

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

Reaction of Benzyne with Benzene and Naphthalene<sup>1</sup>BY ROY G. MILLER<sup>2a</sup> AND MARTIN STILES<sup>2b</sup>

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The pyrolysis of benzenediazonium-2-carboxylate (I) in benzene produces three hydrocarbons: biphenyl, benzocyclooctatetraene and benzobicyclo[2.2.2]octatriene (III). Pyrolysis of I in the presence of naphthalene affords dibenzobicyclo[2.2.2]octatriene as the only recognizable product.

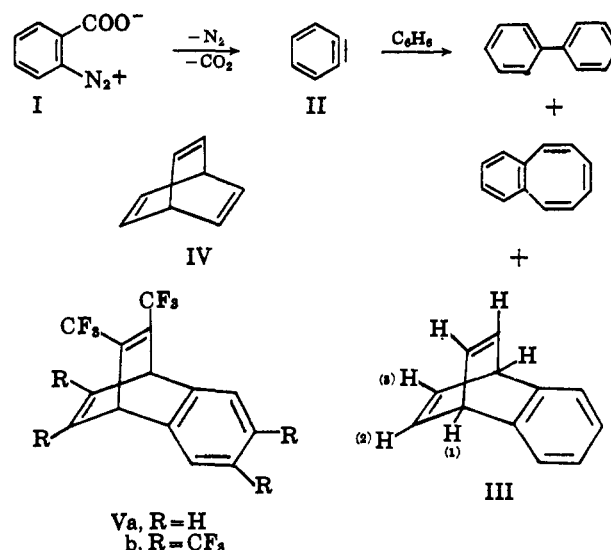
Evidence has been presented that the pyrolysis of benzenediazonium-2-carboxylate (I) leads to benzyne (II) which can be intercepted by various reagents.<sup>3</sup> Aromatic hydrocarbons exhibit relatively low reactivity toward this intermediate and often may be used as media for bringing other reactants into contact with benzyne. However, a close examination of substances formed by the decomposition of the precursor I in pure benzene has revealed the presence of addition products.

Suspensions of I in benzene evolve both nitrogen and carbon dioxide when heated, and a complex mixture of substances is produced.<sup>4</sup> The mixture may be separated into a relatively insoluble amorphous fraction and an oily hydrocarbon fraction. The amorphous material appears to be polymeric and can be shown by infrared spectroscopy to contain ester linkages, but it has not been further characterized. The hydrocarbon fraction was shown by gas chromatography to contain three major components in the ratio of 1:4:3, being eluted in that order from a column of Silicone gum rubber on Chromosorb. The third compound could be easily recognized as biphenyl, on the basis of its retention time. This identification was confirmed by the isolation of small quantities of crystalline biphenyl after careful (but inefficient) chromatography of the hydrocarbon fraction on alumina.

The second hydrocarbon, present in slightly greater amount, was identified as benzocyclooctatetraene. It could be separated from the crude hydrocarbon fraction by treatment with silver nitrate, which caused precipitation of the silver nitrate complex.<sup>5</sup> The pure hydrocarbon, m.p. 49.0–49.5°, could be recovered from the complex and identified by its infrared and ultraviolet spectra, and its characteristic parsley odor.<sup>5</sup>

The remaining hydrocarbon, present in the smallest quantity, was obtained in pure condition by collection of material from the gas chromatogram, followed by sublimation. It melted at 65.0–65.5° and proved to be an isomer of the other two, on the basis of its elemental analysis and mass spectrum.<sup>6</sup> Heating the hydrocarbon at 310° for 1.5 hr. converted it completely to naphthalene (and, presumably, acetylene, although its presence was not proved). The structure which immediately suggested itself was benzobicyclo[2.2.2]octatriene (III). The parent ring compound, bicyclo[2.2.2]octatriene (IV), was recently synthesized by Zimmerman and Paufler<sup>7</sup> and found to undergo cleavage to benzene and acetylene under similar conditions.

