ν_{max} 1040 cm^{-1}; the nmr spectrum showed a triplet at 8.92 (CH_3), a multiplet at 7.25 (CH_2), and a multiplet at 2.48 (ar H) with peak area ratio 3:2:5.

1-Ethoxy-1-phenylthio-2-propyne (26) was prepared from **1** according to the general procedure but with ethanol as solvent. During the reaction a small amount of propargyl aldehyde escaped and was trapped as its 2,4-dinitrophenylhydrazone, mp 120–121°. The product was distilled to give 72% of **26**, bp 60–62° (0.05 mm), $n^{24}D$ 1.5585; ν_{max} 1075 cm^{-1} (C—O); the nmr spectrum showed a triplet at 8.81, a quadruplet at 6.25 (OC_2H_5), and doublets of equal intensity at 7.37 ($C{\equiv}CH$) and 4.44 (CH) besides aromatic absorption.

Anal. Calcd for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.60; H, 6.20.

Trituration of the distillation residue with methanol gave a small amount of diphenyl disulfide, mp 60°, identical with an authentic sample.

Compound **26** was also prepared from **1** and sulfuryl chloride with subsequent treatment with ethanol. The yield was 51%.

1-Chloro-1-phenylthio-2-propyne (27).—A mixture of 1.5 g (10 mmoles) of sulfide **1** and 1 g of sodium bicarbonate in 30 ml of benzene was cooled in an ice bath, and 1.1 g (10 mmoles) of *t*-butyl hypochlorite was added dropwise with stirring. After 1 hr the reaction mixture was filtered and the benzene solution was distilled under reduced pressure. The liquid residue was shown by nmr to consist essentially of starting material and chloride **27** in a ratio of about 4:1; the latter showed doublets of equal intensity at 7.20 ($C{\equiv}CH$) and 4.29 (CHCl) besides aromatic absorption.

Reaction of 1-Phenylthio-2-propyne (1) with *t*-Butyl Hypochlorite in *t*-Butyl Alcohol.—A mixture of 1.5 g (10 mmoles) of sulfide **1** and 1 g of sodium bicarbonate in 30 ml of *t*-butyl alcohol and 6 ml of pentane was cooled to 0°, and 1.1 g (10 mmoles) of *t*-butyl hypochlorite was added with stirring. The reaction was worked up as usual, and the total product (1.6 g) was analyzed by nmr. The product consisted of phenyl propargyl sulfoxide and starting material **1** in a ratio of about 1:3; furthermore, a small amount of diphenyl disulfide was also present, indicating that some α-substitution product may have been formed.

1-Phenylsulfinyl-2-propyne.—A solution of 29.6 (0.2 mole) of sulfide **1** in 50 ml of methylene chloride was stirred and cooled (ice) while a solution of *m*-chloroperbenzoic acid (0.2 mole) was added dropwise over 2 hr. The product was worked up in the usual way. The crude liquid product was shown by glpc to consist essentially of one compound. Attempted distillation resulted in vigorous decomposition. The spectral properties of the crude product are in agreement with the structure for 1-phenylsulfinyl-2-propyne. Infrared data gave 3160, 2090 ($C{\equiv}CH$), and 1045 cm^{-1} (SO); the nmr spectrum showed a triplet at 7.52 ($C{\equiv}CH$), a doublet at 6.40 (CH_2, with J = 2.8 Hz), and complex aromatic absorption centered at 2.4.

Registry No.—**2**, 13864-98-7; **4**, 13864-99-8; **6**, 13865-00-4; **8**, 13865-01-5; **10**, 13865-02-6; **12**, 13865-03-7; **14**, 621-08-9; **15**, 13865-05-9; **17**, 824-86-2; **18**, 13865-06-0; **20**, 833-82-9; **21**, 13865-07-1; **23**, 1193-82-4; **25**, 4170-80-3; **26**, 13865-09-3; **27**, 13865-10-6; 1-phenylsulfinyl-2-propyne, 13865-11-7; *t*-butyl hypochlorite, 507-40-4.

