Electron Impact and Thermal Fragmentation of Biphenylene[1,2]

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Abstract: Electron impact and thermal fragmentation of biphenylene gives benzyne by a minor process; the major process is cleavage of only one bond. Pyrolysis of biphenylene in the liquid phase (~400°) gives an essentially quantitative yield of tetraphenylene. This reaction is catalyzed by stainless steel and is presumed to proceed *via* dimerization of the diradical I. When pyrolysis is conducted in the vapor phase (735°) in a nitrogen stream, a drastically reduced yield of tetraphenylene is observed; but the formation of triphenylene indicates that some benzyne is formed by thermal fragmentation of biphenylene. When vapor phase pyrolysis is carried out in the presence of benzene-d_6, the intermediacy of diradical I is further substantiated by the isolation and characterization of biphenyl-d_2, *o*-terphenyl-d_6, and triphenylene-d_4. In addition, trace amounts of undeuterated triphenylene indicate that benzyne is trapped by I. The electron impact fragmentation pattern bears a striking resemblance to those of anthraquinone and fluorenone. The ion with m/e 152 is probably not biphenylene but an open radical ion.

The mass spectral fragmentation pattern of phthalic anhydride[3] has an intense peak at m/e 76 probably resulting from the sequential loss of carbon dioxide and carbon monoxide. Thermal fragmentation of phthalic anhydride leads to the formation of benzyne,[4-7] showing apparent similarity between the two methods of decomposition.[8] These correlations have also been observed in the formation of benzyne upon electron impact and thermal fragmentation of indantrione[9] and *o*-sulfobenzoic anhydride.[5,10] However, attempts to duplicate the electron impact fragmentation[11] of anthraquinone and fluorenone by pyrolysis[9] have given only traces of hydrocarbons, one of which may be biphenylene.

An abundant m/e 76 ion, observed with both low[12] and high[13] voltage mass spectrometry of the pyrolysis products of *o*-diiodobenzene[12] and the flash photolysis products of benzenediazonium-2-carboxylate,[13] has been assigned to benzyne.[14] Fragmentation of this ion apparently leads to reasonably intense peaks at m/e 50, 39, and 26.[13] An intense m/e 50 ion is also observed in the electron impact fragmentation patterns of phthalic anhydride,[3] indantrione[9c] and *o*-sulfobenzoic anhydride.[10] A supporting metastable ion corresponding to the loss of acetylene from benzyne ($76^+ \rightarrow 50^+ + 26$) is observed in the fragmentation of indantrione.[9c] On the other hand, m/e 39 is absent in the mass spectrum of phthalic anhydride[3] and no mention is made as to its presence or absence from indantrione[9c] and *o*-sulfobenzoic anhydride.[10]

Since biphenylene is the dimer of benzyne, electron impact or thermal fragmentation of biphenylene offers a possible route to benzyne. The mass spectrum (70 eV) of biphenylene is shown in Figure 1. The obvious problem in interpretation of this spectrum is differentiating between m/e 76, $[C_6H_4]\cdot^+$, and m/e 76, $[C_{12}H_8]^{2+}$. Neglecting contributions from the natural isotopic abundance of mass 151 ions,[15] the ion at m/e 76.5 can only be doubly charged parent-plus-one (P + 1) caused by natural isotopic abundance. Therefore, the ratio of the intensity of the peak at m/e 153 to the intensity of the peak at m/e 76.5 is an accurate measure of the ratio of parent ion to doubly charged parent ion. By using this ratio, only 78.7% of the total peak intensity (13.38) can be accounted for by doubly charged parent. By using the appropriate corrections[16] for natural isotopic abundance, the relative intensity of mass 76 ion, $[C_6H_4]\cdot^+$, is at least 2.39. This is presumed to be the ion of benzyne. Ions of m/e 50 (6.8) and 39 (5.0) are consistent with this assignment of structure.

