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Polyethers. XIV. Hydrogen Migration During Oxidative Coupling of 2,6-Xylenol

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An extension of earlier studies of the oxidative coupling of 2,6-xylenol[1] using tritium labels in the 3- or 4- positions indicates that 23% of the 4-H^3 is retained in the polymer, while 16% of the 3-label is lost. To explain these and earlier[1,2] results, we propose a radical coupling mechanism promoted by electron transfer resonance stabilization of the coupled product. The electron transfer process leaves a phenonium ring in which proton migration can occur to give a rearranged phenonium ion in which the 3- and 4-hydrogens have become equivalent.

Extensive investigations of the oxidative coupling of 2,6-xylenol have elucidated many important features of this remarkably facile polymerization.[1,2] It has been established that the reaction proceeds through free radical intermediates,[2c] that it is a stepwise polycondensation,[2b] that conversion of the terminal phenol group to a methyl ether transforms reactive monomers to inert diluents,[2d] and that deuterium substitution on oxygen appreciably affects the rate ($k_{OH}/k_{OD} = 2.52$) while there is almost no similar effect at the *p*-position ($k_{4H}/k_{4D} = 1.05$).[2d]

Because of our prior interest in the preparation of polyxylenol by an alternate route,[3] we have been interested in elucidating the structure and mechanism of formation of this polymer. For this purpose, we have prepared samples of 2,6-xylenol labeled with tritium in the 4- and in the 3-positions. The results lead to new insight into the mechanism of the polymerization reaction.

Discussion

The introduction of tritium at the 4-position of 2,6-xylenol was achieved by equilibration in alkaline tritiated water. Best and Wilson[4] demonstrated that under similar conditions, deuteration occurred exclusively in the *o*- and *p*-positions of phenol. Furthermore, Brodskii[5] showed that side-chain deuteration does not occur with *o*- or *p*-methylphenol. In this case, the label was confined exclusively to the 4-position of 2,6-xylenol as indicated by the loss of activity in the 4-bromo derivative (see Table I).

A more indirect route was required for the preparation of 2,6-xylenol-3-H^3, which was accomplished by equilibration of 4-amino-2,6-xylenol hydrochloride with tritiated water, and subsequent deamination. Best and Wilson[6] showed that aniline undergoes nuclear deuteration under similar circumstances and Brodskii[7] ruled out the possibility of methyl deuteration with toluidines. The activity observed for the 4-bromo and 3,4,5-tribromo derivatives definitely located all the tritium in the 3-position of 2,6-xylenol (see Table I).

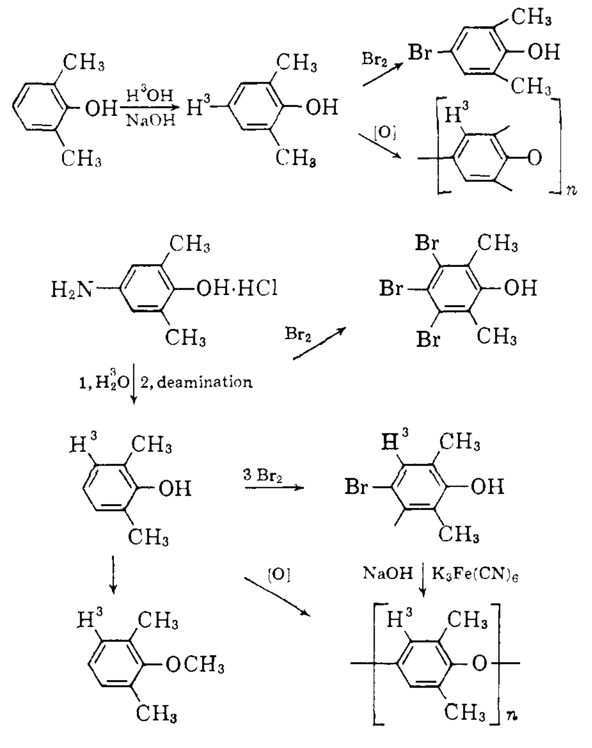
TABLE I

ACTIVITY OF TRITIUM LABELED 2,6-XYLENOLS, DERIVATIVES AND POLYMERS

2,6-Xylenol derivative	S. A., d.p.m./mole	% H^3 lost
4-Tritio-	5.75×10^{10}	..
4-Bromo	3.94×10^{4}	>99.9
Polymer	1.33×10^{10}	76.9
3-Tritio-	3.54×10^{9}	..
Polymer	3.25×10^{9}	8.2
Methyl ether	4.44×10^{8}	< 1[a]
4-Bromo-3-tritio	3.56×10^{9}	0
Polymer	4.31×10^{8}	0[a]
3,4,5-Tribromo	2.33×10^{6}	>99.9

[a] These samples were each diluted *ca.* 8-to-1 with unlabeled material.

