

CHEMICAL REACTIONS IN A CORONA DISCHARGE I. BENZENE

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## INTRODUCTION

Corona discharges (silent) have been used to initiate chemical reactions for well over 150 years with much of the early work being confined to inorganic gases.<sup>2</sup> However, the only commercially significant development over the years has been the process for synthesizing ozone by subjecting oxygen to a corona discharge<sup>3</sup> (ozonizer). Most early investigators encountered serious difficulties in studying the interaction of high voltage electricity with organic molecules. Equipment was unreliable and dangerous, and the complexity of the reaction product mass precluded definitive performance evaluation. Since World War II, technology has advanced to the point where high frequency power can be generated and controlled at reasonable cost and many new dielectric materials such as fused quartz, alumina and mica mat are available.<sup>4</sup> Modern analytical techniques afford the opportunity to determine the composition of the product mix.

Corona electrons are accelerated by the applied voltage to an energy level of 10-20 electron volts, which is sufficient to break the covalent bond. This represents a very efficient approach when compared with high energy radiolysis (m.e.v. range) where the actual chemical work is effected by secondary electrons with an energy of 10-25 e.v., formed after a series of energy-dissipating steps. Potentially, corona energy can deliver electrons to the reaction site at the desired energy level to give products which are not readily obtainable by more conventional means. The energy available in the corona discharge is somewhat above that commonly encountered in photochemistry (up to 6 e.v.).

Bertholot reduced benzene to  $C_6H_8$  in 1876 in what appears to be the first exposure of an aromatic compound to the corona discharge.<sup>5</sup> Losanitsch obtained the following products from benzene in an electrical discharge:  $(C_6H_6)_2$ , biphenyl,  $(C_72H_96)$  and  $(C_6H_6)_{90}$ .<sup>6</sup> Benzene vapor treated at 300° in an ozonizer tube gave resinous products with a 6/4 carbon-hydrogen ratio.<sup>7</sup> Linder and Davis exposed benzene vapor to 37,000 volts and found biphenyl, gaseous products and evidence of polymerization.<sup>8</sup> The early work with benzene reactions in various types of electrical discharges is reviewed in considerable detail by Glocker and Lind.<sup>2</sup> Brown and Ripper investigated the hydrogenation of benzene flowing down the walls of an ozonizer tube and found 1,3- and 1,4-cyclohexadiene, biphenyl, and a resinous mass which gave an infrared spectrum consistent with polystyrene.<sup>9</sup>

In recent years, benzene has been subjected to direct electrode discharge<sup>10</sup> and glow discharges induced by microwave<sup>11</sup> and radiofrequency<sup>12</sup> energy. In this paper, we report some of our observations for the reaction of benzene in a corona discharge.

## APPARATUS

The corona reactor system used in this study is shown in Figure 1 and the reactor details are given in Figure 2. The system is designed to run at atmospheric or reduced pressure and, with slight modification, under recycle conditions. The use of the threaded rod center electrode affords a more uniform and higher treating potential than is obtained with a cylindrical electrode.<sup>13</sup> The electrode threads concentrate surface irregularities thereby eliminating severe discharge points. The copper electrode serves as a cooling coil and affords direct observation of the corona. In a typical run, the benzene reservoir temperature is set at 55°, the helium is adjusted to 100 ml/min. and after a two minute purge, an electrical potential of 15,000 volts is applied. A brilliant blue corona is established, the intensity being a function of helium flow, pressure, benzene content and the applied voltage. Benzene traverses the corona reactor as a vapor and is condensed by the cold water trap and collected. Yellow solids gradually deposit in the flask at the bottom of the reactor and eventually adhere to the dielectric surfaces in the reactor. Some benzene and the more volatile reaction products are condensed in the -70 and -195° traps. See experimental section for further details.

## RESULTS AND DISCUSSION

The excitation of benzene vapor in a corona discharge provides an 8.5% conversion to identifiable products. The major products are a benzene soluble polymer (6%), a benzene insoluble polymer (0.7%), biphenyl (0.3%), and acetylene (1%). The composition of the product mix obtained is given in Table 1. The overall yield obtained under our experimental conditions is similar to that produced in a radiofrequency glow discharge<sup>12</sup> (10%, with longer residence time) and somewhat higher than Streitwieser obtained using a microwave<sup>11</sup> induced glow discharge (5%). The corona discharge gives a considerably higher proportion of polymer than is obtained from these other energy sources. Benzene substitution products such as toluene, phenylacetylene and ethylbenzene were observed in the microwave discharge but were not noted in this study or in the radiofrequency investigation. The high yield of fulvene in the radiofrequency discharge is surprising in view of its tendency to polymerize or add oxygen under rather mild conditions. The sum of the carbon and hydrogen analyses for the polymeric fraction obtained by Stille in the glow discharge of benzene (86-94 per cent) suggests some fixation of oxygen and/or nitrogen during discharge or product work-up.<sup>12</sup> The pressure for these electrodeless glow discharge studies was of the order of 20 mm. or less, while the corona reactor was operated at atmospheric pressure. Schüller, using an electrode discharge in benzene, obtained products similar to those produced in the microwave glow discharge.<sup>10</sup>

The reaction products obtained in this study are roughly categorized as the benzene fraction, biphenyl fraction and polymeric material for purposes of discussion. After initial studies indicated that the components of the -70 and -195° traps were similar to those in the benzene trap, these samples were combined. The acetylene content of the low temperature traps was determined by weight loss prior to mixing with the benzene.

Benzene Fraction

The exposed benzene, as collected in the cold traps, is bright yellow. The following reaction products have been identified in this fraction: 1,3-cyclohexadiene, 1,4-cyclohexadiene, fulvene and cyclohexene. The approximate per cent yield for each of these constituents is given in Table 2. The data were determined using a 100 foot