In attempts to generate benzyne thermally, a 1:1 mixture of biphenylene and anthracene was pyrolyzed in the liquid phase at ~440° in a sealed Vycor tube. It was assumed that the formation of triptycene would be indicative of the presence of benzyne since triptycene remains essentially unchanged under these conditions. Although biphenylene was not recovered, triptycene was not detected. Pyrolysis of a biphenylene–anthracene mixture in the gas phase[17] also showed no evi-

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[1] For a preliminary report of these results see D. F. Lindow and L. Friedman, *J. Am. Chem. Soc.*, **89**, 1271 (1967).

[2] (a) From the Ph.D. Thesis of Donald F. Lindow, Case Institute of Technology, 1968. (b) Supported in part by the Case Research Fund.

[3] F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959).

[4] (a) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965); (b) *J. Org. Chem.*, **31**, 3307 (1966); (c) *Chem. Commun.*, 708 (1966).

[5] M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).

[6] R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, *Australian J. Chem.*, **20**, 139 (1967).

[7] L. Friedman and D. F. Lindow, *J. Am. Chem. Soc.*, **90**, 2329 (1968).

[8] Benzo-2,1,3-selenadiazoles, upon electron impact, have produced ions corresponding to arynes, but pyrolysis was not attempted: N. P. Buu-Hoi, P. Jacquignon, and M. Mangane, *Chem. Commun.*, 624 (1965).

[9] (a) R. F. C. Brown and R. K. Solly, *Chem. Ind.* (London), 181 (1965); (b) *ibid.*, 1462 (1965); (c) *Australian J. Chem.*, **19**, 1045 (1966).

[10] S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).

[11] J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959); J. H. Beynon and A. E. Williams, *Appl. Spectry.*, **14**, 156 (1960).

[12] I. P. Fisher and F. P. Lossing, *J. Am. Chem. Soc.*, **85**, 1018 (1963).

[13] R. S. Berry, J. Clardy, and M. E. Schafer, *ibid.*, **86**, 2738 (1964).

[14] The ion of mass 76, the benzyne ion, is probably best written as an ion radical rather than with the traditional benzyne structure; however, a noncyclic ion formed by cleavage of the benzyne structure is a possible alternative.

[15] The percentage of the intensities of m/e 153 and 76.5 contributed by ions other than the parent ion and its doubly charged analog is very small.

[16] In the limiting case where all of the m/e 75 peak is assumed to be singly charged and all of the m/e 75.5 peak is doubly charged $C_{12}H_7$, the corresponding relative intensity of pure mass 76 ion is calculated to be 2.39. Although the limiting case is undoubtedly not the actual case, it sets a minimum value for the mass 76 ion.

dence for triptycene formation while much of the biphenylene was destroyed.

The sealed tube experiments either in the presence or in the absence of anthracene gave only one major product. This was identified as tetraphenylene[18,19] (tetrabenzocyclooctatetraene) on the basis of melting point and infrared, ultraviolet, and mass spectra. A minor by-product was biphenyl.[20]

Tetraphenylene was obtained in 96% yield by liquid phase pyrolysis (400°) of biphenylene in an evacuated sealed tube.[21] The effects of time and temperature on the course of the reaction are listed in Table I.

Table I. Pyrolysis of Biphenylene in an Evacuated Vycor Tube

			Compn of react. mixture,^{a} %		
Run	Temp, °C	Time, hr	Tetra-phenylene	Bi-phenyl	Bi-phenylene
1	395–408	1	96	4	0
2	430–445	0.5	85	3	0
3	430–445	18	66	5	0
4	330–350^{b}	1	5	0	95
5	330–350^{b}	6	11	1	76
6	330–350^{b}	30	11	6	17
7^{c}	330–350	30	95	1	2
8^{d}	330–350	30	24	6	6

^{a} Glpc % yield (internal standard, triptycene) based on the initial amount of biphenylene. ^{b} Runs 4–6 were carried out concurrently, but the tubes were not attached to the thermocouple. Therefore, the temperatures recorded for these runs may be somewhat erroneous because of temperature gradients in the furnace. ^{c} Reaction tube contained a 14-mm piece of $^{1}/_{8}$-in. stainless steel tubing. ^{d} Control for run 7.