When 2,6-xylenol-4-H^3 was polymerized, 23.1% of the polymer units retained the label. Polymerization of the 3-H^3 monomer resulted in the loss of 8.2% of the original label. Since there are two equivalent 3-positions, and, at the low concentration of tritium involved, only a vanishingly small fraction of molecules can have tritium at both *meta*-positions, this corresponds to a loss of 16.4% of *meta*-hydrogen.



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[1] A. S. Hay, H. S. Blanchard, G. F. Endres and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).

[2] (a) A. S. Hay, Am. Chem. Soc., Div. of Polymer Chem., Preprint booklet, **2**, 319 (Sept., 1961); (b) G. F. Endres, A. S. Hay, J. W. Eustance and J. Kwiatek, *ibid.*, p. 326; (c) H. S. Blanchard, H. L. Finkbeiner and G. F. Endres, *ibid.*, p. 331; (d) H. L. Finkbeiner, G. F. Endres, H. S. Blanchard and J. W. Eustance, *ibid.*, p. 340.

[3] (a) G. D. Staffin and C. C. Price, *ibid.*, **82**, 3632 (1960); (b) C. C. Price and N. S. Chu, *J. Polymer Sci.*, in press (1962).

[4] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 28 (1938).

[5] A. I. Brodskii, L. L. Chervyatsova and G. P. Miklukhin, *Zhur. Fiz. Khim.*, **24**, 968 (1950); *C. A.*, **46**, 8027e (1952).

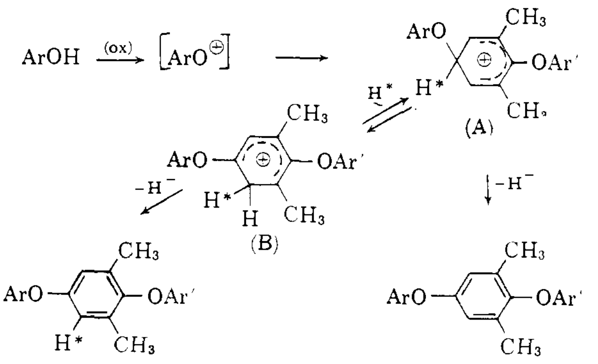
[6] A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946).

[7] A. I. Brodskii, *Izvest. Akad. Nauk S. S. S. R., Odtel. Khim. Nauk*, **3** (1949); *C. A.*, **43**, 5011 (1949).

One possible explanation of these results could be incorporation of about one of every five xylenol units through a 1,3- rather than a 1,4-phenylene oxide structure. However, other evidence reinforces earlier spectral evidence[3] for the almost exclusive occurrence of the 1,4-isomeride. Thus, the infrared spectrum of this polymer is identical with that obtained by the polymerization of 4-bromo-2,6-xylenol,[3] which contains less than 1% bromine and, therefore, must be the 1,4-polyether. Furthermore, the *n.m.r.* spectrum of the polyxylenol shows a single aromatic proton signal at 3.63τ and a single aliphatic proton signal at 7.93τ in the ratio of one to three. The sharpness of these signals demonstrates that all the aromatic protons are equivalent and that both alkyl substituents are located in identical electronic environments. This interpretation is further substantiated by comparison with the spectra of several methyl substituted dimethoxybenzenes[8] from which it is apparent that two signals, separated by at least 0.05τ, should result from the aromatic protons of the 1,3-isomeride. The regular 1,4-structure is also supported by the crystallization of the polymer from hot pinene.[9]

