

where  $\rho$  is the transition dipole moment and  $d_{ij}$  is the effective distance between the electric point dipoles of adjacent ligand molecules in the complex. The mixing coefficients for case c are given by

$$C_A^- = C_B^+ = \frac{\Delta E_1 - \Delta E_2 - K}{2 \left\{ V_{12}^2 + \left( \frac{\Delta E_1 + \Delta E_2 - K}{2} \right)^2 \right\}^{1/2}}$$

$$C_B^- = -C_A^+ = \frac{V_{12}}{\left\{ V_{12}^2 + \left( \frac{\Delta E_1 + \Delta E_2 - K}{2} \right)^2 \right\}^{1/2}}$$

where  $K = \{(-\Delta E_1 - \Delta E_2)^2 + 4V_{12}^2 - 4\Delta E_1\Delta E_2\}^{1/2}$ . Similarly the mixing coefficients for case d are

$$C_1^+ = -C_2^- =$$

$$\frac{-\sqrt{2}V_{13}}{\left\{ 2V_{13}^2 + \left( \frac{\Delta E_1 + V_{12} - \Delta E_3 - L}{2} \right)^2 \right\}^{1/2}}$$

$$C_2^+ = C_1^- =$$

$$\frac{\Delta E_1 + V_{12} - \Delta E_3 - L}{2 \left\{ 2V_{13}^2 + \left( \frac{\Delta E_1 + V_{12} - \Delta E_3 - L}{2} \right)^2 \right\}^{1/2}}$$

where  $L = \{(-\Delta E_1 - \Delta E_3 - V_{12})^2 - 4(\Delta E_1\Delta E_3V_{12} - 2V_{13}^2)\}^{1/2}$ . In these expressions  $\Delta E_n$  refers to the transition energy of the  $n$ th ligand.

## Reactions of Aromatic Compounds at High Temperatures

ELLIS K. FIELDS

*Research and Development Department, Amoco Chemicals Corporation, Whiting, Indiana 46394*

SEYMOUR MEYERSON

*Research and Development Department, American Oil Company, Whiting, Indiana 46394*

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The behavior of aromatic compounds at high temperatures has intrigued chemists for many decades. In the early days of chemistry, as recorded in the first edition of Beilstein,<sup>1</sup> reagents were routinely passed through glowing porcelain or iron tubes and attempts were made to identify the products.

In 1929 Hurd<sup>2</sup> gathered in one volume the pyrolytic reactions of organic molecules. No researcher since has tried to write a comprehensive treatise similar to Hurd's; it would be a formidable task indeed. The reactions at high temperatures of a simple molecule such as toluene would appear predictable, involving scission of only C-H and C-C bonds. Yet in 1960 Badger and Spotswood<sup>3</sup> identified 23 products from toluene at 700°, and an additional 16 unidentified species were detected. Introduction of the heteroatoms O, S, and N vastly increases the complexity of thermal behavior.

A guide to introduce order and predictability into this complexity was obviously most desirable and necessary. A potential guide was found when we observed some striking parallels in the behavior of several compounds on pyrolysis and under electron impact in the mass spectrometer.<sup>4-6</sup> Such parallels had been re-

ported earlier in a few scattered instances, for example, the similarity of the thermal retro-Diels-Alder reaction to that in the mass spectrometer.<sup>7-11</sup> However, the mechanistic implications and synthetic utility for organic chemists of relating thermal and mass spectral fragmentations were not widely realized until very recently.

Mass spectral fragmentation patterns have proven extremely useful to us, not only in explaining the course of some thermal reactions, but also in guiding our experimentation along new lines. Thus, for example, the partial mass spectrum of phthalic anhydride<sup>14</sup> and tentative structures of the ions in the main reaction sequence are as given in Table I. The large amount of  $C_6H_3^+$  formed, most simply formulated as benzyne although the structure is not established, prompted us to try to duplicate this reaction thermally.

(7) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Amer. Chem. Soc.*, **83**, 1401 (1961).

(8) K. Biemann, *Angew. Chem.*, **74**, 102 (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 98 (1962).

(9) H. Audier, M. Fetizon, and W. Vetter, *Bull. Soc. Chim. France*, 1971 (1963).

(10) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(11) R. C. Dougherty [*J. Amer. Chem. Soc.*, **90**, 5780 (1968)] has tried to define the relationships of mass spectral with pyrolytic and photolytic reactions by a perturbation molecular orbital interpretation.<sup>12</sup> Close parallels between mass spectral and pyrolytic decompositions have been rationalized by Brown, *et al.*, as reflecting parallelism of bond energies and vibrational modes in vibrationally excited neutral molecules and their ionized counterparts.<sup>13</sup>

(12) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(13) R. F. C. Brown, G. E. Gream, D. E. Peters, and R. K. Solly, *Australian J. Chem.*, **21**, 2223 (1968).

