 5.26; N, 13.54; Cl, 17.29.

Concentration of the filtrate above gave a tan-brown tar soluble in aqueous alkali. When the tar was added to benzene, an additional 0.01 g. of VII was recovered as a precipitate.

In refluxing dichloroethane, a dark brown reaction mixture was obtained with only a slight amount of VII.

Irradiation in Dichloromethane.—When VI (5 mmoles) was irradiated in purified dichloromethane at room temperature for 100 hours, 90 mg. of VII was obtained as a precipitate.

Irradiation by Ultraviolet Light in Carbon Tetrachloride.—Compound VI (5 mmoles) in 100 ml. of purified carbon tetrachloride was irradiated using a Blak Ray ultraviolet lamp (3660 Å.) at room temperature under nitrogen for 10 days. Toward the end of the reaction period, the reaction mixture consisted of a precipitate and a pale pink solution. The grayish-white precipitate, on filtration and washing with carbon tetrachloride, weighed 0.22 g. and decomposed with bubbling at 116°. The infrared spectrum of the substance was the same as VII.

Evaporation of the filtrate left a viscous oil which was reprecipitated from ether by petroleum ether (30–60°). Gray powder (20 mg.) softening at 140–150° was obtained. No further work was done on this substance.

Irradiation in Benzene.—Compound VI (5 mmoles) in 50 ml. of freshly-distilled benzene was irradiated under nitrogen for 315 hours. Evaporation of the solvent gave 0.8 g. of a mixture of crystals and a red-brown tar. Repeated recrystallization from a 2:3 mixture of dichloromethane and light petroleum ether and then twice from petroleum ether (60–110°), including an active carbon treatment in dichloromethane solution, gave white needles, m.p. 97–98°. The infrared spectrum had two strong peaks at 760 and 698 cm.$^{-1}$ which indicate monosubstitution on the benzene ring, and a triplet (888, 874 and 867 cm.$^{-1}$; all of medium intensity) indicating isolated hydrogen on the benzene ring. Thus the phenolic product is **3,5-dimethyl-4-hydroxybiphenyl** (**VIII**).

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.77; H, 7.12. Found: C, 84.97; H, 6.99.

Thermal Decomposition in Benzene.—Compound VI (5 mmoles) in 50 ml. of purified benzene was heated at 65° under nitrogen in an oil-bath. The reaction mixture turned pale orange after about 20 hours. After 70 hours, the reaction was stopped. The same procedure as described above gave white needles, m.p. 97–98°. The mixed melting point of these two products did not show any depression.

Thermal Decomposition in Chlorobenzene.—Compound VI (5 mmoles) dissolved in 50 ml. of freshly-distilled chlorobenzene was heated at 65–75° for 48 hours under the conditions described above. The reaction was nearly complete in 12 hours, as seen from more than 100 ml. of nitrogen evolution (theoretical, 112 ml., 25°, 1 atm.) and the faded color of the reaction mixture at this stage. The slight amount of precipitate formed was filtered and the solvent was evaporated from the filtrate, leaving a mixture of crystals and a black tar. The precipitate decomposed with bubbling at 113°. The infrared spectrum showed this substance to be VII.

The mixture of crystals and a black tar was subjected to vacuum sublimation twice at 80–100° and the white needles obtained were dried on a porous plate, m.p. 100–130°. Gas chromatographic separation of the crystalline mixture was unsuccessful. On recrystallization from petroleum ether (60–110°), the melting range of the white needles was 132–140° (sintering at 120°).

Anal. Calcd. for a 4:1 mixture of $C_{14}H_{13}OCl$ and $C_{14}H_{14}O$: C, 74.75; H, 5.90; Cl, 12.19. Found: C, 75.40; H, 6.96; Cl, 12.10.