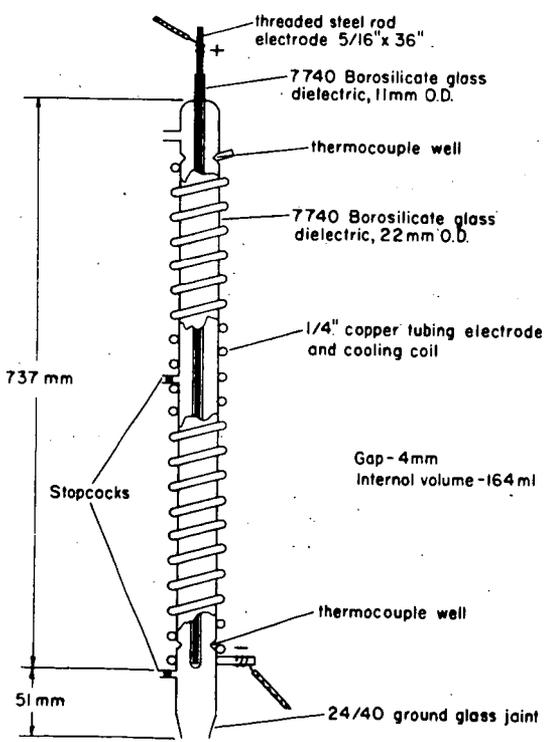
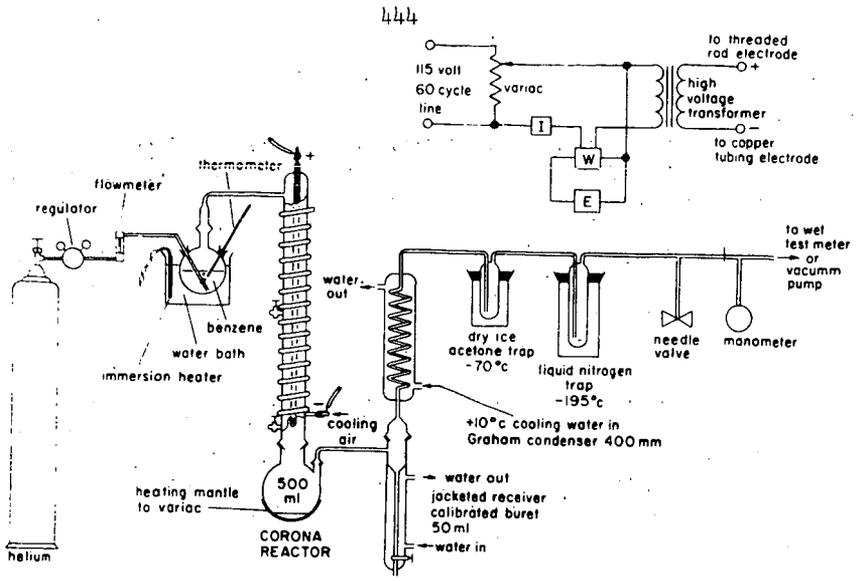


TABLE 1

## Product Distribution in the Corona Discharge of Benzene, 15KV

Product	Yield-Per Cent Benzene Exposed	Yield-Per Cent of Product Mix	Radiofrequency <sup>(c)</sup> Yield, Per Cent
Benzene insoluble polymer	0.7	8.2	N.D. <sup>(d)</sup>
Benzene soluble polymer (a)	6.0	70.5	5.0 <sup>(e)</sup>
Biphenyl	0.3	3.5	2.0
o-, m-, and p-Terphenyl	0.1	1.2	N.D.
Phenyl, benzyl substituted cyclopentenes <sup>(b)</sup>	0.3	3.5	N.D.
1,3-and 1,4-Cyclohexadiene	0.1	1.2	N.D.
Fulvene	0.01	0.1	1.0
Acetylene	1.0	11.8	2.0 <sup>(f)</sup>
TOTAL	8.5	100.0	10.0

(a) Polymer fraction includes materials from 250 molecular weight and up.

(b) Includes several phenyl and benzyl substituted cyclopentenes similar to biphenyl and o-terphenyl in vapor pressure. See discussion.

(c) See reference No. 12.

(d) N. D. -- not determined.

(e) Benzene and toluene soluble polymer.

(f) Acetylene 1%, allene 1%.

support-coated open tubular column with a squalane liquid phase and appropriate calibration standards (Figure 3). No significant change is noted in the cyclohexane content when compared with starting benzene. The increase in the methyl cyclopentane peak is ascribed to its higher vapor pressure thus affording some accumulation of this material in the benzene distillate and a concomitant depletion in the benzene feed stock. Cyclohexene is produced in very low yield, as expected, because of the degree of hydrogenation required during its short residence time in this single pass reactor.

The reduction of benzene to the cyclohexadienes is interesting as 1,3-cyclohexadiene is thermodynamically unstable with respect to benzene, cyclohexene and cyclohexane.<sup>14</sup> The synthesis of 1,3-cyclohexadiene under these conditions is analogous to the conversion of oxygen to ozone which also represents an energetically unfavorable process. The momentary energy input and the rapid removal of the activated species from the reaction zone affords this material in low yield. As expected, the more stable 1,4-cyclohexadiene is produced in higher yield (3/1). Additionally, 1,3-cyclohexadiene would be expected to polymerize at a rapid rate under these conditions. The thermodynamic instability of 1,3-cyclohexadiene is demonstrated by its gradual disappearance from the sample after a few days standing at room temperature. The yields of both the 1,4- and 1,3-cyclohexadiene are somewhat higher than previously reported by Brown and Rippere.<sup>9</sup> The yields reported by these workers after 24 hours exposure to a 15 KV corona discharge in a counter-current hydrogen stream were 0.02 and 0.01 per cent respectively. The major variable in technique which likely accounts for this difference in yields is the use of benzene vapor in our work, versus the hydrogenation of a thin liquid benzene film running down the annular dielectric surface by Brown and Rippere.

The ultraviolet spectrum for the benzene fraction was obtained by running differentially against pure benzene in isooctane. A broad absorption band with a maximum at 258  $\mu$  is ascribed to the 1,3-cyclohexadiene. An additional absorption at 242  $\mu$  and a tailing into the visible region with a broad maximum at 360-370  $\mu$  is also observed. These spectral features are consistent with those reported for fulvene, the non-aromatic isomer of benzene.<sup>15</sup> Blair and Bryce-Smith found fulvene in the photochemical irradiation of benzene in what appears to be the first direct conversion of an aromatic hydrocarbon to a non-aromatic hydrocarbon.<sup>16</sup> Fulvene co-distilled with benzene, but could be separated from benzene using the 100 ft. squalane column (Figure 3). Fulvene prepared by the method of Meuche gave the same retention time and spectral features.<sup>17</sup> Additional evidence for assignment of the fulvene peak included its disappearance from the chromatogram after the sample was refluxed with maleic anhydride (color disappears) or exposure to a free radical catalyst. The Diels-Alder reaction product with maleic anhydride was isolated and hydrolyzed to give the adduct, 7-methylene-5-norbornene -2, 3-dicarboxylic acid. The melting point and infrared data for this adduct were identical with the sample prepared using fulvene synthesized from cyclopentadiene and formaldehyde.<sup>12</sup>