(14) F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959); S. Meyerson, *Record Chem. Progr.*, **26**, 257 (1965).

(1) "Beilstein's Handbuch der Organische Chemie," Vol. 5, Julius Springer, Berlin, 1922, *e.g.*, pp 185, 200, 284, 535.

(2) C. D. Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalogue Co., New York, N. Y., 1929.

(3) G. M. Badger and T. M. Spotswood, *J. Chem. Soc.*, 4420 (1960).

(4) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965).

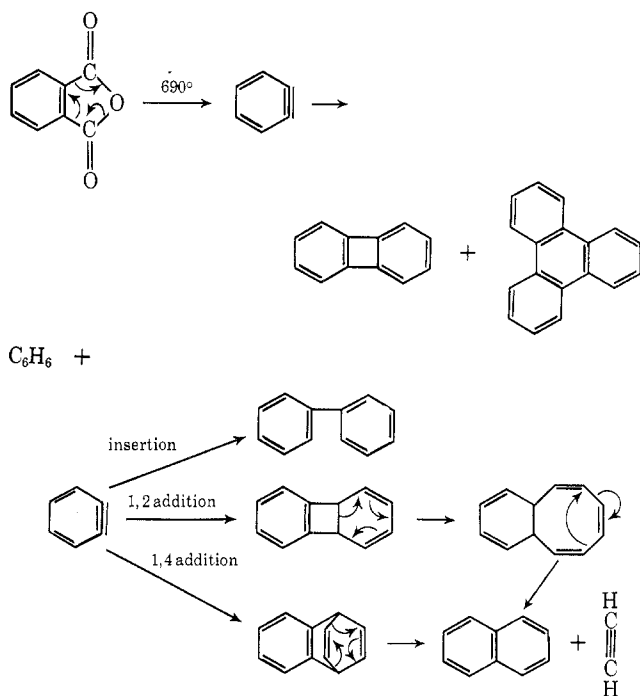
(5) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966).

(6) S. Meyerson and E. K. Fields, *Chem. Commun.*, 275 (1966).

Mass	Relative intensity	Tentative structure
148	47	Parent ion
$-\text{CO}_2$		
104	100	
$-\text{CO}$		
76	85	
$-\text{C}_2\text{H}_2$		
50	40	$[\text{HC}\equiv\text{CC}\equiv\text{CH}]^+$

Accordingly, we pyrolyzed a solution of phthalic anhydride in benzene at  $690^\circ$  under nitrogen. Acetylene was steadily evolved along with carbon dioxide and carbon monoxide in a 1:1 ratio; the pyrolysate, apart from excess benzene and unconverted phthalic anhydride, was essentially a mixture of naphthalene (15%) and biphenyl (85%). Benzene, pyrolyzed under identical conditions, gave no acetylene and only one-tenth as much high-boiling product, which consisted of about 96% biphenyl and 4% terphenyl. Only a trace of naphthalene (about 0.2%) was found.

In addition to naphthalene and biphenyl, about 1% each of biphenylene and triphenylene formed. These products indicated that phthalic anhydride gave benzyne on pyrolysis, and the benzyne subsequently reacted with benzene.<sup>15</sup>



Products clearly derived by way of benzyne as an intermediate were obtained from the reactions of phthalic

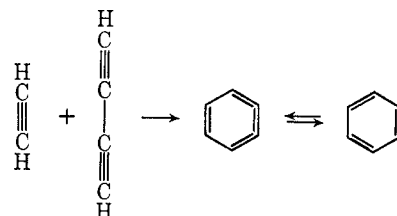
(15) Following our discovery of benzyne and biphenylene formation in the pyrolysis of phthalic anhydride,<sup>4</sup> two separate groups announced isolation of substituted biphenylenes from pyrolysis of substituted phthalic anhydrides: R. F. C. Brown, W. D. Crow, and R. K. Solly *Chem. Ind.* (London), 343 (1966); M. P. Cava, M. S. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).

anhydride at  $700^\circ$  with benzene- $d_6$ , halogenated benzenes, naphthalene, biphenyl, thiophene, benzothio-  
phene, pyridine, quinoline and isoquinoline, and the corresponding deuterated aromatic and heterocyclic compounds.<sup>16,17</sup>

Other aromatic and heterocyclic anhydrides also exhibited parallel behavior under electron impact and upon pyrolysis. Among these are the compounds listed in Table II.<sup>16</sup>