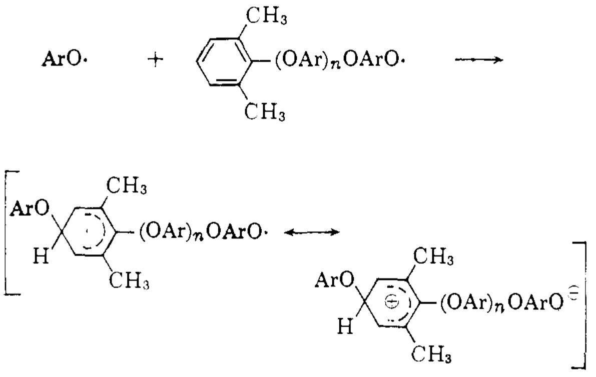
In view of this evidence, the results of polymerization of the tritium-labeled isomer cannot be rationalized as stemming from the occurrence of 1,3-phenylene oxide units. An alternative explanation requires that the hydrogen at C-4 may shift in such a manner that either the hydrogen at carbon 3 or carbon 4 is lost in subsequent reactions. Such a migration of hydrogen immediately suggests the intermediate formation of a carbonium ion at carbon-3.

For some time we considered seriously the possibility that such an intermediate might arise from normal electrophilic attack on the aromatic nucleus by an oxygen cation generated during oxidation.



The phenonium intermediate A could either lose the 4-proton directly to complete the substitution process or undergo proton migration to give intermediate B, in which protons originally in positions 3 and 4 have now become equivalent so that either may now be lost to complete the substitution. Since each isomeric arrangement (A and B) involved equivalent resonance with an ether oxygen, the driving force for conversion of A to B would arise from the greater stability of the carbonium centers on methyl substituted carbons (B) than on hydrogen substituted carbons (A).

The formation of such a phenonium intermediate by attack on a terminal ring by an oxonium ion is untenable, however, in the face of the inert character of the methyl ethers of monomer and dimer,[2d] which we have confirmed by failure to incorporate tritium into polyxylenol prepared in the presence of 3-H^3-2,6-dimethylanisole. We now believe that the phenonium structure A could be formed directly by coupling of two oligomer radicals. The process would be facilitated by the resonance stabilization of the adduct indicated in the equations



Since every atom along the polymer chain has a *p*-orbital, it should be possible to construct a molecular orbital permitting ready transfer of electrons between the two extreme structures represented above. This not only would provide the phenonium structure we deem essential to explain hydrogen migration, but the resonance stabilization would contribute substantially to the ease of coupling of two radicals as contrasted to radical attack on an oligomer molecule, such as a methyl ether. We believe the type of resonance suggested above is more reasonable than, although closely related to, the "uncoupled electron" mechanism proposed earlier.[2d]

Since water is a product of the polymerization, it was necessary to eliminate the possibility of exchange between the water and polymer or some labile intermediate. This possibility was eliminated when it was shown that polymer produced from unlabeled monomer in the presence of equimolar amounts of labeled water did not contain tritium.

The difference between the amount of 4-hydrogen retained and 3-hydrogen lost (23.1% *vs.* 16.4%) can be explained as resulting from a small isotope effect. Thus, tritium may be lost more slowly than hydrogen from the 4-position allowing greater time for rearrangement of A to B. On the other hand, the rate of hydrogen loss from the 4-position may be relatively greater so that less rearrangement and consequently lower loss of tritium results with the 3-labeled xylenol.

An alternative mechanism for the polymerization suggested earlier[2d] was termed the "quinol ether rearrangement" and also involved radical coupling, in this case reversibly to give quinol ethers.

To convert two 50-mers to 100-mer, this would require at least fifty steps and extensive opportunity for equilibration of large and small radicals. This mechanism seems unlikely, however, on the

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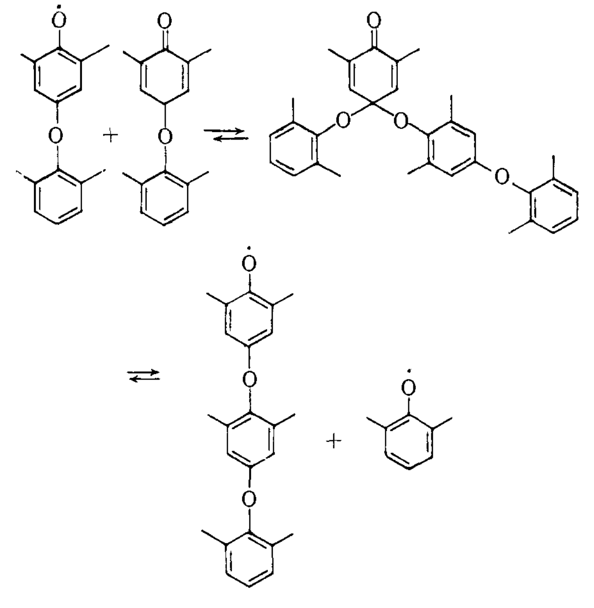
(8) K. D. Kun and H. G. Cassidy, *J. Org. Chem.*, **26**, 3224 (1961).