Further support for the structure III was obtained from the infrared spectrum which showed the presence



of saturated (2990 cm.<sup>-1</sup>), unsaturated (3028 cm.<sup>-1</sup>) and aromatic (3070 cm.<sup>-1</sup>) carbon-hydrogen. The ultraviolet spectrum of the hydrocarbon is summarized in Table I, alongside those of the only known compounds with this fused-ring structure, the trifluoromethyl derivatives Va and Vb, reported by Krespan, McKusick and Cairns.<sup>8</sup>

Confirmation of the structure III came from the n.m.r. spectrum<sup>9</sup> (Fig. 1). Three approximately symmetrical groups of lines appear in the spectrum, two of which overlap. Centered about  $\tau = 5.2$  is the array of lines due to the bridgehead protons; centered about  $\tau = 3.2$  is a strong quartet representing the vinyl protons; overlapping the latter is a complex pattern of 12 lines centering about  $\tau = 3.1$ , closely similar to the naphthalene spectrum<sup>10</sup> and clearly due to the aromatic protons of III. The integrated intensity of the overlapping aromatic and vinyl peaks was 4.0 times that of the higher field signal, in agreement with the structure. The intensities of the vinyl and aromatic peaks could be resolved on the assumption that the aromatic pattern was truly symmetrical, since the lower-field half of the aromatic pattern was free from interference by the vinyl peaks. One concludes on this

TABLE I

ULTRAVIOLET SPECTRA IN ETHANOL

—Compound 111—		—Compound Va <sup>a</sup> —		—Compound Vb <sup>a</sup> —	
$\lambda$ , m $\mu$	$\epsilon$	$\lambda$ , m $\mu$	$\epsilon$	$\lambda$ , m $\mu$	$\epsilon$
276.5	878	272(sh)		277	840
268.5	809	266	370	270	900
262.5	595	259	360		
255(sh)	560				
230(sh)	1280	222	2500	228(sh)	

<sup>a</sup> Reference 8.

(1) (a) Taken from the Ph.D. Thesis of Roy G. Miller, University of Michigan, 1962. (b) This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

(2) (a) E. C. Britton Fellow in Organic Chemistry (Dow Chemical Co.), 1960–1961; Minnesota Mining and Manufacturing Co. Fellow, 1961–1962. (b) Fellow of the Alfred B. Sloan Foundation.

(3) M. Stiles, R. G. Miller and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963). This paper contains references to the previous literature concerning benzyne intermediates.

(4) M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960).

(5) G. Wittig, H. Eggers and P. Duffner, *Ann.*, **619**, 10 (1958).

(6) We are indebted to Dr. Klaus Biemann for this spectrum.

(7) H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

(8) C. G. Krespan, B. C. McKusick and T. L. Cairns, *ibid.*, **88**, 3428 (1961).

(9) Obtained through the courtesy of Dr. Jerry Heeschen of the Dow Chemical Company, using a Varian A-60 instrument.

(10) J. A. Pople, W. G. Schneider and H. J. Bernstein, *Can. J. Chem.*, **35**, 1080 (1957).

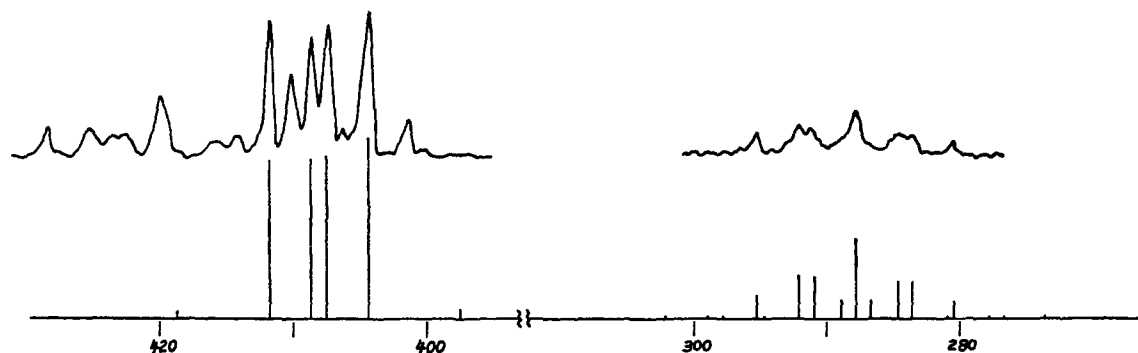
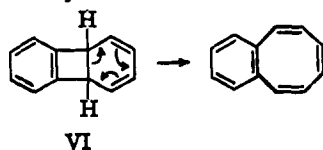