The formation of the 1,3,5-hexatrienyl diradical has been suggested as an intermediate in the photochemical decomposition<sup>18</sup> and the radiofrequency discharge<sup>12</sup> of benzene. Material isolated in the photochemical excitation gave a UV spectrum similar to 1,3,5-hexatriene, but displaced by 7.5  $\mu$  and, more disturbing, the investigators were able to separate the material from benzene by fractional distillation. No experimental evidence was given in the radiofrequency study. In our work, 1,3,5-hexatriene could not be detected (less than 100 ppm) in the benzene fraction using the squalane column. No spectral evidence was noted in the ultraviolet although the region of interest is complicated by the presence of 1,3-cyclohexadiene.<sup>19</sup>

The unidentified peak in the chromatogram (Figure 3) gives a negative test for an acetylenic hydrogen (ammoniacal cuprous chloride solution) and does not disappear after the sample is subjected to free radical catalysis for several hours. Thus, the open chain, acetylenic isomers of benzene, hexa-1, 3-diene-5-yne, 1,4-hexadiyne, 1,5-hexadiyne and 1,5-hexadien-3-yne do not appear to account for this peak. The possibility of valence isomers of benzene such as bicyclo (2.2.0) hexa-2, 5-diene, "Dewar benzene", were excluded based on the observation that the peak was stable to prolonged heating at 100°. The valence isomers would be expected to convert to benzene under such conditions.<sup>20</sup>

TABLE 2

Product Distribution in Discharged Benzene Fraction (a)

<u>Product</u>	<u>Yield % Benzene Exposed</u>
1,3-Cyclohexadiene	0.03
1,4-Cyclohexadiene	0.09
Fulvene	0.01
Cyclohexene	0.01
Unidentified	0.02

(a) Quantitative data obtained by GLC using squalane column and appropriate calibration standards.

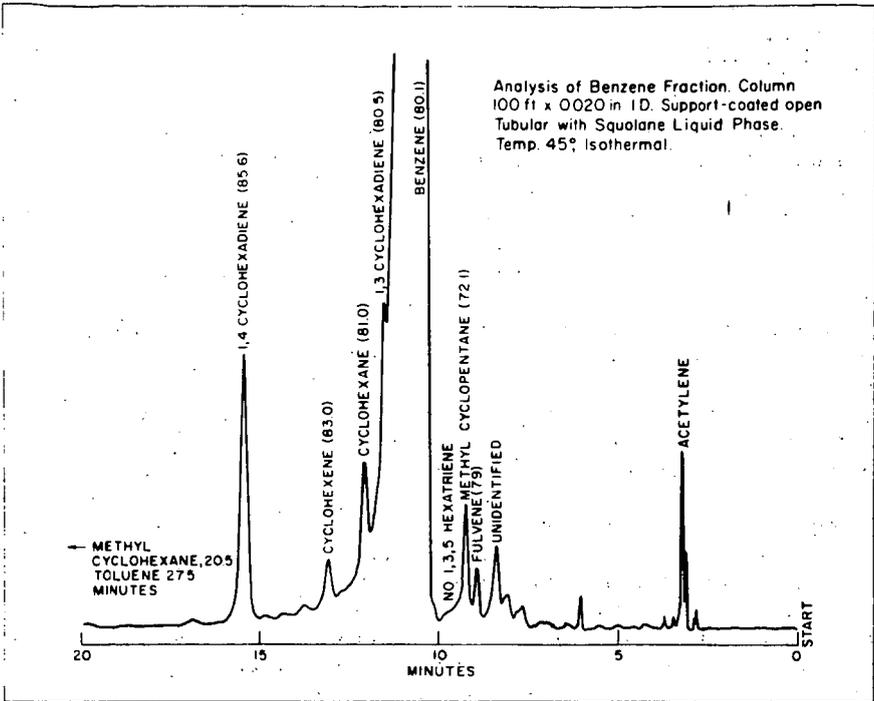


Figure 3

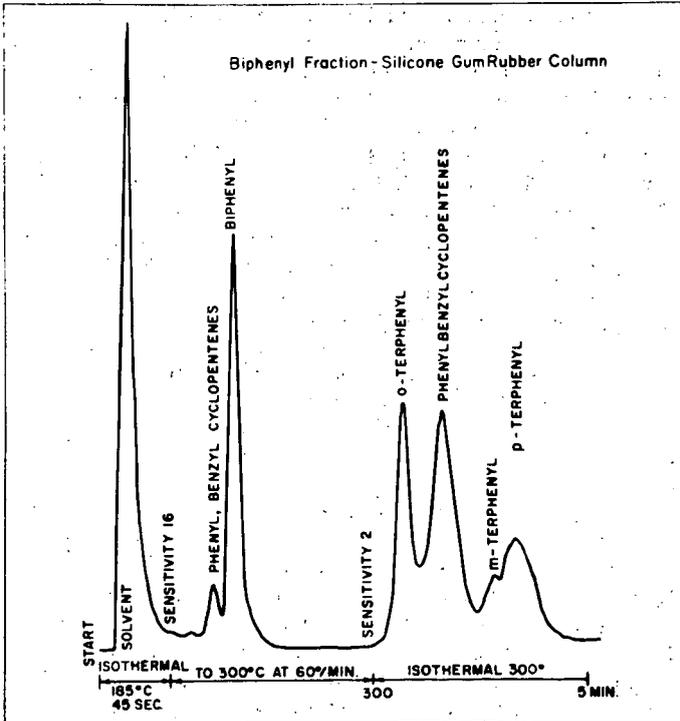


Figure 4

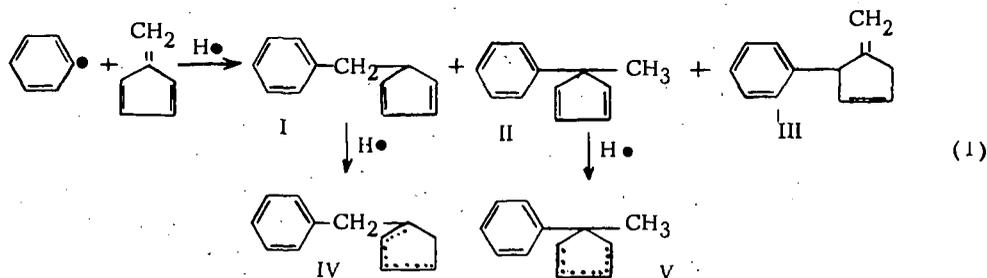
### Biphenyl Fraction

The low molecular weight compounds, soluble in isooctane and hot methanol, were primarily biphenyl and o-, m-, and p-terphenyl. These products were identified by gas-liquid chromatography using a silicone gum rubber column (Figure 4) and a Carbowax 20M column with appropriate standards. The peaks were trapped and analyzed by infrared and NMR spectroscopy for confirmation. Biphenyl was present in sufficient quantity to be readily detected in the initial infrared spectrum and was isolated by sublimation. Quantitative data, obtained using the silicone column with appropriate calibration curves are presented in Table 3. With the possible exception of biphenyl, the yields are very low considering the overall conversion noted. The o-, m- and p-terphenyl ratio (1/0.4/1) indicates a preference for the para position beyond that expected for random attack.