(9) W. A. Butte and C. C. Price, *J. Polymer Sci.*, in press (1962).



basis of a simple experiment described here. Thus, when 2,6-xylenol was partially polymerized in the presence of high molecular weight polymer, no redistribution of phenylene oxide units occurred as evidenced by the isolation of unchanged high polymer and very low molecular weight liquid oligomer. If redistribution had occurred, as proposed above, only low molecular weight material equivalent to that expected for 75% oxygen consumption[2b] should have resulted.

The polymerization of 4-bromo-3-H^3-xylenol by the bromo-displacement mechanism without any loss of tritium is in agreement with the mechanism suggested for this reaction[3] and lends further support to the significance of the hydrogen migration in the oxidative coupling reaction.

Experimental

Experimental Methods.—Isotopic hydrogen content of the materials was determined by liquid scintillation with an automated Packard Tri-Carb spectrophotometer. Samples were dissolved in toluene solution containing diphenyloxazole (primary fluor) and bis-(phenyloxazolyl)-benzene (wave length shifter). Internal standardization was achieved by the addition of standard tritiated toluene; counting efficiency was usually about 20 to 23%. Background correction was determined by the use of blanks. The reported specific activities (S.A.) are an average of at least four independent determinations of disintegrations per minute per mole with an average deviation of less than 2%.

Infrared spectra were determined with 2% solutions in carbon tetrachloride with a Perkin–Elmer instrument. Nuclear magnetic resonance spectra were measured with a Varian instrument using 3–5% solutions in carbon tetrachloride. Viscosities were determined in benzene at 30°. Melting points are not corrected.

2,6-Xylenol-4-H^3.—A solution of 1.22 g. (0.01 mole) of 2,6-xylenol and 0.40 g. (0.01 mole) of sodium hydroxide in 10 ml. of tritiated water was sealed in a Pyrex tube and immersed in a refluxing water-bath. After 18 hours, the solution was cooled and saturated with carbon dioxide. It was then extracted with three 10-ml. portions of diethyl ether. The combined extracts were washed with three 20-ml. portions of cold carbonated water and were dried over sodium sulfate. The ether was removed by distillation and the residue was recrystallized from petroleum ether with Darco to give 1.12 g. (92% recovery) of 2,6-xylenol, S.A. 5.75 × 10^{10} d.p.m./mole.

A portion of the product was brominated in cold glacial acetic acid according to the procedure of Bruice, Kharasch and Winkler.[10] The resulting 4-bromo derivative was washed with water and recrystallized from petroleum ether, S.A. 3.94 × 10^4 d.p.m./mole.

4-Amino-2,6-xylenol-3-H^3.—A Pyrex tube was charged with 3.9 g. (0.02 mole) of 4-amino-2,6-xylenol[11] hydrochloride and 15 ml. of tritiated water. The tube was flushed with nitrogen, sealed and immersed in a boiling water-bath. After 20 hours, the contents were cooled to ice-water temperature. The crystalline material was recovered by filtration and recrystallized twice from 1 *N* hydrochloric acid.

2,6-Xylenol-3-H^3.—A solution of 1.82 g. (0.01 mole) of the 4-amino-2,6-xylenol-3-H^3 hydrochloride was prepared by warming in 1.5 ml. of concentrated hydrochloric acid diluted with 10 ml. of water. The solution was cooled rapidly in an ice–salt mixture and 0.70 g. of sodium nitrite in 5 ml. of water was added dropwise to the cold mixture. Cooling was continued while 0.75 g. of solid zinc chloride was added in five portions. The diazonium chloride–zinc chloride double salt precipitated as straw-colored needles which were separated by filtration and washed with a small quantity of ice-water; m.p. 123° dec.

Without further purification, the double salt and 0.3 g. of zinc oxide were added to 15 ml. of absolute methanol which was kept at gentle reflux temperature for 16 hours. The resulting red solution was steam distilled and the first 15 ml. of distillate was discarded. The next 50 ml. deposited a crystalline solid which was recrystallized from petroleum ether to give 0.33 g. of 2,6-xylenol, m.p. 47–48°. The product was mixed with 2 g. of ordinary 2,6-xylenol and recrystallized again from petroleum ether; S.A. 3.54 × 10^9 d.p.m./mole.