Fig. 1.—Calculated and observed (carbon tetrachloride solution) n.m.r. spectrum of benzobicyclo[2.2.2]octatriene (III), in c.p.s. relative to tetramethylsilane, at 60 Mc.

basis that there are equal numbers of aromatic and vinyl protons.

The observed n.m.r. spectrum agrees closely with that calculated (Fig. 1) for a six-proton system of the  $A_2B_4$  type, where the chemical shifts are 288.0 and 408.0 (in c.p.s. relative to tetramethylsilane) for the bridgehead and vinyl protons, respectively, and  $J_{12} = 6.13$ ,  $J_{13} = 1.27$ ,  $J_{23} = 10.0$ , and all other coupling constants are zero. The aromatic protons were ignored in the calculation, which was carried out essentially as described by Bernstein, Pople and Schneider,<sup>11</sup> using a computer program developed by Bothner-By.<sup>12</sup>

All three of the hydrocarbons isolated from the decomposition of the diazonium carboxylate in benzene are assumed to result from the reaction of benzyne with benzene. There is direct evidence for this path in the case of biphenyl, since both *m*- and *p*-nitrobiphenyl were isolated from a reaction in which 5-nitrobenzenediazonium-2-carboxylate was decomposed in benzene.<sup>3</sup> The other two hydrocarbons apparently arise from cycloaddition of benzyne in either a 1,2- or a 1,4-sense. The latter path gives III directly; the former path would give the dihydrobiphenylene VI, which could easily isomerize to benzocyclooctatetraene.



The reaction of benzyne with benzene emphasizes the "dienophilic" properties of this intermediate, a characteristic first discovered by Wittig.<sup>13</sup> There is little precedent for a 1,4-addition of a dienophile to benzene itself. The reaction of perfluorobutyne with benzene<sup>8</sup> has been rationalized as an initial 1,4-addition, but the product in that case undergoes further transformations which tend to obscure the reaction path.

The 1,2-addition of benzyne to benzene, with over-all expansion of the ring, is reminiscent of the reaction of methylene with benzene to form cycloheptatriene.<sup>14</sup> The recent reports of the light-catalyzed addition of maleic anhydride<sup>15</sup> and acetylenedicarboxylic ester<sup>16</sup> to benzene, particularly the latter, provide close formal analogy for the benzyne-benzene reaction.

The decomposition of the diazonium carboxylate in the presence of a high concentration of naphthalene afforded a 7% yield of dibenzobicyclo[2.2.2]octatriene.

(11) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

(12) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

(13) G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

(14) W. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

(15) H. J. F. Angus and D. Bryce-Smith, *J. Chem. Soc.*, 4791 (1960).

(16) E. Grovenstein, Jr., and D. V. Rao, *Tetrahedron Letters*, No. 4, 148 (1961).

Although one cannot rule out the presence of isomeric hydrocarbons, in view of the difficulty in separating the product from unreacted naphthalene it appears that 1,4-addition to naphthalene predominated.