If hydrogenation of the polyphenyls by hydrogen radicals generated "in situ" is to be considered a primary reaction mechanism, one would expect to see components corresponding to the possible hydrogenated species of biphenyl and the terphenyls. This does not appear to be the case, however, as no significant peak can be ascribed to a hydrogenated o-terphenyl compound. The small peaks before biphenyl and after o-terphenyl in the chromatogram (Figure 4) actually include four or more components present in small proportions which have not been completely identified. The first peak, (eluted before biphenyl) amounting to less than 0.1 per cent of the total yield, was initially ascribed to a mixture of the possible hydrogenation products of biphenyl. On the Carbowax column at lower temperatures this peak is eluted between phenylcyclohexane and 1-phenylcyclohexene. Initial infrared examination of this peak after trapping indicated an intriguing similarity with the peak (s) noted after o-terphenyl and with the polymer fractions. The possibility that this component was a low molecular weight precursor to polymer formation prompted further study. Infrared indicates a phenyl substituted aliphatic compound containing some olefinic unsaturation, and the spectrum is not consistent with the anticipated phenyl cyclohexenes. Careful examination of the spectrum indicates that the following phenyl substituted compounds are not present on the basis of the indicated missing absorptions - phenyl cyclohexane (1010, 1000, 888, 865  $\text{cm}^{-1}$ ), 1-phenylcyclohexene (922, 805  $\text{cm}^{-1}$ ), and 3-phenylcyclohexene (855, 788, 675  $\text{cm}^{-1}$ ).<sup>21</sup> The spectrum is consistent with a non-conjugated benzylcyclopentene system with absorptions at 1070, 1030, and 960  $\text{cm}^{-1}$  and the expected aromatic substitution bands.<sup>21</sup> Two additional absorptions are noted, one at 850  $\text{cm}^{-1}$  which may be attributed to vinyl protons and a phenyl substitution band at 730  $\text{cm}^{-1}$ . This likely results from biphenyl contamination, but it is interesting to note that benzylidenecyclopentane has an absorption at 732  $\text{cm}^{-1}$  with the remainder of the spectrum being similar to the benzylcyclopentenes.

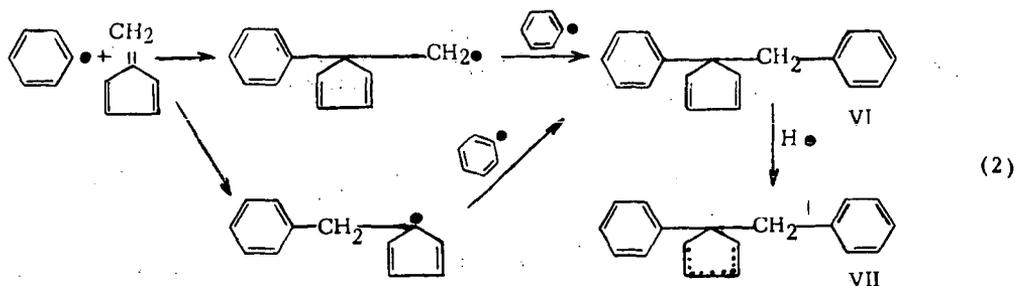
NMR data provides strong evidence for a rigid ring system (non-olefinic protons poorly resolved 1-3 ppm), non-conjugated olefinic protons at 5.7 ppm and phenyl protons at 7.1 ppm. The olefinic protons are complex, giving a closely-spaced doublet superimposed on a broad absorption, suggesting the presence of both ring and exocyclic unsaturation. Additional sharp proton resonances are noted at 1.2 ppm (methyl) and a doublet at 2.7 ppm which is attributed to benzylic protons. The lack of olefinic protons downfield from 5.7 ppm would rule out the benzylidene compounds and likely any similar structures wherein the unsaturation is conjugated with the phenyl moiety. The olefinic protons in cyclopentadiene are found at 6.42 ppm and were not obvious in this fraction. However, absorptions due to a minor component could have escaped detection because of limited sample size. The difficulty encountered in isolating the components of this peak precludes definite structural assignments, but the reaction of phenyl radicals with fulvene followed by H radical termination and hydrogenation to give

phenyl or benzyl substituted cyclopentenes is clearly indicated. The following reaction scheme is proposed to account for the experimental observations:

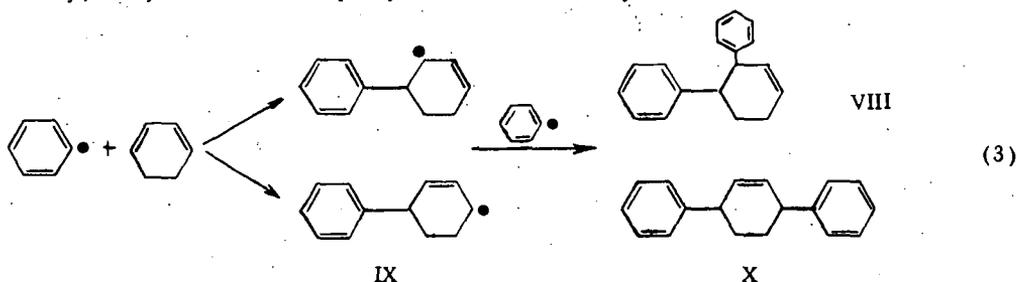


The inherent complexity of the product mix is illustrated by IV above which could be 1-, 3- and 4-benzylcyclopentene. Preliminary mass spectral data for this sample, as isolated from the chromatographic separation, indicates  $m/e$  values of 156 and 158, corresponding to the cyclopentadienes I, II and the cyclopentenes IV, V. Ring substituted compounds such as III would also have a mass of 156. Mass 91, corresponding to the benzyl radical is prominent as is mass 77, the phenyl radical, although this would be expected to arise from the biphenyl (154) contamination. Other features of the spectrum are being evaluated. The low yield is reasonable in view of the limited probability for radical termination and hydrogenation compared with the high reactivity of these olefins (or the diene precursors) under the reaction conditions. The glow discharge work of <sup>10</sup>Schüler indicates the absence of any products with vapor pressure similar to biphenyl and the other related literature generally does not give details beyond biphenyl analysis and gross polymer properties.