Lower yields at higher temperatures and extended reaction times apparently indicate thermal destruction of tetraphenylene (*cf.* runs 1–3). Lower temperatures result in decreased conversion of biphenylene; however, by extending the reaction time, biphenylene is gradually consumed without significant formation of tetraphenylene (*cf.* runs 4–6). The nonvolatile portion of the mixture is polymeric.[22]

Thus, at higher temperatures, it seems most likely that efficient dimerization occurs in the liquid phase as a result of a relatively high steady-state concentration of diradical I. At lower temperatures, the concentration of I would be smaller; consequently dimerization would be less favored, and other radical reactions would presumably occur to produce polymeric material. Recyclization may occur when I undergoes an appropriate energy-releasing collision.

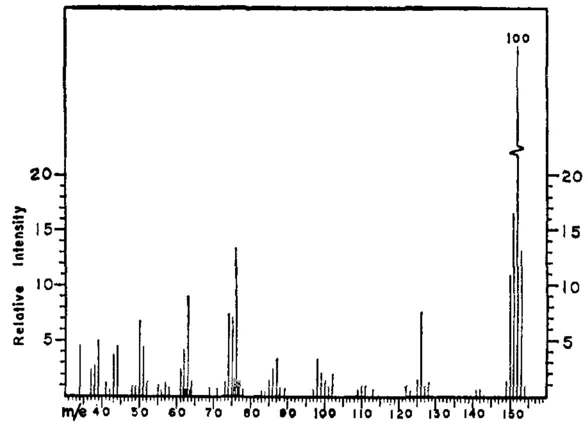
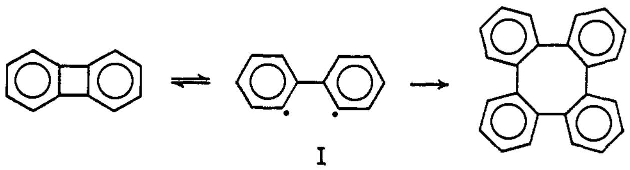


Figure 1. Mass spectrum of biphenylene at 70 eV.



I

Large-scale (20 g) pyrolyses of biphenylene were conducted in a 40-ml, stainless steel bomb at 375° for 1 hr.[23] Since the optimum temperature was lower when the stainless steel bomb was used, pyrolysis was carried out in a sealed Vycor tube in the presence of a small piece of stainless steel tubing. The results of these experiments (Table I, runs 7 and 8) show that the formation of tetraphenylene by liquid phase pyrolysis of biphenylene is catalyzed by a stainless steel surface.[24] Stainless steel could catalyze formation of I, dimerization of I on the surface, or both.

Other evidence for the intermediacy of I was obtained by vapor phase pyrolysis of biphenylene (0.1 *M*) in benzene. For example, at 650° (contact times of 3–5 sec), in addition to unreacted biphenylene (~70%), three major products were obtained: biphenyl, triphenylene (1.3%), and *o*-terphenyl (2.1%).[25] Only trace amounts of tetraphenylene were detected. At 730° the results were qualitatively the same but more biphenylene was consumed. In the absence of biphenylene, smaller amounts of biphenyl and *o*-terphenyl were formed.[26]

Biphenyl and *o*-terphenyl may be formed either by reaction of biphenylene with benzene or by pyrolysis of benzene alone. Although the relative importance of each path may be determined by the difference in product yield between a biphenylene–benzene pyrolysis and a blank pyrolysis of benzene alone, the reproducibility of this method was not satisfactory. Therefore, pyrolysis was conducted in benzene-d_6 so that there would be no doubt as to the origin of the reaction

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(17) Reaction effected in an oven (helium atmosphere) connected directly to a dual column (7 ft × 0.25 in. o.d. 3% GE SF 1093 on acid-washed DMCS-treated Chromosorb G, 70–80 mesh) F & M gas chromatograph. The authors acknowledge with thanks Dr. Stephen S. Hirsch and Mr. Gazie K. Ragep, Chemstrand Research Corp., for performing these experiments.