### Experimental

**Decomposition of Benzenediazonium-2-carboxylate (I) in Benzene.**—Three hundred milligrams (2.03 mmoles) of benzenediazonium-2-carboxylate<sup>3</sup> was stirred in 60 ml. of dry benzene for 34 hr. at 45°. During this period 0.052 g. (58%) of carbon dioxide was evolved and the mixture became homogeneous and dark reddish brown. The solution was washed with four 15-ml. portions of 5% sodium bicarbonate, then with water, and dried over magnesium sulfate. After removal of most of the benzene at reduced pressure the residue was analyzed by gas chromatography, utilizing an F. and M. model 500 instrument, equipped with a 15-ft. column of 20% Silicone gum rubber on Chromosorb, with temperature programmed from 150° at 2.9°/min. In the temperature range 200–230° three substances were eluted, showing well resolved peaks, the integrated intensities of which were in the ratio 1:4:3. Another smaller peak (not identified) was eluted near 300°, but no more than traces of other substances could be detected. By adding weighed quantities of naphthalene to the crude reaction mixture, the yields of the three major components (which proved to be isomers of  $C_{12}H_{10}$ ) could be determined to be approximately 2, 8 and 6%,<sup>17</sup> based upon the weight of diazonium carboxylate.

Before attempting isolation of the three products, the reaction was carried out repeatedly until, after removal of polymeric materials on an alumina column, 0.694 g. of crude hydrocarbon was accumulated. This oil was stirred with 3 ml. of a 10% solution of silver nitrate in 50% aqueous alcohol, the mixture was cooled in ice, and the white crystalline precipitate (0.217 g.) was collected and dried *in vacuo*. Recrystallization from absolute alcohol afforded 0.2 g. of white needles, m.p. 168° dec. (reported<sup>6</sup> for silver nitrate complex of benzocyclooctatetraene, m.p. 167.0–167.5° dec.). The silver nitrate complex was decomposed with 4 ml. of concentrated aqueous ammonia, and the hydrocarbon product was extracted into ether. Evaporation of the dried ether solution left 0.063 g. of benzocyclooctatetraene, m.p. 46.5–48.5° (Köfler). Sublimation raised the melting point to 49.0–49.5° (reported<sup>6</sup> m.p. 50–51°). The infrared spectrum of the hydrocarbon agreed with that reported previously<sup>6</sup>; ultraviolet absorption:  $\lambda_{max}$  232.5  $\mu$  ( $\epsilon$  23,300) and  $\lambda$  (shoulder) 275  $\mu$  ( $\epsilon$  1030). The retention time of this compound in the gas chromatographic procedure identified it as the second of the three peaks.

The hydrocarbon mixture remaining after silver nitrate treatment still contained appreciable quantities of benzocyclooctatetraene as well as the other two components, as revealed by gas chromatography. Microdistillation (Kugelrohr) separated the material into two fractions, the second of which crystallized, m.p. 70.1–70.6°, and proved identical with authentic biphenyl.

For isolation of the third component, a portion of the crude hydrocarbon mixture was chromatographed on Florisil. Elution with petroleum ether (30–60°) afforded early fractions which were relatively rich in the third component. Gas chromatography, using the conditions described above, afforded colorless needles, 0.020 g., collected in the temperature range 205–210°. After sublimation at 45° (0.2 mm.) the hydrocarbon melted at 65.0–65.5° (Köfler).

(17) The yields of biphenyl (6%) and benzocyclooctatetraene (8%) are fairly accurate since standard mixtures of these compounds with naphthalene were analyzed to establish the relationship between mole ratio and relative signal intensity. The yield of benzobicyclo[2.2.2]octatriene was estimated from signal intensity only.

*Anal.* Calcd. for  $C_{12}H_{10}$ : C, 93.46; H, 6.54. Found<sup>18</sup>: C, 93.65; H, 6.48.

The mass spectrum of the compound (major peaks at  $m/e = 154, 153, 152, 128, 76, 63, 51, 39, 28$ ) indicated a molecular weight of 154. The infrared spectrum ( $CS_2$  solution) contained bands at 655(s), 690(s), 747(s), 789(s), 1330(m), 1612(w), 2990(w), 3028(w) and 3070(w)  $cm^{-1}$ , as well as several weak bands in the 850–1250  $cm^{-1}$  region. The ultraviolet spectrum is summarized in Table I, and the n.m.r. spectrum is shown in Fig. 1. The hydrocarbon is assigned the structure, benzobicyclo[2.2.2]octatriene.