A portion of the product was converted to the 3,4,5-tribromo derivative by the procedure of von Auwers and Markowitz[12] providing an 80% yield of fine, white needles, m.p. 201–202° (lit.[6] 200–201°), S.A. 2.33 × 10^6 d.p.m./mole.

4-Bromo-2,6-xylenol-3-H^3 was prepared by bromination of 2,6-xylenol-3-H^3 according to the method of Bruice, Kharasch and Winkler.[4] The product had a specific activity of 3.56 × 10^9 d.p.m./mole. A sample diluted *ca.* 8-to-1 (S.A. 4.26 × 10^8 d.p.m./mole) was polymerized by alkaline ferricyanide[3b] to give 95% of polyxylenol, m.p. 210–230°, S.A. 4.31 × 10^8 d.p.m./mole (for polymers the S.A. is reported in activity per C_8H_8O unit).

The polymerization procedure is essentially that of Hay, *et al.*[1] To 15 ml. of nitrobenzene and 4.5 ml. of pyridine in a 50-ml. flask connected to an oxygen buret was added 20 mg. of finely divided cuprous chloride. The mixture was stirred vigorously for 15 min. After this time, the absorption of oxygen had ceased and a dark green solution resulted. Then 0.489 g. (0.004 mole) of 2,6-xylenol was added and stirring was continued. A rapid uptake of oxygen began almost immediately accompanied by the development of orange color. After 20 min., the theoretical amount of oxygen had been consumed and the reaction abated. Stirring was continued for 20 min. longer, during which time a small additional amount of oxygen was absorbed and the orange color almost disappeared.

The polymeric product was precipitated by adding the reaction mixture dropwise to 65 ml. of methanol acidified with 0.65 ml. of concentrated hydrochloric acid. The pale yellow polymer was collected by filtration and washed by resuspending in acidified methanol. It was reprecipitated twice from solution in 10 ml. of benzene by addition to 40 ml. of methanol. Finally, a solution of the product in 20 ml. of benzene was washed with two 10-ml. portions of water and freeze-dried at 1 mm. pressure.

This procedure consistently gave 90 ± 2% yields of polymer with intrinsic viscosity of 1.0 ± 0.1 dl./g. The specific activity of the polymers from the tritiated xylenols is summarized in Table I.

Tritium Exchange during Polymerization.—The procedure described above was conducted with the addition of 36.0 μl. of tritiated water (S.A. 6.5 × 10^{10} d.p.m./mole) at the start. The polymeric product did not contain any of the

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[10] T. C. Bruice, N. Kharasch and R. Winkler, *J. Org. Chem.*, **18**, 89 (1953).

[11] L. I. Smith and W. B. Irwin, *J. Am. Chem. Soc.*, **63**, 1036 (1941).

[12] K. von Auwers and T. Markowitz, *Ber.*, **41**, 2339 (1908).

label (92 c.p.m. *vs.* 98 c.p.m. for a blank solution). Similar results were obtained when tritiated water was added to a solution of polyxylenol under polymerizing conditions.

2,6-Dimethylanisole-3-H^3.—A solution of 0.15 g. of 2,6-xylenol-3-H^3 (3.54×10^9 d.p.m./mole) and 1.05 g. of ordinary 2,6-xylenol was dissolved in 5.5 ml. of 2 *N* sodium hydroxide solution. The temperature was kept below 40° while 1.26 g. of dimethyl sulfate was added dropwise with stirring. An additional 3 ml. of 2 *N* sodium hydroxide solution was then added followed by 0.63 g. of dimethyl sulfate. The reaction mixture was heated for 30 min. on a steam-bath. Upon cooling, it was extracted with two 10-ml. portions of diethyl ether. The extracts were dried over sodium sulfate and distilled. A colorless oil was collected; b.p. 82.5–84° (30 mm.), yield 1.1 g. (80%), S.A. 4.44×10^8 d.p.m./mole.

Polymerization in the Presence of 2,6-Dimethylanisole-3-H^3.—To the standard polymerization mixture described previously was added 0.54 g. (0.004 mole) of 2,6-dimethylanisole-3-H^3 together with the 2,6-xylenol (0.49 g.). The resulting polymer was isolated and purified in the usual manner. The tritium content of this polymer was too low (49.5 c.p.m./mg.) to be distinguished as significantly above the natural background (47 c.p.m./mg.)