Arylation by Aromatic Nitro Compounds at High Temperatures. III. Reactions of Nitrobenzene with Aromatic Fluorine Derivatives

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Nitrobenzene phenylates fluorobenzene, *p*-difluorobenzene, benzotrifluoride, and hexafluorobenzene in a flow system at 600°. Minor reactions, paralleling the behavior of nitrobenzene under electron impact in the mass spectrometer, lead to the formation of phenol and naphthalene derivatives. Hexafluorobenzene gives product distributions that differ markedly from those of the other three fluoroaromatics as well as those from benzene-d_6. In the reaction with hexafluorobenzene, the phenyl radical from benzoyl peroxide shows greater discrimination than that from nitrobenzene.

The previous paper[1] described formation of the phenyl radical by the thermal decomposition of nitrobenzene and the products from nitrobenzene, alone and in admixture with benzene and benzene-d_6. This article is concerned with the reaction of nitrobenzene with four aromatic fluorine derivatives at 600° to give fluorinated biphenyls and terphenyls, as well as products derived by rearrangement of nitrobenzene to phenyl nitrite and formation of phenoxy radicals.

Experimental Section

Arylations were run in a Vycor tube filled with Vycor beads in an electric furnace maintained at 600 ± 1° under pure dry nitrogen with contact times of 25 ± 3 sec. The vapors were condensed in a bulb at −60°, the condensate was distilled to recover unreacted material, and the residue was analyzed. Analyses were performed with a Consolidated Model 21-103c mass spectrometer with the inlet system at 250 or 325°, with a directly coupled gas chromatograph–mass spectrometer combination[2] also employing a 21–103c instrument with an electron multiplier in place of the Faraday-cup detector, and by gas chromatography on a column of polyethylene glycol sebacate on Chromosorb W. Mass spectra were measured at the conventional 70 ionizing v and at low voltage (7.5 v, uncorrected). For the low-voltage measurements, the repellers were maintained at an average potential of 3 v, the exact values being selected to give maximum sensitivity. The reagents and standards for gas chromatography were purchased from Aldrich Chemicals and used as received. Where purity was critical, the reagent was analyzed and, if necessary, purified by distillation, crystallization, and gas chromatography.

In a typical experiment, a solution of 2.044 ml (0.02 mole) of nitrobenzene in 9.6 g (0.1 mole) of fluorobenzene was passed through a Vycor tube at 600° under nitrogen flowing at 45 cc/min. Contact time was 25 sec. The vapors were condensed in a bulb at −60° and the condensate was distilled to recover 4.9 g of fluorobenzene and give 4.1 g of products, the composition of which is shown in Table I. To compare the products of arylation of hexafluorobenzene by nitrobenzene with those

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

(2) R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L. Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1135 (1964).

TABLE I

RELATIVE CONCENTRATIONS[a] OF THE PRODUCTS OF THE REACTION OF NITROBENZENE WITH AROMATIC FLUORINE DERIVATIVES[b]

Fluorobenzene

	Nitrobenzene, moles	
	0.02	0
	Total wt of products, g	
Products	4.1	0.05
Fluorobiphenyl	100	100
Difluorobiphenyl	112	244
Terphenyl	30	...
Fluoroterphenyl	95	7
Difluoroterphenyl	135	17

p-Difluorobenzene

	Nitrobenzene, moles		
	0.02	0.2	0
	Total wt of products, g		
Products	4.0	10.75	0.01
Phenol	41	385	...
Biphenyl	15	135	...
Dibenzofuran	22	175	...
Fluorobiphenyl	57	65	...
Fluorodibenzofuran	22	53	...
Difluorobiphenyl	100	100	100
Difluorodibenzofuran	15	18	...
Trifluorobiphenyl	45	12	7700
Tetrafluorobiphenyl	29	4	7000
Difluoroterphenyl	15	19	...
Trifluoroterphenyl	15	4	...
Tetrafluoroterphenyl	11	2	...
Pentafluoroterphenyl	3	12	...
Hexafluoroterphenyl	2	4	...

Benzotrifluoride

	Nitrobenzene, moles	
	0.02	0
	Total wt of products, g	
Products	4.8	0.1
Phenol	7	...
Biphenyl	25	75
Nitrobiphenyl	12	...
Trifluoromethylbiphenyl	100	100
Trifluoromethyldibenzofuran	11	...
Bistrifluoromethylbiphenyl	46	88
Terphenyl	5	10
Trifluoromethylterphenyl	21	8
Bistrifluoromethylterphenyl	21	5

Hexafluorobenzene

	Nitrobenzene, moles		
	0.02	0.067	0
	Total wt of products, g		
Products	6.6	9.56	0.005
Tetrafluorobiphenyl	12	37	...
Pentafluorobiphenyl	100	100	...
Hexafluorobiphenyl	92	37	...
Nonafluorobiphenyl	12	10	1[c]
Decafluorobiphenyl	52	27	3[c]
Tetrafluoroterphenyl	3	23	...
Pentafluoroterphenyl	4	27	...
Hexafluoroterphenyl	1	...	...
Octafluoroterphenyl	1	...	...
Nonafluoroterphenyl	12	20	...
Decafluoroterphenyl	60	27	...