(18) G. Wittig and G. Lehmann, *Chem. Ber.*, 90, 875 (1957).

(19) (a) In an excellent paper on biphenylene chemistry, it was stated that "diphenylene is extraordinarily stable—it is is formed at 350°." However, in the discussion J. Chatt reported that biphenylene and bis(triphenylphosphino)nickel dicarbonyl at 100° for 7 hr gave tetraphenylene (~10%) as the only isolable product: W. Baker and J. F. W. McOmie, "Diphenylene and the Cyclobutadiene Problem," in the Chemical Society Symposia, Bristol, 1958; Special Publication No. 12, The Chemical Society, London, 1958, pp 49–67; (b) J. Chatt, R. G. Guy, and H. R. Watson, *J. Chem. Soc.*, 2332 (1961).

(20) Another possible by-product, *o*-quaterphenyl, was not separable from tetraphenylene by glpc; but on the basis of infrared analysis (ultraviolet analysis does not distinguish between them) not more than 1% could be present in the crude tetraphenylene. Mass spectral analysis, however, did not indicate the presence of *o*-quaterphenyl, but did show a definite small (<1%), poorly resolved peak at approximately *m/e* 456 to 458 indicative of hexaphenylene or *o*-sexiphenyl.

(21) Small amounts (~1%) of tetraphenylene were also obtained by photolysis of biphenylene (0.066 *M*) in hexane at 2538 and 3500 Å. Solid films were unaffected.

(22) The nature of this substance is presently under investigation.

(23) The procedure for large-scale preparations of tetraphenylene in a stainless steel bomb was developed by Peter Rabideau.

(24) Metal catalysis of biphenylene dimerization is currently under investigation.

(25) Typical data.

(26) For examples of pyrolytic coupling reactions of aromatic compounds see: G. M. Badger, *Progr. Phys. Org. Chem.*, 3, 1 (1966).

Table II. Products from Pyrolysis of Biphenylene in Benzene-d_6

Products	Pyrolysis temp, °C	Deuterium composition, mole %: d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	d_{13}	d_{14}
Biphenylene[a]	650	84.4	13.9	1.5	0.2											
Biphenyl		0.5	3.7	28.3	5.5	0.7	0.4	0.8	0.4	0.4	2.1	57.2				
o-Terphenyl		0.8	0.1	0.2	0.3	0.4	8.0[b]	65.0	19.7	3.0	0.6	0.8	0.6	0.1	0.1	0.2
Triphenylene		5.2	2.8	1.1	2.6	59.6	22.6	5.1	1.0							
Biphenylene[a]	730	48.7	32.5	13.6	3.9	0.9	0.4									
Biphenyl		0.1	1.4	11.8	9.2	4.0	1.4	1.0	0.5	0.4	4.5	65.7				
o-Terphenyl					0.9	0.6	4.1	36.7	33.6	16.4	5.6	2.1				1.8[c]
Triphenylene		0.9	1.3	1.3	2.2	29.6	32.8	19.6	8.3	2.8	0.8	0.3	0.1			
Biphenylene[a]	650[d]	95.2	4.5	0.2												
Biphenyl		11	25	7.9	0.9						4	52				
o-Terphenyl							24	67	9							
Triphenylene		3.1	0.6	0.8	2.3	83.5	8.7	1.2								

[a] Recovered. [b] Very poorly resolved peak. [c] Not considered in total of 100%. [d] Protium-contaminated C_6D_6.

products. The extent of deuteration of the products is shown in Table II.