Anhydride	Aryne intermediate
Trimellitic	Carboxybenzyne
Naphthalene-2,3-dicarboxylic	2,3-Naphthalene
1,8-Naphthalic	peri-Naphthalene
Pyromellitic	Benzadiyne
Mellophanic	Benzadiyne
Naphthalene-1,4,5,8-tetracarboxylic	Naphthaladiyne
Tetraphenylphthalic	Tetraphenylbenzyne
Quinolinic	2,3-Pyridyne

Benzyne is formed not only from aromatic compounds but also, apparently, from acetylene. Phthalic anhydride and acetylene gave similar products, some in about the same concentrations, with benzene,<sup>18</sup> hexafluorobenzene,<sup>18</sup> and pyridine<sup>17</sup> at  $700^\circ$ . Benzyne may result by cycloaddition, concerted or stepwise, of acetylene to diacetylene, a known pyrolysis product of acetylene.<sup>19,20</sup>



This evidence that benzyne is at least one of the intermediates in acetylene pyrolysis suggests the possible involvement of acetylene in the formation of polycyclic aromatic hydrocarbons in high-temperature reactions of tobacco, petroleum products, and other organic materials.

Benzyne is also formed in good yield by pyrolysis of *o*-sulfobenzoic anhydride,<sup>5</sup> and to some extent in the pyrolysis of chlorobenzene and bromobenzene.<sup>17,21</sup> This elimination of groups such as  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ , and  $\text{HX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) also parallels similar fragmentations under electron impact and emphasizes the utility of this guide. These eliminations prompted us to study also the pyrolysis of nitrobenzene. Although nitrobenzene was well characterized 135 years ago<sup>22</sup> and has

(16) E. K. Fields and S. Meyerson, *Advan. Phys. Org. Chem.*, **6**, 1 (1968).

(17) E. K. Fields and S. Meyerson, in press.

(18) E. K. Fields and S. Meyerson, *Tetrahedron Letters*, 571 (1967).

(19) E. F. Greene, R. L. Taylor, and W. L. Patterson, *J. Phys. Chem.*, **62**, 238 (1958).

(20) H. R. Linden and J. M. Reid, *Chem. Eng. Progr.*, **55** (3), 71 (1959); C. F. Aten and E. F. Greene, *Combustion Flame*, **5**, 55 (1961).

(21) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 3388 (1966).

(22) E. A. Mitscherlich, *Ann. Physik*, **31**, 625 (1834).

been the subject of many liquid-phase reactions as well as a bountiful source of useful chemicals, its behavior at high temperatures in the gas phase has hitherto been almost unknown.

### Pyrolysis of Nitrobenzene

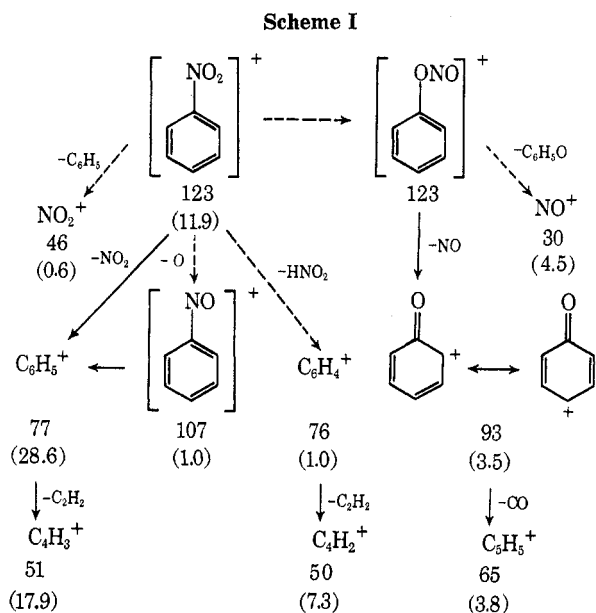
After 20 sec at 600°, nitrobenzene was completely decomposed and gave a 30 wt % yield of the products shown in Table III. To help explain the formation of

**Table III**  
Products from Nitrobenzene

Product	Relative concentration <sup>a</sup>	Product	Relative concentration <sup>a</sup>
Benzene	5.0	Phenyl ether	0.7
Aniline	1.4	Aminobiphenyl	0.7
Phenol	27.2	Hydroxybiphenyl	3.7
Naphthalene	0.2	Nitrobiphenyl	2.5
Quinoline	2.2	<i>o</i> -Terphenyl	1.6
Biphenyl	20.1	<i>m</i> -Terphenyl	3.0
Carbazole	0.5	<i>p</i> -Terphenyl	3.9
Dibenzofuran	15.1	Quaterphenyl	1.6

<sup>a</sup> Determined by gas chromatography.