[a] Relative intensities in the low-voltage (7.5 v, uncorrected) mass spectrum, normalized for each fluorine compound to the phenyl derivative = 100. These were for fluorobenzene, fluorobiphenyl; for p-difluorobenzene, difluorobiphenyl; for benzotrifluoride, trifluoromethylbiphenyl; and for hexafluorobenzene, pentafluorobiphenyl. [b] Reaction conditions: temp, 60°; contact time, 25 ± 3 sec; fluorine derivative, 0.1 mole. [c] No penta- or hexafluorobiphenyl was formed. The numbers shown are based on hexafluorobenzene = 100.

formed by benzoyl peroxide, a solution of 2.42 g (0.01 mole) of benzoyl peroxide in 11.8 ml (0.1 mole) of hexafluorobenzene was refluxed at 84° under 50-mm pressure for 24 hr. The mixture was distilled to recover 9.2 ml of hexafluorobenzene and obtain a residue of 5.4 g whose analysis is shown in Table II.

TABLE II

COMPARISON OF HEXAFLUOROBENZENE ARYLATION BY NITROBENZENE AND BENZOYL PEROXIDE

	Relative concn[a]	
	Total wt of products, g	
Products	Nitrobenzene, 6.6	Benzoyl peroxide, 5.4
Biphenyl	0	13
Terphenyl	0	3
Pentafluorobiphenyl	100	100
Hexafluorobiphenyl	92	0.4
Tetrafluoroterphenyl	3	2
Pentafluoroterphenyl	4	15

[a] Relative intensities in the low-voltage mass spectrum, normalized to pentafluorobiphenyl = 100.

Results and Discussion

Table I lists the products from the reactions of nitrobenzene with aromatic fluorine derivatives. For comparison, the total amount, as well as the relative concentrations, of products formed from the same amount of fluorine compound alone under identical conditions is shown. For p-difluorobenzene and hexafluorobenzene, the products from reaction with higher concentrations of nitrobenzene are also listed. The total amounts of products from the fluorinated aromatics alone were small, 0.1–2% of the amounts formed in the nitrobenzene reactions. In addition, the product distributions were quite different—evidence that different reactions were involved in the two series.

The proportions of phenylated fluoroaromatic/fluoroaromatic dimer/phenylated dimer for fluorobenzene differ substantially from those for the other three compounds in Table I. The relative yields listed in Table III include those products that clearly arose from arylation with loss of fluorine. Thus, for example, the respective product groupings from p-difluorobenzene were taken to be fluoro- and difluorobiphenyls, trifluoro- and tetrafluorobiphenyls, and trifluoro- and tetrafluoroterphenyls. The differing product distributions are most simply accounted for by a steric effect. The fluoroaromatic radical produced by the abstraction of a hydrogen (eq 1) can most readily add to another fluoroaromatic in the case of fluorobenzene, where more unhindered positions are available.

TABLE III

	Relative yield, %		
Fluoroaromatic	Phenylated fluoroaromatic	Fluoroaromatic dimer	Phenylated dimer
Fluorobenzene	1.0	1.12	1.35
p-Difluorobenzene	1.0	0.47	0.17
Benzotrifluoride	1.0	0.46	0.21
Hexafluorobenzene	1.0	0.31	0.36

$$RH \xrightarrow[\text{or } NO_2]{C_6H_5\cdot} R\cdot + C_6H_6 \text{ or } HNO_2 \qquad (1)$$