The peak after *o*-terphenyl (Figure 4) actually consists of 3-4 components when analyzed by varying the chromatographic conditions. This peak has the same retention time as diphenyl fulvene and is in the same general range as noted for a commercially available hydrogenated terphenyl, Monsanto HB-40. This complex peak was trapped (with trace *o*-terphenyl contamination) as a yellow liquid which gave an infrared spectrum identical to the polymer fractions and very similar to the peak before biphenyl. Again, phenylbenzylcyclopentenes are indicated and the spectrum bears little resemblance to the hydrogenated terphenyl spectrum. The NMR spectrum in carbon tetrachloride showed aromatic protons at 7.1 ppm, a broadened olefinic proton resonance at 5.7 ppm and non-olefinic protons from 0.8-3.5 ppm with poor resolution. These extremely complex olefinic and non-olefinic resonances are typical of protons in a fixed ring system such as cyclopentene. The integration for these resonances allows approximation of an average structure containing a cyclopentene ring system substituted with one phenyl and one benzyl group. The reactions appear analogous to those responsible for the components of the peak before biphenyl with termination being with a phenyl radical rather than the hydrogen radical. The mass spectrum for this material as trapped from the chromatographic analysis shows prominent peaks at mass 232 and 234 corresponding to VI and VII below. The benzyl and phenyl radical peaks are also evident at mass values of 91 and 77 respectively. Evaluation of the final structure details is continuing. The following is believed to be representative of the many reactions which are possible under the experimental conditions, to give a variety of closely related compounds:



The actual structural definition must await isolation of sufficient quantities of the components for NMR studies under various conditions. The possibility of a hydrogenated *p*-terphenyl was carefully considered, but the only structure even remotely consistent with the infrared and NMR data would require that the center ring of *p*-terphenyl be non-aromatic with mono-substituted phenyl groups attached. Such a material could be formed by preferential hydrogenation of the center ring of *p*-terphenyl (statistically unlikely) or by the reaction of phenyl radicals and 1,3-cyclohexadiene as follows:



This mechanism requires the formation of hydrogenated ortho terphenyl derivatives such as VIII, which were not noted by gas-liquid chromatography or infrared.

TABLE 3

## Biphenyl Fraction (a)

	Yield % Exposed Benzene	Yield % Reaction Products
Biphenyl	0.30	3.5
<i>o</i> -Terphenyl	0.05	0.6
<i>m</i> -Terphenyl	0.02	0.2
<i>p</i> -Terphenyl	0.05	0.6
Benzyl and phenyl cyclopentenes (C <sub>12</sub> )	0.05	0.6
Phenylbenzylcyclopentenes (C <sub>18</sub> )	0.25	2.9
TOTAL	0.72	8.4

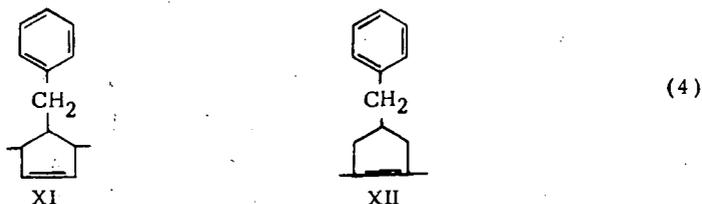
(a) Quantitative data were obtained by GLC, using a silicone gum rubber column with appropriate standard calibration curves based on peak height.

## Polymeric Products

The material which adheres to the glass dielectric surface in the reactor is a high melting solid ( $>320^\circ$ ), insoluble in benzene and all common solvents. The infrared spectrum and the carbon-hydrogen ratio are essentially the same as noted for the benzene soluble material. The benzene soluble polymer was fractionated into three molecular weight ranges based on solubility in isoctane. The polymers are all yellow with the intensity increasing as the molecular weight decreases. The ultraviolet spectrum for the low molecular weight polymer shows a gradual tailing into the visible region. The physical property data for the polymeric fractions are summarized in Table 4.

Infrared data indicate that the polymeric fractions are structurally similar to the low molecular weight products identified as benzyl and phenyl substituted cyclopentenes. The infrared evidence already presented for the low molecular weight products is applicable to the polymeric products and need not be repeated. The data are consistent with an average repeating unit containing the cyclopentene ring structure substituted with phenyl or benzyl groups. NMR data for the polymers were obtained in carbon tetrachloride at the cell holder temperature ( $40^\circ$ ). The spectrum obtained for the 300 molecular weight polymer fraction is presented in Figure 5. The extreme broadening of the proton resonances is associated with the complex, long range proton coupling in a rigid system and the motional averaging commonly noted in polymers.<sup>22</sup> Scanning the same sample at  $90^\circ$  in tetrachloroethylene did not significantly improve the resolution. The NMR spectrum of the polymer in pyridine (Figure 5) gives some improvement in the high field proton resolution, indicating a doublet at 2.6 ppm (benzylic protons) and a complex methyl proton resonance. The spectra are similar to those obtained for the low molecular weight precursors containing unresolved ring protons. The NMR spectra generally eliminate polymer formation by way of phenyl and hexatrienyl radicals as suggested for the radiolysis of benzene.<sup>23</sup> The aliphatic proton portion of the spectrum is very similar to that reported for cyclopentadiene polymers by Davies and Wassermann.<sup>24</sup> The cyclopentadiene polymers had a molecular weight range of 1200-2300, a  $\lambda$  max. at 320-360 m $\mu$  and non-olefinic proton to olefinic proton ratio of approximately 3/1.

The data are consistent with polymer formation by way of phenyl radical (or excited benzene) reaction with the fulvene produced to give phenyl or benzyl substituted cyclopentadienes which then polymerize to give a polycyclopentene chain with pendant phenyl and/or benzyl groups. The average non-olefinic to olefinic proton ratio of 2.9 indicates that the many possible structures similar to XI (5/2) predominate over the alternate type structures, XII (7/0),<sup>24</sup> assuming our analogy to cyclopentadiene type polymers is valid.



Many similar structures must be considered, including those derived from phenyl attack on the ring with polymerization through the exocyclic vinyl group of fulvene.