The infrared spectra before and after recrystallization were taken and compared with that of VIII. In the region from 700 to 1100 cm.$^{-1}$, the following peaks decreased in intensity after recrystallizations, 698(vs), 745(s), 762(vs), 942(m), 983(w), 1000(vw) and 1130(m) cm.$^{-1}$, while the following were relatively unchanged, 715(vw), 726(w), 828(vs), 877(m), 1010(m), 1075(m) and 1090(s) cm.$^{-1}$. All the weakened peaks were found in the spectrum of VIII. Following Bellamy,[11] some of the peaks were assigned as follows: 698 cm.$^{-1}$, C–H out-of-plane deformation for the monosubstituted benzene ring; 715 and 726 cm.$^{-1}$, probably C–Cl stretching (similar peaks were found in the spectrum of 2,6-dimethyl-5-chlorophenol, but not in that of the 4-bromo derivative); 745 and 762 cm.$^{-1}$, C–H out-of-plane deformation for monosubstitution; 828 cm.$^{-1}$, C–H out-of-plane deformation for two adjacent hydrogens on aromatic rings (839 cm.$^{-1}$ in 4-chlorobiphenyl[12]); 877 cm.$^{-1}$, C–H out-of-plane deformation for an isolated hydrogen.

Apparently, the crystalline mixture was composed of two substances—VIII and 3,5-dimethyl-4-hydroxy-4′-chlorobiphenyl (IX)—and the former substance was lost to some extent on recrystallization. This fact was confirmed by the rise in the melting range and by elementary analysis. No peaks corresponding to the 2′-chloro derivative were found.

Polymerization by Irradiation in Tetrahydrofuran (**DZ-2**).—Compound VI (5 mmoles) dissolved in 50 ml. of dry tetrahydrofuran (refluxed and distilled over calcium hydride) was irradiated with magnetic stirring under nitrogen at room temperature. The evolved nitrogen was led to a gas buret filled with water through a bubble counter. The buret reading remained constant at 130 ml. after 95 hours. The irradiation was continued for 102 hours. The reaction mixture was concentrated to about 10 ml. and poured into excess methanol to give a yellow amorphous precipitate, which was dried under vacuum; yield 0.24 g., softening point 55–70°. Reprecipitation from benzene and methanol was repeated. The infrared spectrum showed a band at 3620-(w) cm.$^{-1}$ due to a small amount of hydroxyl group and at 855-(w) cm.$^{-1}$ due to out-of-plane deformation for an isolated aromatic hydrogen, but much weaker than in poly-(2,6-dimethylphenylene oxide). The n.m.r. spectrum showed the ratio of intensities of 2 (τ_{arom} 3.19, 3.60), 4.2 (τ_{OCH_2} 6.20, triplet), 11.5 (τ_{CH_3,CH_2} 7.80, 7.95, 8.10).

There remained an insoluble thin film on the wall of the reaction vessel up to the level of the reaction mixture. It weighed 50

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(5) M. J. S. Dewar and A. N. James, *J. Chem. Soc.*, 917 (1958).

(6) G. D. Staffin and C. C. Price, *J. Am. Chem. Soc.*, **82**, 3632 (1960); C. J. Kurian and C. C. Price, *J. Polymer Sci.*, **49**, 267 (1961).

(7) A. S. Hay, *ibid.*, **58**, 581 (1962).

(8) B. O. Lindgren, *Acta Chem. Scand.*, **14**, 1203 (1960).

(9) A. Hantzsch and W. Davidson, *Ber.*, **29**, 1522 (1896).

(10) W. Ried and R. Dietrich, *ibid.*, **94**, 387 (1961).

(11) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

(12) D. R. Augood, J. I. G. Cadogan, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 3412 (1953).

mg. and was not soluble in common organic solvents, but gave a dark colored solution in concentrated sulfuric acid. The substance became transparent at 160–170°. The X-ray diffraction pattern gave spacings corresponding to 5.67(w), 5.63(w), 4.70(s), 3.97(m), 3.69(m), 3.28(w), 2.92(w), 2.73(w) Å. and still weaker diffractions at higher angles.

When a THF solution of the soluble product was kept for a few days at room temperature, no precipitation occurred.

Thermal Polymerization in THF.—Compound VI (5 mmoles) was heated in THF under nitrogen for varying intervals. The solvent was removed under vacuum, leaving a pale orange viscous oil, which was dissolved in ether or benzene, washed with aqueous alkali and extracted with Claisen alkali.[13] Benzene solutions of the extracted and unextracted portions were subjected to freeze-drying. The results are shown in Table I, together with the data obtained in irradiation experiments. Elementary analyses for some of the polymeric products are shown in Table II.