Phenol Formation.—Phenol formed in some reactions in varying amounts. It probably arose by a rearrangement observed previously in thermal decomposition of nitrobenzene as well as under electron impact in the mass spectrometer[1] (eq 2). No phenol formed

$$C_6H_5NO_2 \rightarrow C_6H_5ONO \rightarrow C_6H_5O\cdot + NO \qquad (2)$$

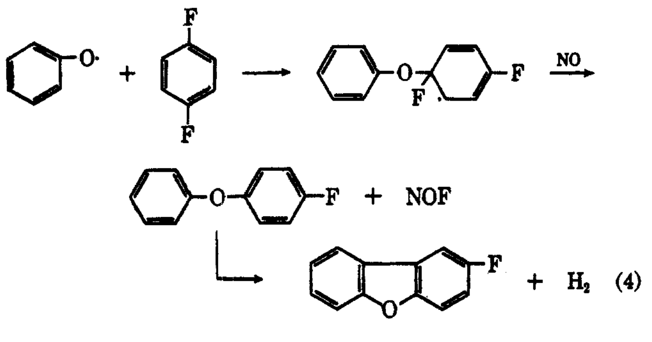
in the reaction of nitrobenzene with fluorobenzene, a little formed with benzotrifluoride, much more with *p*-difluorobenzene, and none with hexafluorobenzene. The results with fluorobenzene, benzotrifluoride, and *p*-difluorobenzene can be rationalized by assuming that, if the phenyl radical cannot add quickly to the aromatic substrate, it regenerates nitrobenzene, which then rearranges and goes to phenol, as, *e.g.*, in the presence of *p*-difluorobenzene (eq 3). However, this picture cannot account for the hexafluorobenzene results.

$$\begin{array}{l} C_6H_5NO_2 \overset{\text{fast}}{\rightleftharpoons} C_6H_5\cdot + NO_2 \\ \Big\downarrow \text{slower} \\ C_6H_5ONO \end{array} \qquad (3)$$

The absence of phenol here, even at the higher nitrobenzene/hexafluorobenzene mole ratio of 1:1.5, 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 the other fluoroaromatic compounds studied.

Dibenzofuran formed apparently by addition of the phenoxy radical to nitrobenzene (eq 4); it was found among the products of nitrobenzene alone at 600°.[1] Fluorodibenzofuran in the products from *p*-difluorobenzene probably arose by attack of the phenoxy radical at a carbon attached to a fluorine atom. Formation of difluorodibenzofuran similarly implies phenoxy radical attack at an unsubstituted position on the *p*-difluorobenzene. Dibenzofuran and derivatives evidently derived from the fluoroaromatic compounds under study were found only in the two systems that gave rise also to phenol, as would be expected if the reaction sequences leading to these products involve a common intermediate. In fact, the yields of total dibenzofurans relative to those of phenol in the two systems are very nearly equal—1.4 from *p*-difluorobenzene and 1.6 from benzotrifluoride.

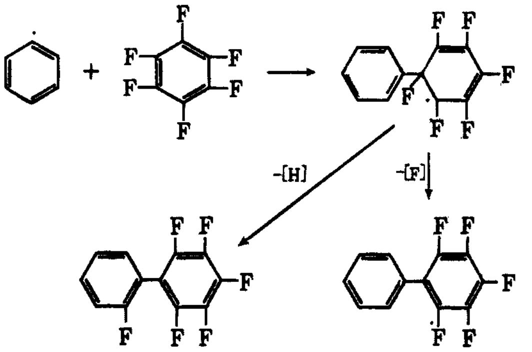
$$C_6H_5ONO \longrightarrow C_6H_5O\cdot + NO$$



(4)

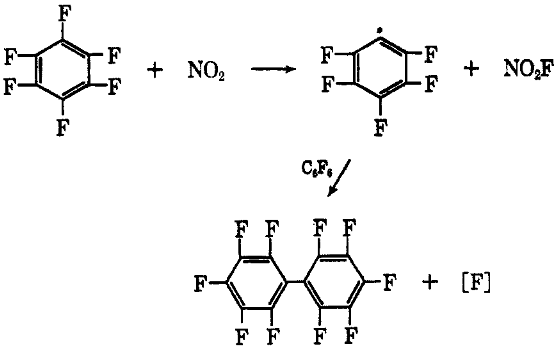
The reaction scheme for the formation of dibenzofurans shows diphenyl ethers as intermediates. These are stable species and should survive the reaction conditions to some extent. Indeed, small amounts of fluoro- and difluorodiphenyl ethers were found among the reaction products of nitrobenzene with *p*-difluorobenzene. We are presently studying the rate and extent of dehydrogenation of substituted and unsubstituted diphenyl ethers and *o*-hydroxybiphenyls to dibenzofurans at 600°.