Test of "Quinol Ether Rearrangement."[2d]—The polymerization procedure described above was utilized. One-half (9.75 ml.) of the reaction mixture was withdrawn and treated in the usual manner to give 0.22 g. (92%) of purified product, $[\eta]$ 0.93 dl./g.

To the remaining reaction mixture was added 0.245 g. (0.002 mole) of 2,6-xylenol and the reaction was resumed with the development of an orange color. After 50% of the theoretical oxygen was absorbed, the reaction was quenched by the addition of 15 ml. of 1 *N* hydrochloric acid. The product was isolated as before, yielding 0.21 g. (88%) of polymer, $[\eta]$ 0.75 dl./g.

The filtrate from this second portion was steam distilled until all volatile material had been removed. The residue consisted of a brown gum (0.20 g., 85% based on the 0.245 g. of additional xylenol), which was not polymeric, $[\eta]$ 0.02 dl./g.

[Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Conn., and Department of Chemistry, The University of Michigan, Ann Arbor, Mich.

The Absorption Spectrum of Gaseous Benzyne

By R. Stephen Berry,[1a] G. Neil Spokes[1a] and Martin Stiles[1b]

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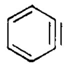
Flash photolysis has been carried out on thin solid films of two substances known to give benzyne under other conditions. Transient and final product ultraviolet gas phase spectra have been recorded and at least one reaction has been observed, with butadiene. On the basis of the observed final products, the reactions and the appearance of a transient continuous spectrum, it is concluded that gaseous benzyne is produced and that it probably is responsible for the transient absorption spectrum.

I. Introduction

The molecular fragment 1,2-dehydrobenzene (hereinafter called benzyne) (I) has been the subject of intensive study in its role as an intermediate in organic reactions. The chemistry of benzyne has been reviewed recently.[2–5] In contrast to our present extensive knowledge of the chemical properties of benzyne in solution, very little headway has been made in the examination of the species itself, either in terms of its physical properties or of its chemical reactions in the gas phase. Some preliminary theoretical estimates have been made in order to get a qualitative idea of the structure and properties of benzyne.[6,7] No detailed calculations have been reported which attempt to investigate electronic energy states and the relation between the structure of benzyne and that of benzene, for example.

The work described here was, in large part, suggested by the recent discovery of two new paths for the apparent production of benzyne. These paths are based on the precursors benzenediazonium-2-carboxylate[8] and on *o*-iodophenylmercury compounds.[9] Benzenediazonium-2-carboxylate (II) leads to benzyne under very mild conditions; it is very sensitive to heat or shock, detonating when warmed quickly or struck. It is a strong absorber of ultraviolet light, and is non-volatile.



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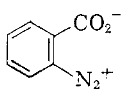
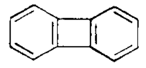


II

These observations led to a series of experiments in which solid films of II were flash-photolyzed and the ultraviolet absorption spectra of transient and final products were observed. The results, already reported in part in a preliminary communication,[10] indicated the presence of gaseous benzyne, because one could observe the formation of biphenylene (III), the dimer of benzyne, in the gas phase. Moreover the transient spectrum which was recorded clearly differed from that of ordinary biphenylene, and was tentatively assigned as the spectrum of benzyne.



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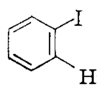

IV

Since that time, similar methods have been applied in the flash photolysis of *o*-iodophenylmercuric iodide (IV), a compound whose role as a benzyne precursor had been shown by Wittig and Ebel.[9] The results obtained from these experiments have provided strong support for attributing the transient spectrum to benzyne.

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[1] (a) Yale University; (b) University of Michigan.

[2] (a) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); (b) J. D. Roberts, *Chem. Soc. (London) Spec. Publ. No.* **12**, 115 (1958).

[3] R. Huisgen, Chapter 2 in "Organometallic Chemistry," H. H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 36.

[4] J. F. Bunnett, *J. Chem. Ed.*, **38**, 278 (1961).

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[6] C. A. Coulson, *Chem. Soc. (London) Spec. Publ. No.* **12**, 85 (1958).

[7] H. G. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

[8] M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960).

[9] G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960).

[10] R. S. Berry, G. N. Spokes and R. M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960).