these products, we also reexamined the decomposition under electron impact in the mass spectrometer.<sup>23a</sup> The major paths in the mass spectrum of nitrobenzene are shown in Scheme I (solid arrows denote reaction

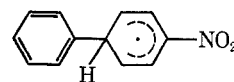


steps supported by metastable peaks; the relative intensities of the different species, expressed as fractions of the total ion yield of mass 29 and higher, are shown in parentheses). The major single process thus is loss of NO<sub>2</sub>, directly and to some extent by a two-step sequence, to give C<sub>6</sub>H<sub>5</sub><sup>+</sup>, accompanied by the complementary loss of C<sub>6</sub>H<sub>5</sub> to give NO<sub>2</sub>. The C<sub>6</sub>H<sub>5</sub><sup>+</sup> ion splits out acetylene and goes to C<sub>4</sub>H<sub>3</sub><sup>+</sup>. A significant fraction of the nitrobenzene parent ions forms phenoxy ion by loss of NO or NO<sup>+</sup> by loss of a phenoxy radical, presumably through an intermediate nitro-nitrite arrangement;<sup>23</sup>

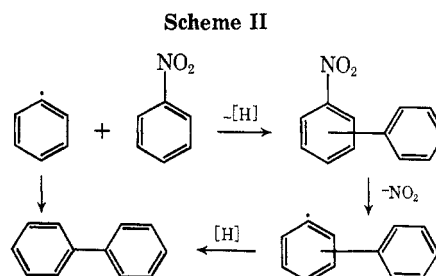
(23) (a) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964); (b) S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966).

summing the intensities for C<sub>6</sub>H<sub>5</sub>O<sup>+</sup>, C<sub>5</sub>H<sub>5</sub><sup>+</sup>, C<sub>3</sub>H<sub>3</sub><sup>+</sup> (which most likely arises chiefly by loss of acetylene from C<sub>5</sub>H<sub>5</sub><sup>+</sup><sup>7,24</sup>), and NO<sup>+</sup> leads to an estimate of 14.8% for the fraction of nitrobenzene ions that react by this pair of complementary paths.

The thermolysis products can be rationalized in similar fashion. Phenyl radical, formed by breaking of the phenyl-nitro bond, can give benzene by abstraction of hydrogen from another molecule of nitrobenzene. This abstraction is probably from an adduct such as

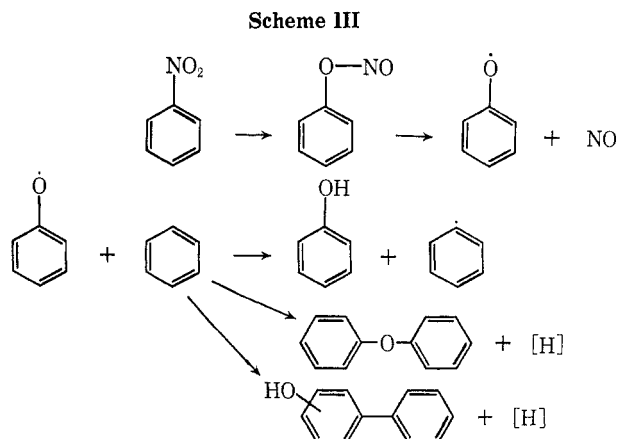


rather than from nitrobenzene directly. In Scheme II and subsequently in this paper, the symbol [H] is used to represent a hydrogen atom gained or lost from a cyclohexadienyl radical formed by prior addition of an aryl or aryloxy radical to an aromatic system.



Hydrogen abstraction by the phenyl radical is, however, only a minor reaction. Phenyl prefers to dimerize to biphenyl or to add to the aromatic system, as in solution chemistry,<sup>25</sup> to give nitrobiphenyls (Scheme II). At 600° little nitrobiphenyl survives; it decomposes to give biphenyl by hydrogen abstraction probably as described above, quaterphenyl by dimerization, and hydrobiphenyl by rearrangement; it also alkylates nitrobenzene and nitrobiphenyl.

Phenol—and probably some of the hydroxybiphenyl—arises by a nitro-nitrite rearrangement paralleling the process under electron impact (Scheme III).



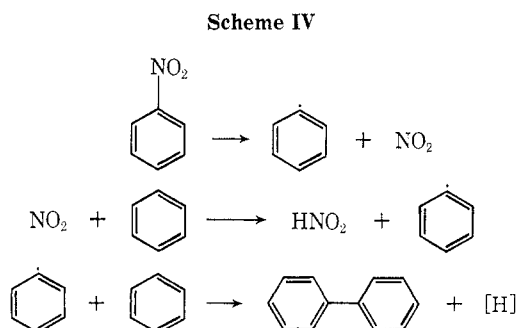
(24) S. Meyerson, *ibid.*, **85**, 3340 (1963).