Formation of Biphenyls and Terphenyls.—Nitrobenzene with hexafluorobenzene at a mole ratio of 1:5 gave three major products. Pentafluorobiphenyl would be the expected arylation product; the formation of as much hexafluorobiphenyl strongly suggests that in reaction 5 the intermediate phenylcyclohexadienyl radical has a lifetime sufficiently long to exchange hydrogen and fluorine atoms before it is restored to full aromaticity. This phenomenon has been observed before in the reaction of nitrobenzene with benzene-d_6,[1] although it is perhaps not so surprising in the latter case, as protium and deuterium atoms have more nearly the same bond strengths and mobility than do hydrogen and fluorine atoms.



(5)

Aromaticity was restored to I by plucking off an allylic fluorine atom. This must have been accomplished either by a phenyl radical to give fluorobenzene or by NO_2 to give nitryl fluoride. Fluorobenzene was indeed formed, but in quantity far too low to account for all the pentafluorobiphenyl. The NO_2 radical was apparently the principal aromatizing reagent; it was also probably responsible for abstracting a fluorine from hexafluorobenzene to give nitryl fluoride and the pentafluorophenyl radical, and subsequently decafluorobiphenyl[3,4] (eq 6). Two mechanisms can be suggested for the formation of decafluorobiphenyl: fluorine abstraction and arylation of hexafluorobenzene by



(6)

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[3] 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).

[4] A similar attack by NO_2 on pentafluorobiphenyl can account for the observed tetrafluorobiphenyl as well as for the increased yield of this species at the higher nitrobenzene concentration.

the pentafluorophenyl radical thus formed and a high-temperature reaction of hexafluorobenzene as through a perfluorophenylcyclohexadiene followed by intramolecular loss of fluorine, paralleling the formation of biphenyl in pyrolysis of benzene.[5] 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.[6]

Nitryl fluoride could form readily from NO_2 and hexafluorobenzene, just at it forms from N_2O_5 and sodium fluoride,[7] but would not be expected to survive. It is a strong nitrating agent, ionizing as $NO_2^+F^-$,[8] and would readily nitrate the unsubstituted rings of the fluorinated biphenyls. Hydrogen fluoride was always present in the reaction products of nitrobenzene with hexafluorobenzene, as evidenced by etching of the Vycor reaction tubes and by the presence of silicon tetrafluoride in the gaseous products.

At a nitrobenzene/hexafluorobenzene mole ratio of 1:1.5, the ratio of the "normal" arylation product to the "scrambled" increased from 1:1 to 3:1, in accord with our proposed mechanism. Increasing the concentration of radicals that can remove an allylic fluorine atom leads to faster rearomatization of the phenylcyclohexadienyl radical and thus allows less time for hydrogen–fluorine interchange.

Four fluorinated terphenyls were formed in the reaction at the higher ratio of nitrobenzene with hexafluorobenzene in the amounts shown in Table IV. If we make the grossly oversimplified assumption that the ratio of pentafluorobiphenyl to hexafluorobiphenyl measures the relative tendency of the arylation intermediate to lose a fluorine or a hydrogen atom in the rearomatization step, the relative amounts of fluorinated terphenyls formed by attack of phenyl and pentafluorophenyl radicals on the five fluorinated biphenyls in Table I would be those given in Table V.

Table IV

Terphenyl	Relative concn[a]
Tetrafluoro-	23
Pentafluoro-	27
Nonafluoro-	20
Decafluoro-	27

[a] From relative intensities in the low-voltage mass spectrum, normalized to pentafluorobiphenyl = 100.

Table V

	x in terphenyl-F_x (relative abundance, %)	
	Attacking radical	
x in biphenyl-F_x	$C_6H_5\cdot$	$C_6F_5\cdot$
4	3 (27); 4 (10)	8 (27); 9 (10)
5	4 (75); 5 (25)	9 (75); 10 (25)
6	5 (27); 6 (10)	10 (27); 11 (10)
9	8 (8); 9 (3)	. . . . . .
10	9 (21); 10 (6)	. . . . . .