TABLE 4

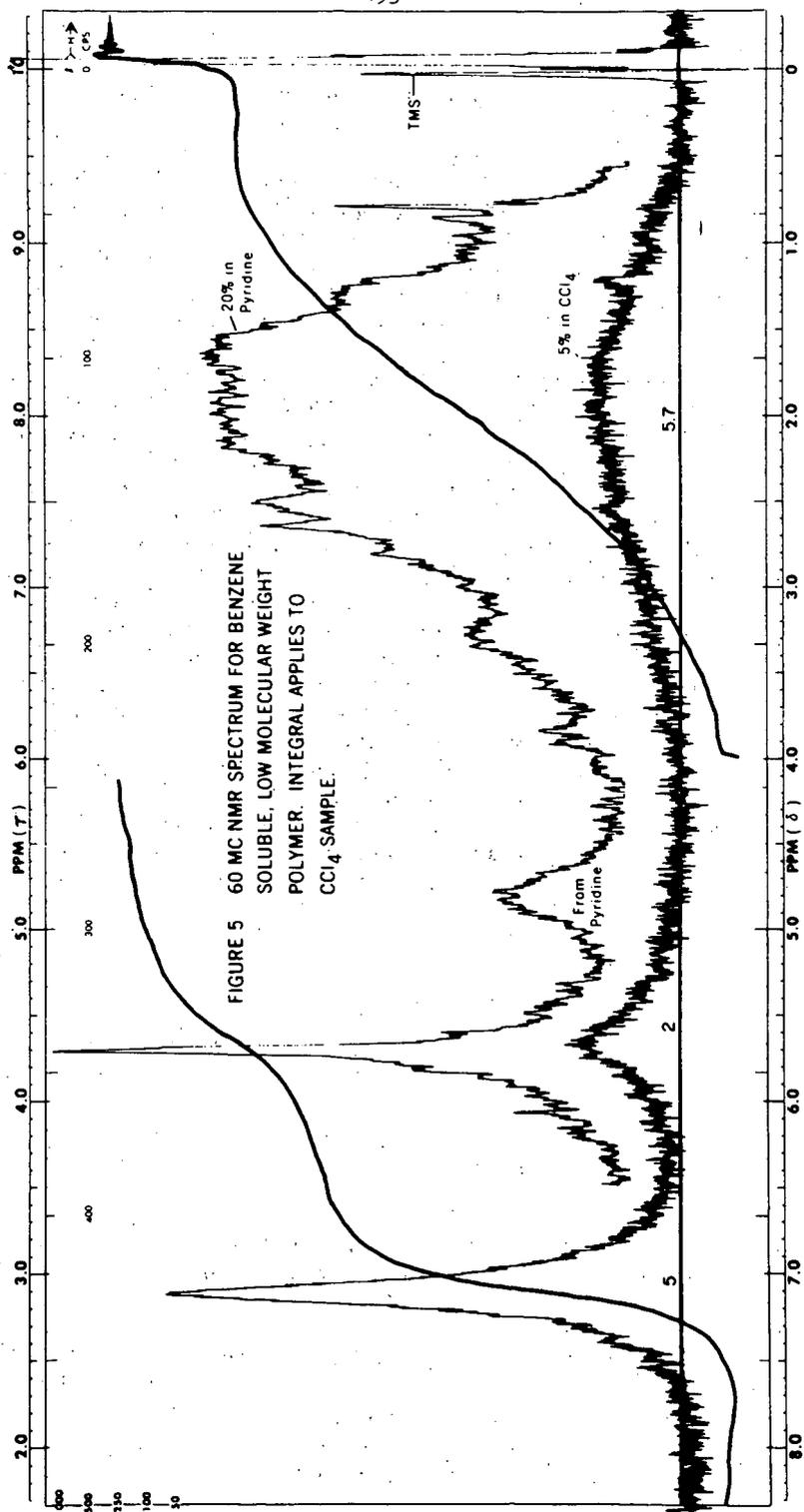
Properties of Polymers Produced  
in Corona Discharge of Benzene

	% C	% H	C/H	M. W. (a)	Infrared cm <sup>-1</sup>	(b)		
						Aromatic	Protons Olefinic	Non-olefinic
Benzene insol.	86.95	7.17	1.01	---	755, 695	---	---	---
Benzene sol. 1	88.32	7.18	1.02	4360	755, 695	5	2	5.8
2	87.26	7.09	1.03	1555	755, 695	5	2	5.7
3	87.23	7.09	1.03	305	755, 695	5	2	5.7

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(a) Vapor pressure osmometry in benzene solution.

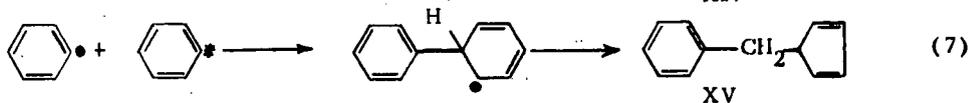
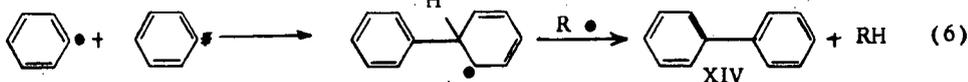
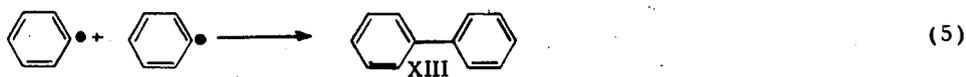
(b) Aromatic proton resonance assigned five protons.



## Mechanism

The available evidence is thus not consistent with the generally proposed mechanism of polymer formation based on the random build-up of a poly (phenylene) chain accompanied by hydrogenation,<sup>9</sup> or the interaction with the hexatrienyl diradical.<sup>23</sup> In the radiofrequency discharge of benzene, evidence was presented which clearly indicated that the polymer contained consecutive para linkages suggesting poly (p-phenylenes) as the predominant structure.<sup>12</sup> Schüller observed that the polymer (C/H 1.03, M.W. 503) was a phenyl substituted aliphatic chain based on infrared evidence.<sup>10</sup> Patrick and Burton have demonstrated that hydrogen atoms are not involved to any significant extent in polymer formation when liquid benzene is irradiated with a 1.5 m.e.v. source.<sup>24</sup>