**Pyrolysis of Benzobicyclo[2.2.2]octatriene.**—The hydrocarbon (1.5 mg.) was sealed under vacuum in a Pyrex tube and heated at 310° for 1.5 hr. Upon cooling to room temperature the liquid product crystallized to a solid mass of naphthalene, m.p. and mixed m.p. 78–79°, identity confirmed by the ultraviolet spectrum.

**Decomposition of Benzenediazonium-2-carboxylate in the Presence of Naphthalene.**—Sufficient anhydrous ether was added

(18) Spang Microanalytical Laboratory, Ann Arbor, Mich.

to 10 g. of naphthalene to dissolve it at the reflux temperature. In this solution 0.35 g. (2.4 mmoles) of the diazonium carboxylate I was stirred for 63 hr. at reflux. The ether was removed under reduced pressure and the product was chromatographed on 350 g. of ordinary alumina, using petroleum ether (30–60°)–benzene mixtures as eluent. After the elution of naphthalene there was obtained, in the 2:1 petroleum ether–benzene eluates, a series of colorless crystalline fractions. Combination of this material and sublimation at 98° (0.6 mm.) provided 0.034 g. (7%) of dibenzobicyclo[2.2.2]octatriene, m.p. 119.5–120.5° (reported 118.5–119°, 119–120°<sup>20</sup>) identical by mixed m.p. and infrared spectrum with an authentic sample.<sup>20</sup>

**Acknowledgment.**—We are grateful to Dr. A. A. Bothner-By for advice and assistance in calculating the n.m.r. spectrum.

(19) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).

(20) W. R. Vaughan and A. C. Schoenthaler, *ibid.*, **80**, 1956 (1958). We are grateful to Dr. Vaughan for a comparison sample of this compound.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

## Dicarbonium Ions of the Triarylmethyl Type. Ions from *o*-, *m*- and *p*-Xylylene Glycols<sup>1</sup>

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Tetraphenyl-*p*-xylylene glycol and tetraphenylphthalan have *i*-factors in sulfuric acid of 7 and 5, respectively, indicating that each ionizes to the corresponding dicarbonium ion in that solvent. From the spectra of tetraphenyl-*o*-, *m*- and *p*-xylylene glycols in varying concentrations of aqueous sulfuric acid, values of  $pK_{R^+}$  (glycol to monocarbonium ion) for the latter two and  $pK_{R^{++}}$  (mono- to dicarbonium ion) for all three were determined. Values of  $pK_{R^+}$  for the *m*- and *p*-glycols were -7.9 and -8.1;  $pK_{R^{++}}$  for the *o*-, *m*- and *p*-isomers were -16.4, -9.9 and -10.5, respectively. The monocation from the *o*-glycol is undoubtedly in the colorless, cyclic oxonium ion form; this accounts in great measure for the 10<sup>6</sup> difference in difficulty of formation of the *o*-*vis-à-vis* the *m*- and *p*-dicarbonium ions. The electronic spectra of the three dicarbonium ions are compared. Hydrolysis or methanolysis of the *m*- or *p*-dications gave the glycols or their dimethyl ethers. Hydrolysis of the *o*-dication gave tetraphenylphthalan as expected, but methanolysis gave 9-methoxy-9,10,10-triphenyl-9,10-dihydroanthracene *via* rapid intramolecular alkylation. Tetra-*p*-anisyl-*p*-xylylene glycol is completely ionized to dicarbonium ion in about 0.2–0.4% sulfuric acid–acetic acid.