(25) D. H. Hey, A. Nechvatal, and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951); T. Inukai, K. Kobayashi, and O. Simamura, *Bull. Chem. Soc. Japan*, **35**, 1576 (1962).

Dibenzofuran forms from phenyl ether, *o*-hydroxybiphenyl, or both, by intramolecular loss of hydrogen. It does not come directly from phenol itself, because phenol alone under identical conditions is converted in only 0.5% yield to a mixture of phenyl ether, hydroxybiphenyls, and dibenzofuran.

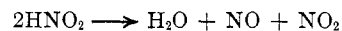
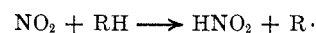
### Reaction of Nitrobenzene with Benzene

The  $C_6H_5$  ion or radical is therefore the major primary decomposition product from nitrobenzene both under electron impact and in thermolysis. This conclusion led us to investigate reactions of nitrobenzene with other aromatic compounds at 600°. Benzene alone under these conditions, 600° and 9-sec contact time, was almost all recovered; it gave only 0.01 wt % of biphenyl. Nitrobenzene with benzene gave the products shown in Table IV. Phenol is a minor product, suggesting that the decomposition of nitrobenzene to phenyl radical and nitrogen dioxide is unimolecular, but that the nitro-nitrite rearrangement may be of higher order. The yields of products are considerably different for the reactions at the two different concentration ratios, and thus give a clue to the mechanism of biphenyl formation. The increasing proportion of biphenyl with decreasing concentration of nitrobenzene (yields based on moles of nitrobenzene) implies that most of the biphenyl arises by reaction with benzene rather than by dimerization of the phenyl radical from nitrobenzene decomposition. At a nitrobenzene:benzene mole ratio of 1:5, the yield of biphenyl and terphenyl combined, as measured by gas chromatography, was 85 mole % based on 1 mole of phenyl radical produced per mole of nitrobenzene decomposed. At a mole ratio of 1:25 the yield on the same basis jumped to 170%. Both the phenyl radical and the nitrogen dioxide from the nitrobenzene may have been involved. The probable sequence of reactions is given in Scheme IV.



The gases from the reaction of nitrobenzene with benzene consisted almost entirely of NO, with small amounts of CO,  $N_2O$ ,  $N_2$ , and  $H_2$ . The  $NO_2$  fragment of the nitrobenzene molecule apparently ends up chiefly as nitric oxide, either by direct reduction or *via* a series of free-radical hydrogen abstractions and decompositions<sup>26</sup>

(26) For the structure of nitrous acid in the gas phase and its dissociation products, see A. P. Cox and R. L. Kuczowski, *J. Amer. Chem. Soc.*, **88**, 5071 (1966), and references cited therein.



### Reaction of Nitrobenzene with Benzene- $d_6$

In order to understand more clearly the interaction of nitrobenzene fragments, nitrobenzene was decomposed at 600° in benzene- $d_6$  and the isotopic distribution of the products was determined, as shown in Table

**Table IV**  
Reaction of Nitrobenzene with Benzene<sup>a</sup>

Product	Relative concentration <sup>b</sup> at nitrobenzene:benzene <sup>c</sup>	
	1:5	1:25
Phenol	1.8	1
Naphthalene	0.3	
Biphenyl	100.0	100
Dibenzofuran	11.5	1
Phenyl ether, hydroxybiphenyl	3.4	3
Terphenyl	44.4	23
Phenyldibenzofuran	7.3	
Phenyl diphenyl ether	1.0	
Quaterphenyl	8.2	2
Diphenyldibenzofuran	1.8	
Biphenyl ether	0.3	
Quinquephenyl	0.9	
Triphenyldibenzofuran	0.3	

<sup>a</sup> At 600°, contact time 9 sec, total pressure 1 atm, as were all pyrolyses described in this article. <sup>b</sup> Relative intensity of the parent peaks of components in the low-voltage (7.5 V, uncorrected) mass spectra normalized to biphenyl = 100. <sup>c</sup> Mole ratio.