TABLE I

DECOMPOSITION OF DIAZOÖXIDE VI IN TETRAHYDROFURAN[a] AND DIOXANE

No.	Condition	Reaction time	Yield, g.	Softening point, °C.	Mol. wt.[j]
DZ-2	U.v.	95 hr.	0.24	55–70	1380
			.05[g]	160–210	. .
DZ-12	U.v.[b]	215 hr.	.46[i]	Sticky solid	760
DZ-17	50°[c]	14 days	.12[h]	Viscous oil	630
			.20[i]	Viscous oil	450
DZ-14	Reflux[d]	20 hr.	.25[h]	Viscous oil	900
			.25[i]	Viscous oil	840
DZ-19	Reflux	20 hr.	.13[h]	Viscous oil	720
			.30[i]	Viscous oil	820
DZ-21	Reflux[e]	5 days	.26[h]	Viscous oil	470
			.22[i]	60-65°	1250
DZ-23	70°[f]	52 hr.	.08[h]	Viscous oil	. .
			.79[i]	Viscous oil	500

[a] VI (5 mmoles) in 50 ml. of the solvent. [b] 10 mole % of $CuSO_4$ present. [c] 20 mole % of triethylboron present; 25 ml. of the solvent. [d] 10 mole % of 2,6-dimethyl-4-bromophenol present. [e] 10 ml. of the solvent. [f] 50 ml. of dioxane as solvent. [g] THF-insoluble crystalline product. [h] Soluble in Claisen alkali, after washing with aq. alkali. [i] Insoluble in Claisen alkali. [j] Measured by a vapor phase osmometer (Mechrolab, Calif.) in benzene.

TABLE II

ELEMENTARY ANALYSES OF POLYMERS

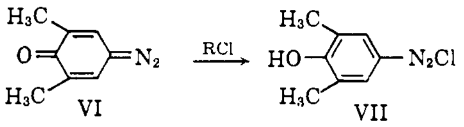
Sample	Carbon, %	Hydrogen, %	Nitrogen, %
DZ-2 THF-sol.	72.57	8.46	0.45
DZ-2 THF-insol.	72.86	8.02	. .
DZ-21 unextracted	74.39	7.52	1.58
Calcd. for $C_8H_8OC_4H_8O$	74.88	8.50	. .
DZ-23 unextracted	69.73	8.05	0.11
Calcd. for $C_8H_8OC_4H_8O_2$	69.21	7.74	. .

Formation of a Complex with Boron Trifluoride.—Into a solution of 5 mmoles of VI in 50 ml. of purified dioxane was added an excess of boron trifluoride etherate, forming a white precipitate instantly with the disappearance of the initial red-orange color. The precipitate was collected by filtration, washed with dioxane and dried; yield 0.83 g. Recrystallization twice from a 4:1 mixture of dioxane and ethanol gave pure white needles, m.p. 126–127° (decomposition with bubbling, sintering at 80°). The crystals were soluble in acetone (colorless), diglyme (colorless), ethanol (colorless), pyridine (pale yellow) and water (pale yellow) and sparingly soluble in dioxane and THF. The infrared spectrum (Nujol) showed a peak at 2250 cm.$^{-1}$, which is characteristic of diazonium salts.

Anal. Calcd. for $C_8H_8N_2OBF_3\cdot 2H_2O$: C, 38.14; H, 4.80; N, 11.12. Found: C, 38.20; H, 4.78; N, 11.10.

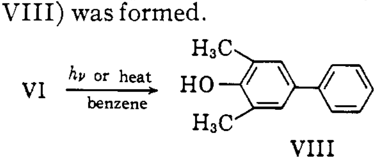
Discussion

Decomposition in Non-polar Solvents.—In chlorinated solvents, such as dichloromethane and *s*-dichloroethane, VI eliminated chlorine from the solvents to give the corresponding diazonium chloride VII.



This result was observed both with heating and with irradiation. The remainder of the product was black tar, soluble in the respective solvents and in aqueous alkali, from which no definite products were isolated. Irradiation in carbon tetrachloride gave VII and a slight amount of a gray amorphous soluble powder softening at 140–150°. In this case, the hydrogen atom necessary for the formation of VII must have been eliminated from another molecule of VI.