At 650°, the biphenyl consisted of mainly d_2 and d_{10} species. Biphenyl-d_2 was formed from I and benzene-d_6 by deuterium abstraction, while biphenyl-d_{10} arose from pyrolytic coupling of benzene-d_6. The presence of other deuterated species is a result of deuterium–protium exchange[27] between benzene-d_6 and biphenylene and/or biphenyl-d_2. Triphenylene and *o*-terphenyl contained mainly four and six deuterium atoms per molecule, respectively, and lesser amounts of more highly deuterated species formed by exchange reactions. The degree of exchange observed for all of the materials recovered from these pyrolysis reactions was similar (*cf.* Table II). At 730°, the anticipated increase in deuterium–protium exchange was observed.

The formation of undeuterated triphenylene, when pyrolysis of biphenylene was carried out in benzene-d_6, is best explained by reaction of I with benzyne-d_0. Benzyne was presumably generated by fragmentation of biphenylene or preferably I. To support this contention, biphenylene was pyrolyzed in a nitrogen stream at 735°. In addition to recovered biphenylene (relative peak area, 100) and tars, the products were biphenyl (44), tetraphenylene (1.2), triphenylene (7.4), and at least six other unidentified, longer retained hydrocarbons (~50). Since tetraphenylene is not converted to triphenylene by pyrolysis in benzene at 650°, it is difficult to conceive of any process whereby biphenylene is converted to triphenylene without generation of benzyne. This route may account for the formation of triphenylene by the supposed trimerization of benzyne.[4a,9c,28]

Pyrolysis of biphenylene with inadvertently contaminated benzene-d_6 (with a nonbenzene protium source)[29] sheds a great deal of light on the actual mechanism of the reaction of diradical I with benzene. Triphenylene-d_4 is evidently formed by 1,2 addition of I to benzene-d_6 with subsequent aromatization by loss of two deuterium atoms. The reaction carried out in the presence of protium source impurity evidently only decreased the amount of deuterium–protium exchange (Table II).[30] This is consistent with the mechanism proposed.

Diradical-derived biphenyl could result from simultaneous or stepwise abstraction of two deuteriums from the same benzene-d_6. However, the large amounts of monodeuterated and undeuterated biphenyl formed with impure benzene-d_6 indicate that stepwise deuterium abstraction from different molecules of benzene-d_6 is the major reaction.

o-Terphenyl isolated from the same reaction mixture shows less deuterium–hydrogen exchange, as expected, and a somewhat larger amount of d_5 species. Since the amount of less highly deuterated *o*-terphenyl does not approach that observed in biphenyl, it is probable that much of the *o*-terphenyl arises by addition of the elements of benzene across the diradical in either a stepwise or simultaneous process. A stepwise mechanism is more attractive since, with impure benzene-d_6, part of the *o*-terphenyl is formed from three different molecules. However, it is impossible to determine whether the initial attack is at a deuterium or a carbon. Possible mechanisms for the formation of biphenyl, *o*-terphenyl, and triphenylene are outlined in Figure 2. Interconversion of *o*-terphenyl and triphenylene is excluded since, under the reaction conditions, pyrolysis of either fails to produce the other.

m- and *p*-terphenyls, which were also expected to be formed *via* coupling of benzene,[26] were found both in the presence and absence of biphenylene. On the basis of mass spectral data and expectation of their formation by coupling of benzene and biphenylene, two other products of biphenylene–benzene-d_0 reactions were tentatively identified as the isomeric phenylbiphenylenes. Five other extremely minor, as yet unidentified, products were also noted by glpc.

The low-voltage mass spectrum of the mixture of four products from benzene-d_6 reactions (Table III), previously designated as the isomeric phenylbiphenyl-

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(27) E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 21 (1966).