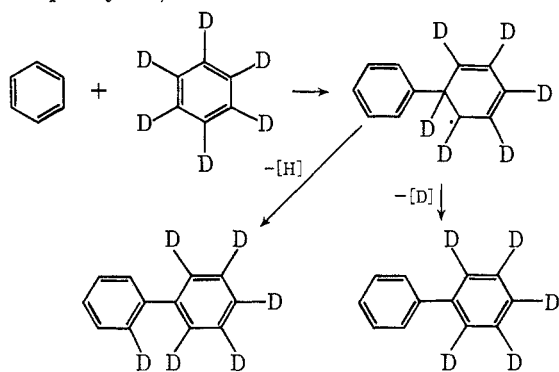
**Table V**  
Reaction of Nitrobenzene with Benzene- $d_6$ <sup>a</sup>

Product	Isotopic distribution, <sup>b</sup> %	Total concentration <sup>c</sup>
	Benzene	
Phenol	0.9 $d_0$	4.4
	2.4 $d_1$	
	1.7 $d_2$	
	0.8 $d_3$	
	2.2 $d_4$	
	17.3 $d_5$	
	74.7 $d_6$	
	29.1 $d_0$	
	19.8 $d_1$	
	9.9 $d_2$	
10.6 $d_3$	20.6	
11.2 $d_4$		
5.2 $d_5$		
0.8 $d_6$		
0.7 $d_0$		
1.3 $d_1$		
1.6 $d_2$		
1.6 $d_3$		
4.4 $d_4$		
18.2 $d_5$		
16.4 $d_6$		
8.5 $d_7$		
5.8 $d_8$		
14.4 $d_9$		
	27.1 $d_{10}$	

<sup>a</sup> At 600°; contact time, 9.3 sec; mole ratio nitrobenzene:benzene = 1:5; isotopic composition of benzene: 0.2%  $d_4$ , 5.7%  $d_5$ , 94.1%  $d_6$ . <sup>b</sup> Derived from low-voltage mass spectrum. <sup>c</sup> Summed relative intensity for each chemical species in the low-voltage spectrum, normalized to benzene = 100.0.

V. Despite some inevitable scrambling of protium and deuterium,<sup>27,28</sup> the results are revealing.

Biphenyl consisted mainly of four species:  $d_5$ ,  $d_6$ ,  $d_8$ , and  $d_{10}$ . Only 0.7% was unlabeled; this measures roughly the extent of dimerization of the phenyl radical derived from nitrobenzene. Almost 40 times as much was biphenyl- $d_{10}$ , formed presumably by abstraction of a deuterium atom from the benzene- $d_6$  by either fragment of the decomposed nitrobenzene, followed by dimerization of the phenyl- $d_5$  radical or arylation of benzene- $d_6$  by phenyl- $d_5$  radical. The appreciable amount of biphenyl- $d_8$  probably forms in part, at least, by arylation of benzene- $d_6$  by unlabeled phenyl radical. Arylation of benzene- $d_6$  by unlabeled phenyl radical should give biphenyl- $d_5$ ; the formation of almost as much bi-



phenyl- $d_6$  suggests that in the reaction the intermediate phenylcyclohexadienyl radical has a lifetime sufficiently long to exchange protium and deuterium intramolecularly before it is restored to full aromaticity. This is perhaps not too surprising, in view of the evidence for a phenylcyclohexadienyl intermediate in scrambling of protium and deuterium in the pyrolysis of benzene- $d$ .<sup>27</sup>

The isotopic composition of the phenol is unexpected. A reactive aromatic system such as phenol should exchange ring hydrogens with benzene- $d_6$  more readily than would benzene, and the formation of phenol- $d$  would be predicted to exceed by far that of the unlabeled phenol, if abstraction by the phenoxy radical occurred with equal ease from benzene- $d_6$  or nitrobenzene. However, formation of more unlabeled than monodeuterated phenol suggests that reaction of phenoxy radicals is much faster with nitrobenzene than with benzene. Relative reactivities toward aryl radicals in the gas phase, to be described in a forthcoming publication, roughly parallel those in solution, in which nitrobenzene is more reactive than benzene.

The phenol:biphenyl ratio in Table IV is 0.018; in Table V it is 0.214. Reaction conditions are essentially the same except that the data in Table V refer to reaction with benzene- $d_6$ . Thus, the isotope effects introduced by replacing unlabeled benzene with benzene- $d_6$

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

(28) To estimate the extent of scrambling to be expected, an equimolar mixture of benzene and benzene- $d_6$  (0.2%  $d_4$ , 5.7%  $d_5$ , 94.1%  $d_6$ ) was heated at 600° for 9 sec. The percentage isotopic composition of the recovered benzene was:  $d_0$ , 46.2;  $d_1$ , 4.0;  $d_2$ , 0.4;  $d_3$ , 0.1;  $d_4$ , 0.7;  $d_5$ , 6.8;  $d_6$ , 41.8. The scrambling is low enough to permit drawing mechanistic conclusions from the reaction of nitrobenzene with benzene- $d_6$ .

appear preferentially to inhibit biphenyl formation or, by default, to favor phenol.