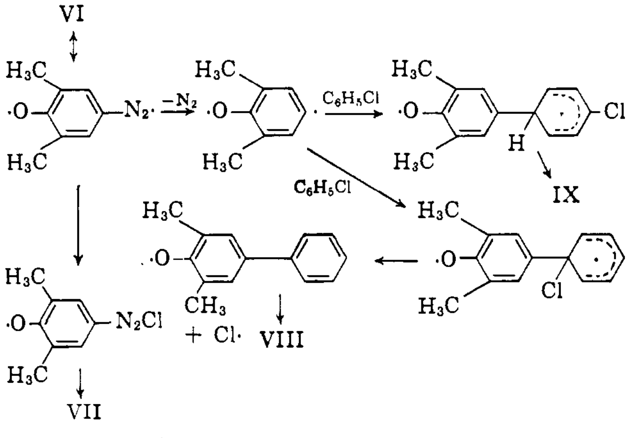
When a benzene solution of VI was refluxed or irradiated at room temperature, 3,5-dimethyl-4-hydroxybiphenyl (VIII) was formed.



The results agree with those obtained by Süs, *et al.*,[2] for photodecompositions of benzene-*p*-diazoöxide and the 3,5-dibromo derivative in benzene. No polymeric material was isolated, unlike Wang's result.[2]

The thermal decomposition of VI in chlorobenzene at around 70° gave three identified products. These are VII, VIII and 3,5-dimethyl-4-hydroxy-4′-chlorobiphenyl (IX). The formation of VII, as in chlorinated hydrocarbons, fits with the formation of the non-chlorinated biphenyl. While Dewar and James[5] had obtained a polymer by the decomposition of 3,5-dibromobenzene-1,4-diazoöxide in chlorobenzene, no polymer separated on reprecipitation from benzene and methanol. Furthermore, the 2′-chloro isomer of the biphenyl was not detected.

That chlorine elimination was observed in several chlorine-containing solvents, including carbon tetrachloride and chlorobenzene, suggests a free radical reaction path. In non-polar solvents, it would appear that both VI and the reactive intermediate formed from it by loss of nitrogen react in their diradical forms.



The formation of a diradical intermediate was also postulated by Dewar and James.[5]

Decomposition in Cyclic Ethers.—Decompositions of VI in THF or dioxane gave polymeric substances with molecular weights up to 1380, as summarized in Table I.

Irradiation in THF (DZ-2) gave a pale orange solid softening at 55–70° (mol. wt. 1380) and a small amount of an insoluble, crystalline film. The addition of cupric sulfate, which is known to catalyze the decomposition of diazo compounds, slightly decreased the molecular weight.

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[13] L. Claisen and O. Eisleb, *Ann.*, **401**, 38 (1913).

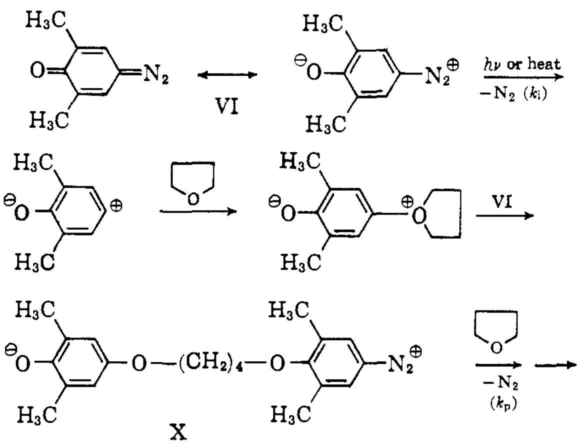
When VI was heated in refluxing THF (DZ-19), the product was separated into two parts by extraction with Claisen alkali. However, the infrared spectra of these portions were identical, including small hydroxyl peaks. Addition of triethylboron (DZ-17) or of 2,6-dimethyl-4-bromophenol (DZ-14) as possible initiators, did not affect the results significantly, while the use of less solvent increased the molecular weight of the product to some extent. Thermal decomposition in dioxane gave a viscous oil of low molecular weight.

Elementary analyses for some of the polymeric products, shown in Table II, gave lower carbon and higher hydrogen contents than expected from poly-(2,6-dimethylphenylene oxide), indicating a large amount of the solvent incorporated in the products. If a one-to-one copolymer with the solvent is assumed, the calculated values are fairly close to the analytical data found.