(28) (a) Although naphthalene-d_4 is the major reaction product of benzyne and benzene-d_6 in the absence of other benzyne traps,[7] it is not surprising that naphthalene-d_4 was not found in these reactions since benzyne is known to be a discriminating reagent[28b,c] and presumably reacts selectively with I in preference to benzene. (b) Decomposition of benzenediazonium-2-carboxylate in the presence of equimolar concentrations of anthracene and iodine produces mainly *o*-diiodobenzene showing that benzyne reacts preferentially with iodine: F. M. Logullo, Ph.D. Dissertation, Case Institute of Technology, 1965. (c) Although benzene, in large excess, has been used as a solvent for benzyne reactions, in the *absence* of other reactants, benzyne does react with benzene: M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963); R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963); L. Friedman, *ibid.*, **89**, 3071 (1967).

(29) Contaminated with tetrahydrofuran and/or its pyrolysis products.

(30) This coupled with the fact that the level of exchange is similar for all of the compounds studied (including recovered biphenylene) shows that intermolecular H–D exchanged undoubtedly prevails over intramolecular exchange.

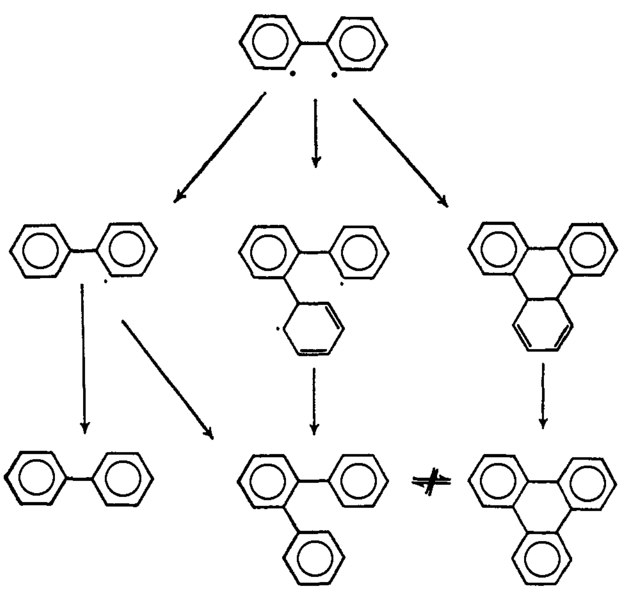

Figure 2.

enes and *m*- and *p*-terphenyls, tends to confirm the assignment of these structures since *m/e* 233, equivalent to phenylbiphenylene-d_5, has the largest intensity. In addition, approximately 60% of the *m*- and *p*-terphenyl may be formed from phenylbiphenylenes in the same manner as biphenyl is formed from biphenylene, because *m/e* 237 and higher mass species formed by exchange may be assigned to terphenyl-d_7. Some *o*-terphenyl-d_7 (Table II) may have been formed from 1-phenylbiphenylene by the same mechanism.

Table III. Low-Voltage Mass Spectrum of a Product Mixture from Pyrolysis of Biphenylene and Benzene-d_6 at 730°

m/e	Intensity[a]	Structure assignment
232	2.1	
233	25.2	Phenylbiphenylene-d_5
234	22.4	Phenylbiphenylene-$d_6{}^{b,c}$
235	10.6	Phenylbiphenylene-$d_7{}^{b}$
236	5.4	Phenylbiphenylene-$d_8{}^{b}$
237	8.6	Terphenyl-d_7 and phenylbiphenylene-$d_9{}^{b}$
238	7.2	Terphenyl-$d_8{}^{b,c}$
239	3.7	Terphenyl-$d_9{}^{b}$
240	1.5	Terphenyl-$d_{10}{}^{b}$
241	0.7	
242	0.5	
243	1.4	
244	9.7	Terphenyl-d_{14}

[a] Corrected for natural isotopic abundances. [b] D-H exchange products; the level of D-H exchange is similar to that observed for all other products at this temperature. [c] It is conceivable, although unlikely, that these products may also be formed by attack of a molecule or radical on benzene-d_6 followed by intramolecular deuterium migration; *cf.* E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 3224 (1967).