### Reaction of Nitrobenzene with Hexafluorobenzene

To find if phenol would be formed in the presence of reagents other than benzene and generally how the reaction paths change with substituted benzenes, we allowed nitrobenzene to react with hexafluorobenzene. The products are listed in Table VI. Phenol was ab-

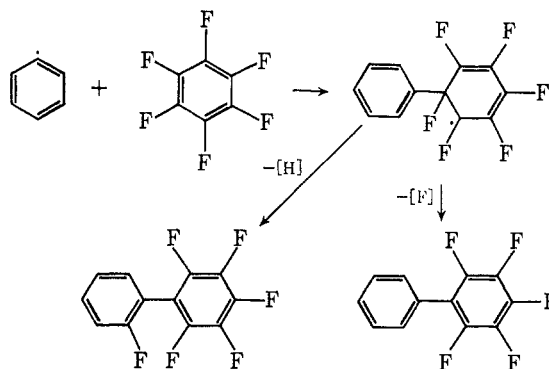
**Table VI**  
Reaction of Nitrobenzene with Hexafluorobenzene<sup>a</sup>

Product	Relative concentration <sup>b</sup>	Product	Relative concentration <sup>b</sup>
Tetrafluorobiphenyl	12	Tetrafluoroterphenyl	3
Pentafluorobiphenyl	100	Pentafluoroterphenyl	4
Hexafluorobiphenyl	92	Hexafluoroterphenyl	1
Nonafluorobiphenyl	12 <sup>c</sup>	Octafluoroterphenyl	1
Decafluorobiphenyl	52 <sup>c</sup>	Nonafluoroterphenyl	12
		Decafluoroterphenyl	60

<sup>a</sup> Temperature 600°, contact time 25 sec, 0.02 mol of nitrobenzene, 0.1 mol of hexafluorobenzene, total weight of products 6.6 g. <sup>b</sup> Relative intensity in the low-voltage mass spectrum normalized to pentafluorobiphenyl = 100. <sup>c</sup> These were the only products from 0.1 mol of hexafluorobenzene alone; total yield, about 10<sup>-5</sup> g in a 1:3 ratio of nonafluorobiphenyl:decafluorobiphenyl.

sent even at a nitrobenzene:hexafluorobenzene mole ratio of 1:1.5, far higher than that shown in the table. This suggests perhaps a "solvated" or strongly complexed nitrobenzene in the vapor phase. In other respects as well, product distributions from hexafluorobenzene give evidence for behavior markedly different from that of other fluoroaromatic compounds studied.<sup>29</sup>

Nitrobenzene with hexafluorobenzene gave four major products: pentafluorobiphenyl, hexafluorobiphenyl, decafluorobiphenyl, and decafluoroterphenyl. Pentafluorobiphenyl would be the expected arylation product; the formation of as much hexafluorobiphenyl suggests that in the reaction



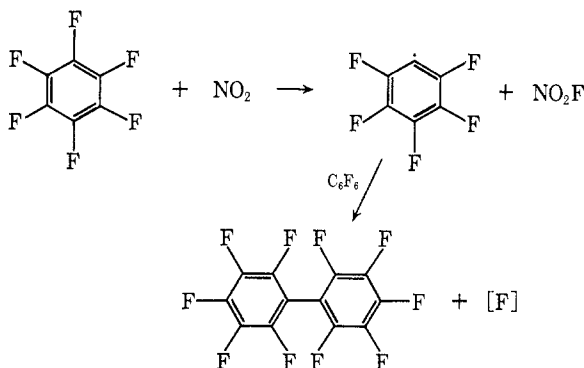
the intermediate phenylcyclohexadienyl radical has a lifetime sufficiently long to exchange hydrogen and fluorine atoms before it is restored to full aromaticity. This is the same behavior that we observed in the reaction of nitrobenzene with benzene- $d_6$ ,<sup>30</sup> although it is

(29) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **32**, 3114 (1967).

(30) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967).

perhaps not so surprising in the latter case, as protium and deuterium atoms are more nearly alike in bond strength and mobility than are hydrogen and fluorine atoms.

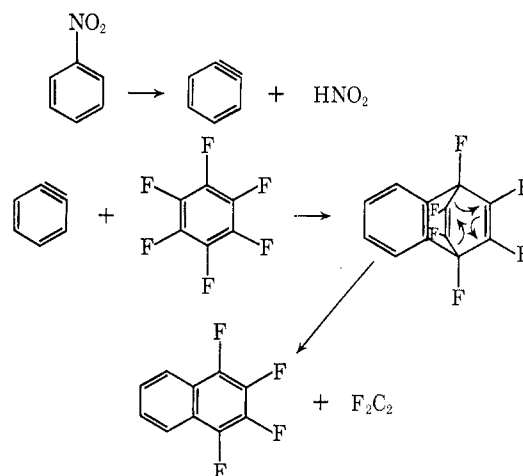
Aromaticity was restored *via* one path by plucking off a fluorine atom. This must have been accomplished either by a phenyl radical to give fluorobenzene or by  $\text{NO}_2$  to give nitryl fluoride. Fluorobenzene was indeed formed, but in quantity far too low to account for all the pentafluorobiphenyl (the fluorobenzene:pentafluorobiphenyl ratio was 1:10). The  $\text{NO}_2$  radical was apparently the principal aromatizing reagent; it may also have been responsible for abstracting a fluorine from hexafluorobenzene to give nitryl fluoride and the pentafluorophenyl radical, and subsequently decafluorobiphenyl.<sup>31,32</sup>