### Introduction

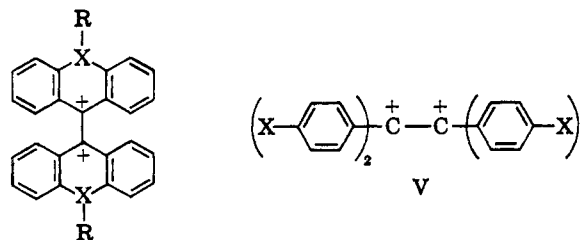
Evidence for several structurally different types of stable multicharged carbonium ions now exists. The ionization of certain benzotrihalides proceeds with the loss of two halide ions from a single carbon, giving ions of type I.<sup>2–4</sup> The cyclobutene dication II,<sup>2a,5</sup> which



may be considered as the homolog of the cyclopropenium cation,<sup>6</sup> was produced by loss of two halide ions from adjacent carbon atoms.

Multicharged carbonium ions with more classical structures have also been described, but in most examples one has the option of representing the ion with charges on carbon or on some more electronegative element, usually nitrogen, oxygen or sulfur. Bis-xanthylum (III)<sup>7–11</sup> and acridinium (IV)<sup>12</sup> salts and

certain of their non-benzo analogs<sup>13,14</sup> are known, although their chemistry has been investigated only briefly. Substituted tetraarylethylene dications (V, X = OCH<sub>3</sub>,<sup>15–18</sup> N(CH<sub>3</sub>)<sub>2</sub><sup>15,16,19</sup>) are known but the



III, X = O or S, R = electron pair

IV, X = N, R = alkyl

parent dication (V, X = H) has not yet been prepared.<sup>20</sup> Finally, one must mention the many triaryl-

(1) We are indebted to the National Science Foundation, Grant 14289 (T. S.), and the Petroleum Research Fund of the American Chemical Society, Grant 488C (R. R. R.), for financial support.

(2) (a) H. Hart and R. W. Fish, *J. Am. Chem. Soc.*, **82**, 5419 (1960); (b) **83**, 4460 (1961).

(3) H. Hart and J. S. Fleming, *Tetrahedron Letters*, 983 (1962).

(4) Similar ions may be produced by addition of two protons to arylacetylenes, but the evidence is not yet as firm as with 1, where crystalline salts have been isolated<sup>2</sup>; see M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 600 (1962).

(5) H. H. Freedman and A. M. Frantz, Jr., *J. Am. Chem. Soc.*, **84**, 4165 (1962).

(6) See R. Breslow, H. Höver and H. W. Chang, *ibid.*, **84**, 3168 (1962), and earlier references cited there.

(7) A. Werner, *Chem. Ber.*, **34**, 3300 (1901).

(8) A. Werner *Ann.*, **322**, 296 (1902).

(9) A. Schönberg and S. Nickel, *Chem. Ber.*, **67**, 1795 (1934).

(10) A. Schönberg and W. Asker, *J. Chem. Soc.*, 272 (1942).

(11) R. Wizinger and Y. Al-Atter, *Helv. Chim. Acta*, **30**, 189 (1947).

(12) R. M. Acheson, "Acridines," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 280–285.

(13) F. Arndt, P. Nachtweg and E. Scholz, *Chem. Ber.*, **57**, 1903 (1924).

(14) F. Arndt and C. Lorenz, *ibid.*, **63**, 3121 (1930).

(15) R. Wizinger and J. Fontaine, *ibid.*, **60B**, 1377 (1927).

(16) R. E. Buckles and N. A. Meinhardt, *J. Am. Chem. Soc.*, **74**, 1171 (1952).

(17) R. E. Buckles and W. D. Womer, *ibid.*, **80**, 5055 (1958).

(18) R. E. Buckles, R. E. Erickson, J. D. Snyder and W. B. Person, *ibid.*, **82**, 2444 (1960).

(19) D. H. Anderson, R. M. Eloffson, H. S. Gutowsky, S. Levine and R. B. Sandin, *ibid.*, **83**, 3157 (1961).

(20) Tetraphenylethylene dichloride, with silver tetrafluoroborate in liquid sulfur dioxide, gave purple solutions from which the predominant product (about 47%) was 9,10-diphenylphenanthrene: H. Hart and H. Tanida, unpublished results.