Since a number of relatively intense peaks other than those attributed to benzyne and the parent ion are observed in the electron impact fragmentation pattern of biphenylene, it deserves further comment. There is a striking similarity between the fragmentation patterns of biphenylene and anthraquinone.[11] The only real difference between them from *m/e* 50 to 154 is the presence of an ion with *m/e* 90 from anthraquinone. The ion at *m/e* 90 is undoubtedly a doubly charged ion of mass 180. Fluorenone also has essentially the same fragmentation pattern.[11a] While the relative intensities are not exactly the same, the similarities are great enough to suggest that an ion derived from biphenylene is an intermediate in the electron impact fragmentation of anthraquinone and fluorenone.

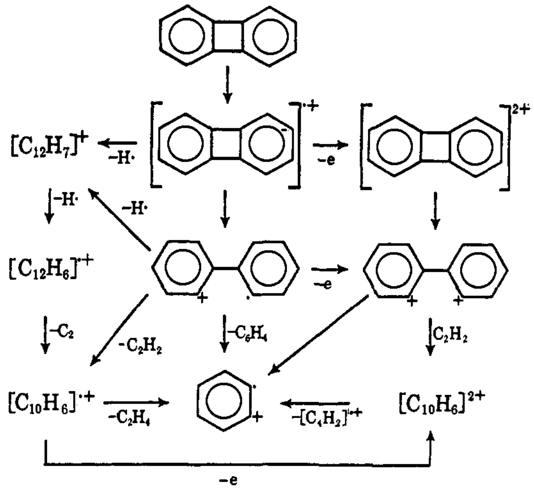

Figure 3.

The possible modes of decomposition of biphenylene upon electron impact are shown in Figure 3. A metastable peak was observed at *m/e* 150, confirming the transition 152 → 151.

Obviously, there is doubt as to whether or not the parent ion has an intact four-membered ring. If we make the inevitable comparison to the thermal data, it seems likely that many, if not most, of the ions with *m/e* 152 have an opened structure. The same argument should apply to doubly charged ions with *m/e* 76. It is premature to speculate about the structure of other fragment ions.

Thus, electron impact and thermal fragmentation of biphenylene apparently parallel each other insofar as formation of benzyne is concerned. It is not surprising that benzyne formation is not the major process since it is unlikely that both bonds will break simultaneously. Thermal cleavage of one bond to form I or electron impact induced cleavage of one bond to form an ion radical analogous to I are energetically more favorable processes. Although these intermediates can and apparently do undergo further fragmentation to form benzyne and benzyne ion, respectively, other reactions are more favorable. Thermal fragmentation of I to form benzyne apparently takes place to a greater extent in the gas phase when dimerization and other bimolecular reactions are minimized. These conditions more closely approximate the unimolecular decomposition conditions present in a mass spectrometer, leading to closer agreement between the two methods of fragmentation.

Experimental Section

Materials. Benzene, analytical reagent, was used without further purification. Concentration of 1 l. of benzene to 5 ml did not reveal the presence of any of the pyrolysis products (glpc). Benzene-d_6 (Merck Sharp and Dohme) was recovered by distillation and reused. Recovered benzene-d_6 from later runs contained less than 4% benzene-d_5 (mass spectral data). The balance was completely deuterated. Biphenylene was prepared from benzenediazonium-2-carboxylate *via* benzyne dimerization.[31]

Instrumentation. The electron impact fragmentation pattern was obtained on a C.E.C. 21-103C mass spectrometer. Low-voltage mass spectral analysis of the pyrolysis products were made on the same model spectrometer. Glpc was performed on a F & M 500 gas chromatograph. Infrared and ultraviolet spectra were obtained using Beckman IR-8 and Beckman DB spectrophotometers, respectively.