Two mechanisms can be suggested for the formation of decafluorobiphenyl: fluorine abstraction and arylation of hexafluorobenzene by the pentafluorophenyl radical thus formed, and a high-temperature reaction paralleling the formation of biphenyl in pyrolysis of benzene,<sup>27</sup> in which hexafluorobenzene gives perfluorophenylcyclohexadiene followed by intramolecular loss of fluorine. That it was almost all by the first reaction was demonstrated by heating hexafluorobenzene alone at 600° for 30 sec; only 0.7% as much decafluorobiphenyl was obtained as in the nitrobenzene reaction. In any case, elemental fluorine would be energetically unlikely to form, either inter- or intramolecularly.<sup>33</sup>

In the reaction of nitrobenzene with hexafluorobenzene, tetrafluoronaphthalene was produced in small amounts that were approximately proportional to the nitrobenzene concentration. The implied loss of  $\text{HNO}_2$  from nitrobenzene at high temperatures to yield benzyne parallels a minor decomposition path in the mass spectrum of nitrobenzene to give  $\text{C}_6\text{H}_4^+$  ion. Tetrafluoronaphthalene was a major product in the reaction of benzyne from phthalic anhydride at 690° with hexafluorobenzene, by 1,4 and 1,2 addition and elimination

of difluoroacetylene.<sup>34</sup> It was most likely formed in the nitrobenzene reaction in the same way.



The amount of tetrafluoronaphthalene formed in the reaction of nitrobenzene with hexafluorobenzene at a 1:1.5 mole ratio, although a minor product, was about 100 times as great as naphthalene or naphthalene derivatives formed in the decomposition of nitrobenzene alone or in its reaction with benzene at 600°; it also far exceeded the amounts formed from other fluorine derivatives. This result suggests that intramolecular loss of  $\text{HNO}_2$  to give benzyne was somehow enhanced by the presence of hexafluorobenzene.

### Conclusion

Our studies of the reactions of aromatic compounds at high temperatures have proven fruitful, leading to the discovery, among others, of (a) arylcyclohexadienes as intermediates in biaryl formation;<sup>27</sup> (b) a bimolecular complex as the intermediate in toluene pyrolysis at 1 atm and demonstration of methyl diphenylmethane and bitolyl formation along with bibenzyl in that pyrolysis;<sup>35</sup> (c) benzyne as an intermediate in the pyrolysis of acetylene to aromatic hydrocarbons;<sup>18</sup> (d) intramolecular loss of  $\text{HX}$  from substituted aromatics to give arynes; (e) intramolecular shifts of deuterium or fluorine with protium in arylcyclohexadienyl radicals; and (f) the formation of benzyne almost as universally in the pyrolysis of aromatic compounds as that of acetylene in the pyrolysis of aliphatic compounds.<sup>18,21</sup>

In addition, two general syntheses of wide scope and considerable utility have been developed: the formation of arynes from aromatic anhydrides<sup>16</sup> and the generation of aryl and heterocyclic radicals from nitro derivatives.<sup>36</sup> A tremendous number of nitro compounds are readily available, and these are being used for preparing and studying aryl radicals and their reactions in the gas phase.

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(31) Decafluorobiphenyl also results from the photolysis of hexafluorobenzene in cyclohexane: D. Bryce-Smith, B. E. Connett, A. Gilbert, and E. Kendrick, *Chem. Ind.* (London), 855 (1966).

(32) A similar attack by  $\text{NO}_2$  on pentafluorobiphenyl can account for the observed tetrafluorobiphenyl as well as for the increased yields of this species at the higher nitrobenzene concentration.

(33)  $D(\text{C}_6\text{F}_5-\text{F}) = \sim 140$  kcal/mol,  $D(\text{F}-\text{F}) = 36$  kcal/mol: T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co. (Publishers), Ltd., London, 1958, pp 275, 281.

(34) E. K. Fields and S. Meyerson, *Chem. Ind.* (London), 1230 (1966).

(35) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **33**, 2315 (1968).

(36) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 724 (1967).