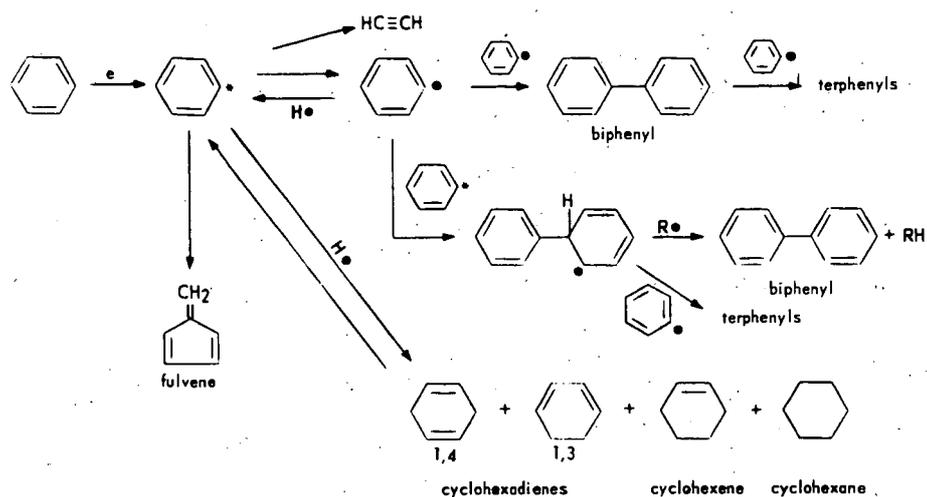
In the corona discharge many types of energy transfer are occurring, varying from photolysis (visible corona) to relatively high energy electrons responsible for fragmentation. The low yield of biphenyl in this single pass reactor suggests that phenyl radical production through loss of a hydrogen radical is not the primary reaction route leading to polymer formation. Considerable energy should be available to excite benzene to relatively high vibrational levels which would be somewhat below that energy required to actually separate the H radical. At any given time the number of these excited benzene molecules should greatly exceed the phenyl radical population. Fulvene is produced from benzene by ultraviolet energy (200 m $\mu$ , about 112 kcals, or 4.9 electron volts).<sup>25</sup> Thus, the formation of this benzene isomer with a resonance energy (11-12 kcals/mole) intermediate between benzene and 1,3 cyclohexadiene may be energetically favorable in the corona environment. Fulvene has been shown to polymerize rapidly under similar conditions with no reversion to benzene.<sup>25</sup> The uniformity of the phenyl (benzyl) - cyclopentene ratio throughout all polymer fractions makes it difficult to accept a mechanism based solely on random attack by phenyl radicals on the growing fulvene polymer. The initial synthesis of a monomeric unit comprised of the benzylcyclopentadiene system with subsequent diene type polymerization is consistent with all our observations. The phenyl radical produced in the discharge should collide with the nearest benzene molecule which will be excited to a relatively high vibrational energy level. The following reaction sequences are suggested for the phenyl radical:



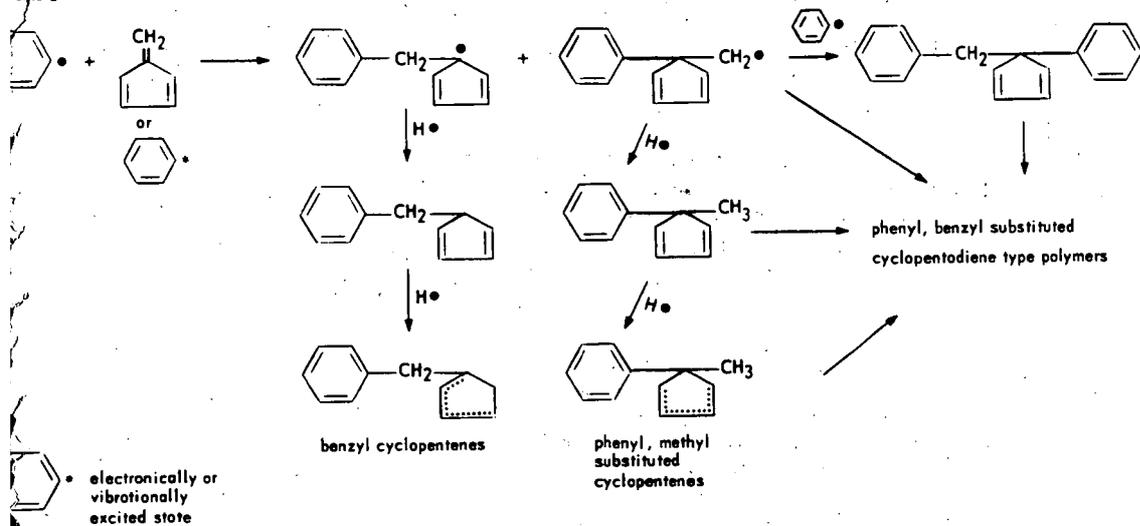
Reaction (5) is the typical termination reaction by radical coupling leading to biphenyl. The intermediate radical in (6) would be expected to lose hydrogen more readily than it would add to another benzene molecule to give polymer formation.<sup>26</sup> The possibility of ring contraction in the excited intermediate, accompanied by an intramolecular shift of a hydrogen atom is suggested in reaction (7). The benzylcyclopentadiene XV so obtained would be a very active monomer leading to the polymeric products observed. Although our data support polymer formation by the mechanism indicated, we cannot rule out participation by the cyclohexadienes and acetylene, both of these being noted in the benzene fraction and the low temperature traps.

FIGURE 6 PROPOSED REACTION MECHANISMS

Scheme 1



Scheme 2



The relatively low yield and the complexity of the reaction products does not allow an unequivocal designation of reaction mechanism or of the mode of energy transfer in the corona environment. However, where possible, we have proposed reaction mechanisms which are consistent with our results to date. These mechanisms are summarized in Figure 6. Studies are underway to obtain deuterium exchange data in the corona reactor, and mass spectral data are being evaluated. Investigation of the utility of corona chemistry will be extended to other volatile compounds.

## EXPERIMENTAL

Materials: Fisher thiophene-free benzene contained trace quantities of methyl cyclopentane, cyclohexane and toluene. Chromatogram (squalane) of original material was used as reference for irradiated benzene evaluation under the same GLC conditions.

Reference materials for chromatographic identification were generally used as obtained from commercial sources. Most of these materials were of sufficient purity to identify the major peak. However, mono-phenyl fulvene, obtained from Aldrich, gave no peak on the silicone column and infrared indicated extensive hydroxyl and carbonyl absorptions. 1,3,5-hexatriene from Aldrich gave two major and two minor peaks on the squalane column. Infrared<sup>27</sup> indicated largely the trans isomer with only a small cis absorption at  $818\text{ cm}^{-1}$ .

Fulvene was prepared by the method of Meuche.<sup>17</sup> Infrared ( $1662, 925, 890, 765\text{ cm}^{-1}$ ) and ultraviolet ( $\lambda_1 = 242\text{ mu}, \lambda_2 = 360\text{ mu}$ ) were in good agreement with literature values.<sup>15</sup>

### Reaction Conditions

The equipment used in these experiments was presented in Figures 1 and 2. Helium was bubbled through the benzene reservoir ( $55^\circ$ ) at  $100\text{ ml/min.}$  to carry  $4.2\text{ gm.}$  ( $0.054\text{ moles}$ ) benzene through the corona reactor per hour. The reactor temperature was  $45^\circ \pm 2^\circ$ . A total of  $101\text{ gm.}$  ( $1.3\text{ moles}$ ) benzene was passed through the  $15\text{ KV, } 60\text{ cycle,}$  corona discharge in  $23.7\text{ hours.}$  A small helium purge was maintained throughout all sampling operations and necessary downtime to preclude oxidation.