Solvent incorporation is supported also by physical data, such as n.m.r. and infrared spectra. The n.m.r. spectrum of the soluble part of DZ-2, showed a triplet at τ 6.20, which is characteristic of a methylene proton adjacent to ether oxygen and split by adjacent methylene protons. The ratio of intensities for the three groups of peaks (aliphatic, next-to-oxygen aliphatic and aromatic) was 11.5:4.2:2. While the ratio for a one-to-one copolymer should be 10:4:2, the comparatively low molecular weight of the product with the consequent sensitivity to different terminal groups may explain this discrepancy. The n.m.r. spectrum of the polymer sample prepared in dioxane showed three aromatic peaks at τ 3.1, 3.3 and 3.5, a complex methylene band centered at τ 6.2 and a methyl band at τ 7.8, with relative intensities of 2.0:6.9:5.0, close to the expected ratio of 2:8:6. There were also two additional bands at τ 2.7 and 8.2 with relative intensities 1.0 and 1.6. According to Jackman,[14] the aliphatic methylene groups should absorb at $\tau \simeq 8$, while those with oxygen attached should absorb at $\tau \simeq 6$. We found the aromatic hydrogens of poly-(xylenol) to absorb at $\tau = 3.38$, the methyl groups at 7.89.

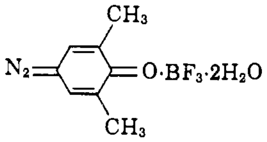
The infrared spectra of these polymeric products showed that a small amount of hydroxy group was present, that C–H out-of-plane deformation for an isolated hydrogen on the benzene ring was much weaker than in poly-(2,6-dimethylphenylene oxide), and that no particular peaks suggesting the presence of the cyclic THF group were present.

The assumption that the copolymer has an essentially regular structure with alternating phenylene oxide and tetramethylene oxide (for THF solvent) units is supported by fairly good analytical data fitting with the copolymeric structure, independent of the reaction conditions used, and by the formation of a crystalline product as seen from its X-ray diffraction pattern. However, no crystalline precipitates were obtained when THF solutions of some of the soluble products were kept for several days at room temperature. Presumably, the crystalline polymer is of considerably higher molecular weight than the soluble samples. In order for this scheme to produce polymer, conversion of X to the THF oxonium salt (k_p) must occur more rapidly than for VI (k_i).

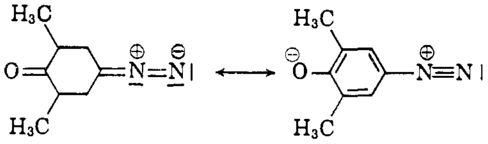


X

Complex Formation with Boron Trifluoride. Boron trifluoride etherate was added to VI in dioxane for the purpose of catalyzing polymer formation, as the compound is an efficient catalyst for the polymerization of diazomethane.[15] No polymerization or nitrogen evolution was observed. With an excess of boron trifluoride, a white crystalline precipitate was formed, which proved to be the dihydrate of a stable 1:1 complex. It has been proposed that the electronic structure of diazooxides is a resonance hybrid of the two extreme structures[16]



$N_2{=}C_6H_2(CH_3)_2{=}O{\cdot}BF_3{\cdot}2H_2O$



The N–N stretching peak in the infrared spectrum shifts to a higher frequency as the bond order increases from azo compounds (bond order 2) to diazonium salts (bond order 3).[11] This peak for VI occurs at 2060 cm.$^{-1}$ in accordance with the data for other diazoöxides.[10] Therefore, the bond order for diazoöxides must be close to that of diazomethane (2100 cm.$^{-1}$). On the other hand, the boron fluoride complex gave a shifted peak at 2250 cm.$^{-1}$, which is in the region for the peak of diazonium salts. Thus it can be concluded that when the oxygen coördinates with boron fluoride in the complex, VI assumes the highly polar structure on the right side to a very large extent. The solubility of the complex in polar solvents, such as water, ethanol, diglyme and acetone, as against the poor solubility in less polar THF and dioxane, is further supporting evidence of the ionic structure with considerable covalent bonding between boron and oxygen.

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