Pyrolysis Apparatus. Pyrolyses were effected in a vertically mounted fused quartz tube (diameter 1.7 cm) having a thermocouple well which was centrally located and extended half the length of the heating zone. The 30-cm heating zone was packed with fused quartz chips to leave free volume of ~25 ml. The tube was heated externally by an insulated, electrical furnace having a brass heat sink. Solutions were added to the tube dropwise through a dropping funnel equipped with a stopcock-operated bypass line. Most of the pyrolysate was collected in the first trap which was cooled by a mixture of ice and water. An additional trap, cooled by a Dry Ice-acetone bath, was attached to the outlet of the first trap. A bubbler was connected to the outlet of the second trap.

Typical Pyrolysis Run. The apparatus was purged with nitrogen for at least 30 min. After closing the bypass stopcock, a solution of biphenylene in benzene or benzene-d_6 was added at a constant rate so that the drops fell directly into the heating zone. After the solution was added, the apparatus was purged with nitrogen for 1 min, before the traps were disconnected. Between runs all parts of the apparatus were thoroughly rinsed with benzene and dried. The pyrolysis tube was filled with air and heated at pyrolysis temperatures for at least 1 hr to remove any carbonaceous material. Pyrolyses were carried out at an average temperature of either 650 or 730°. A temperature drop of about 5° was normal for a typical 5-ml run.

Analysis of Pyrolysates. Most of the benzene or benzene-d_6 was removed from the pyrolysate by distillation through a short Vigreux column. The resulting mixtures were then analysed on a 4 ft × 0.25 in. SF 1093 silicone fluid on silanized Chromosorb G (60–80 mesh) column programmed from 75° at 11°/min. Products were identified by retention time and comparison of the infrared and ultraviolet spectra of glpc collected samples with spectra of known materials. The extent of deuteration was obtained by low-voltage mass spectrometry of glpc collected products. All mass spectral data was corrected for natural isotopic abundances.

Vapor Phase Pyrolysis of Biphenylene. The pyrolysis apparatus was modified by replacing the dropping funnel with a distilling flask and turning the pyrolysis tube to an almost horizontal position. A nitrogen inlet tube was attached so that it extended almost to the bottom of the flask. Biphenylene was placed in the distilling flask, and with the pyrolysis tube at 735° the apparatus was purged with nitrogen for 30 min. The appropriate inlet areas were heated with heating tape to prevent condensation of biphenylene. When the distilling flask was heated, biphenylene melted and was carried through the pyrolysis tube in a stream of nitrogen. No attempt was made to optimize the conditions. The pyrolysate was analyzed by glpc. Triphenylene was identified by retention time and uv spectrometry.

Sealed-Tube Pyrolysis. Solid biphenylene (or a 1:1 mixture of biphenylene and anthracene) was added to a 20 cm × 7 mm Vycor tube which had previously been sealed on one end. The tube was evacuated to approximately 1 mm and sealed. The tube or tubes were attached to a chromel-alumel thermocouple and placed in a previously heated muffle furnace. The temperature was read periodically at the high and low points in the cycle. The temperature variation was found to be between 10 and 15°. The pyrolysate was dissolved in methylene chloride and analyzed by glpc using triptycene as an internal standard. As much as 1 g of biphenylene was converted to tetraphenylene using tubes of this size.

Large-Scale Preparation of Tetraphenylene.[28] Biphenylene (20 g) was placed in a 40-ml stainless steel bomb. The bomb was filled with nitrogen after first removing the air by alternate evacuation and purging with nitrogen. By using a small furnace the bomb was heated to between 365 and 375° and maintained at that temperature for 1 hr. Crude tetraphenylene was recrystallized from acetone and dried under vacuum (water aspirator) at 110° (toluene) to remove the 0.5 mol of acetone of crystallization. This afforded 18 g (90%) of powdered, white tetraphenylene (mp 232–233° cor). Higher reaction temperatures result in decreased yields of poorer quality material which may be purified by chromatography on alumina.

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(31) L. Friedman and A. Seitz, in press.