### Product Isolation and Analysis

At the conclusion of the run, the reactor was partially filled with benzene and refluxed on a steam bath for 2 hours. The benzene soluble material from the column was combined with the yellow brown solid which collected in the lower receiver. The insoluble material was swelled by benzene and generally loosened from the glass dielectric surface. This insoluble material was filtered off, washed several times with chloroform and dried overnight at  $70^\circ$  in a vacuum oven. The reactor was cleaned with a 5 per cent hydrofluoric acid solution to remove final traces of polymer after each run. Benzene insoluble polymer -  $0.7\text{ gm.}$  yellow brown color, % C 86.95, % H 7.17, C/H 1.01.

The benzene containing all solid products from the reactor and pot residue was reduced to  $30\text{ ml.}$  volume by vacuum distillation at  $50^\circ$ . Considerable foaming was encountered, requiring careful control of the distillation. The  $30\text{ ml.}$  of

brown benzene solution was added to 300 ml. isooctane at room temperature. A yellow solid precipitated immediately and was collected by filtration. After several washings with hot methanol, the material was dried for 8 hours at 70° in a vacuum oven. Benzene soluble polymer - Fraction 1, 2.3 gm., M. W. 4360, %C 88.32, %H 7.18, C/H 1.02.

The isooctane-methanol solution was reduced to 100 ml. volume (all methanol removed) by vacuum distillation at 60°. The solution was a brilliant yellow color at this point. On cooling to room temperature, a small proportion of a deep yellow polymeric solid precipitated and was collected by filtration. After washing with hot methanol, this yellow material was dried at 70° for 8 hours in a vacuum oven. Benzene soluble fraction 2, 0.2 gm., M.W. 1555, %C 87.26, %H 7.09, C/H 1.03.

The isooctane-methanol soluble portion was reduced to 20 gm. by vacuum distillation and sufficient benzene added to insure solubility of all components. The per cent solids was determined for this sample, being careful to limit sublimation of biphenyl (about 2 hours at 70° in a vacuum oven). This sample contains the low molecular weight products and a yellow resinous polymer. Qualitative analysis for the low molecular weight components was accomplished by gas-liquid chromatography using the following liquid phases: silicone gum rubber, Carbowax 20 M, and Reoplex 400. Quantitative data were obtained on the silicone column (Figure 4) using calibration curves (peak height) prepared from appropriate standards. The concentration of the small peak eluted before biphenyl was estimated using the biphenyl calibration curve and the peak after o-terphenyl was estimated using a commercial hydrogenated terphenyl mixture (Monsanto HB-40) as a reference. The F & M 500 gas-liquid chromatograph equipped with a standard thermoconductivity detector was used for these analyses. These low molecular weight products (biphenyl, o-, m-, p-terphenyl and phenylcycloalkenes, M. W. up to ~250) amount to 0.72 gms. (See Table 3). Peak confirmation was provided by infrared and NMR analysis after fraction collection from the chromatographic separation.

The concentration of the low molecular weight resinous polymer was determined by subtracting the total biphenyl fraction weight from the total isooctane-methanol soluble material. A sample of this material was placed in the vacuum oven at 100° until the GLC trace indicated negligible biphenyl content and the molecular weight was determined. Benzene soluble fraction 3, 3.5 gm., M. W. 305, %C 87.23, %H 7.09, C/H 1.03. Prolonged heating at 150° in air gives a hard, brittle yellow film. Infrared analysis indicates oxidation is involved in the drying process.

The benzene fraction was initially examined by GLC using 100 ft. support coated open tubular columns containing Carbowax 1540 poly (ethylene glycol) and squalane (Figure 3) as the liquid phase. Quantitative data were obtained at 45° on the squalane column with a helium flow of 3.0 ml/min. The Perkin Elmer Model 380 gas-liquid chromatograph, equipped with a stream splitting device and hydrogen flame detector was used for these analyses. Peak identification was by comparison with commercial standards and the synthesized fulvene. Additionally, the benzene fraction was refluxed in pressure bottles with maleic anhydride, azobisisobutyronitrile, and ammoniacal cuprous chloride solution prior to chromatographic analysis to note peak changes due to adduct formation, polymerization or presence of acetylenic hydrogen. Acetylene content was estimated from weight loss of the -70° and -195° traps. The vapor space above those cold traps and the gas stream directly below the corona were analyzed by infrared using an 8 cm. gas cell. Although the study was not exhaustive, several samplings were made and only acetylene was detected.

Methylacetylene, allene and butadiene were not present in sufficient quantity to be detected.

The yellow benzene from several runs (1000 ml.) was fractionated and 900 ml. distillate obtained from 79-80°. The distillate was refluxed with maleic anhydride until colorless and the benzene removed at reduced pressure. Dilute sodium hydroxide solution was added and the resulting solution was extracted several times with chloroform. After acidification with dilute hydrochloric acid, the solution was extracted with ether. The ether was removed after drying to give a white solid which, on recrystallization from chloroform and pet ether, gave the adduct 7-methylene-5-norbornene-2, 3-dicarboxylic acid which melted at 146°-150°. The infrared showed maxima at 1553, 875 and 710  $\text{cm}^{-1}$ , (lit <sup>(12)</sup> 1555, 874, 712  $\text{cm}^{-1}$ ). Fulvene was prepared in low yield (less than one per cent) from cyclopentadiene and formaldehyde with sodium ethoxide catalyst. <sup>17</sup> The adduct was prepared by adding maleic anhydride to the crude fulvene reaction product in Freon 113 (b.p. 47.6°) and refluxing until colorless. After removal of the solvent, hydrolysis and recrystallization yielded the adduct, m.p. 147-150°, which gave properties identical with the fulvene adduct obtained from the corona discharge. Bryce-Smith obtained a melting range of 105-110° for this adduct which was likely a mixture of the exo and endo isomers. <sup>25</sup> Stille prepared the fulvene-maleic anhydride adduct with a melting point of 149-150° which may be a single isomer. <sup>12</sup>

Through the courtesy of the Perkin Elmer Company at Norwalk, Connecticut, the discharged benzene was analyzed by combination of gas-liquid chromatography and mass spectroscopy. The peak attributed to fulvene gave a parent mass of 78 and fragments at m/e 77, 52, 51, 50 and 39 in good agreement with the literature. <sup>17</sup> Confirmation of other assignments was obtained by this technique and the one unidentified component on the squalane column gave a parent mass of 78.

Molecular weight and carbon-hydrogen determinations were made by Schwarzkopf Microanalytical Laboratories, New York, New York. Molecular weight was determined in benzene by vapor pressure osmometry.

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