The totals of the calculated relative amounts in parentheses are given in Table VI. The absence of terphenyls containing 13 and 14 fluorine atoms indicates the reluctance of pentafluorophenyl radical to add to a highly fluorinated biphenyl. Tetra- and pentafluoroterphenyls arise by reaction of fluorinated biphenyls with phenyl radical; the major portion of nona- and decafluorobiphenyls evidently comes from reaction of penta- and hexafluorobiphenyl with pentafluorophenyl radical. Calculated and observed values for terphenyls, although far from quantitative, are roughly parallel. The species predicted to be least abundant—terphenyls containing 3, 6, 8, and 11 fluorine atoms—are present in no more than trace amounts.

Table VI

	Total relative abundance, %	
	Attacking radical	
x in terphenyl-F_x	$C_6H_5\cdot$	$C_6F_5\cdot$
3	27	. . .
4	85	. . .
5	52	. . .
6	10	. . .
8	8	27
9	24	85
10	6	52
11	. . .	10

Naphthalene Formation—Varying amounts of naphthalene and naphthalene derivatives were formed in the nitrobenzene arylations. These are summarized in Table VII, which also shows naphthalenes formed from some aromatic fluorine compounds alone. In the reaction of nitrobenzene with hexafluorobenzene, tetrafluoronaphthalene was produced in appreciable amounts that were approximately proportional to the nitrobenzene concentration. The implied loss of HNO_2 from nitrobenzene at high temperatures to yield benzyne parallels a minor decomposition path in the mass spectrum of nitrobenzene to give the $C_6H_4^+$ ion.[1]

Fluorobenzene, either alone or with nitrobenzene, gave no discernible naphthalene or fluoronaphthalene at 600°. At 690° for 40 sec alone, it gave a very small amount of both products. *p*-Difluorobenzene with nitrobenzene gave naphthalene, presumably derived from nitrobenzene itself, and fluoronaphthalene. The absence of difluoronaphthalene among the reaction products from either nitrobenzene/*p*-difluorobenzene concentration ratio further illustrates the strong preference shown by benzyne to add 1,4 rather than 1,2 and to avoid adding at carbon atoms bearing a halogen substituent. This effect was originally found in the reactions of benzyne from phthalic anhydride with dichlorobenzene isomers.[9]

Benzotrifluoride gave no naphthalene or derivative at 600° for 25 sec; at 690° for 40 sec it yielded both naphthalene and trifluoromethylnaphthalene in equal amounts. This behavior differs markedly from that of toluene under similar conditions. Toluene readily lost benzylic hydrogen and gave dibenzyl and stilbene as the major products; it showed little tendency to lose methane and go to benzyne.[10] Benzotrifluoride evi-

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

(6) (a) $D(C_6F_5–F) = \sim 140$ kcal/mole and $D(F–F) = 36$ kcal/mole.[b] (b) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth and Co., Ltd., London, 1958, pp 275, 281.

(7) J. E. Ogg and J. D. Ray, *J. Chem. Phys.*, **25**, 797 (1956).

(8) G. Hetherington and P. L. Robinson, *Chem. Soc.* (London), *Spec. Publ.*, **10**, 23 (1957).

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

(10) E. K. Fields and S. Meyerson, in preparation.

TABLE VII
NAPHTHALENES FROM AROMATIC FLUORINE COMPOUNDS[a]

Fluorine compd	Nitrobenzene, moles	Naphthalene or substituted naphthalene	Relative concn[b]
Fluorobenzene	0	Naphthalene	1[c]
		Fluoronaphthalene	2[c]
	0.02	...	
p-Difluorobenzene	0	...	
	0.02	Naphthalene	2
	0.2	Naphthalene	12
		Fluoronaphthalene	4
Benzotrifluoride	0	Naphthalene	6[c]
		Trifluoromethylnaphthalene	6[c]
	0.02	Naphthalene	2
Hexafluorobenzene	0	...	
	0.02	Tetrafluoronaphthalene	8
	0.067	Tetrafluoronaphthalene	20
Benzene[d]	0.02	Naphthalene	0.3

[a] Reaction conditions are the same as given in Table I. [b] Relative intensities in the low-voltage mass spectrum normalized as in footnote a, Table I. [c] At 690° for 40 sec. [d] See ref 1.

dently lost CF_3 easily and, to a lesser extent, HCF_3 to give benzyne, the presumed intermediate in formation of naphthalene and trifluoromethylnaphthalene (Tables I and VII). No evidence was found for the loss of benzylic fluorine (Scheme I). This difference is consistent with the available data for bond-dissociation energies given in Table VIII.

SCHEME I

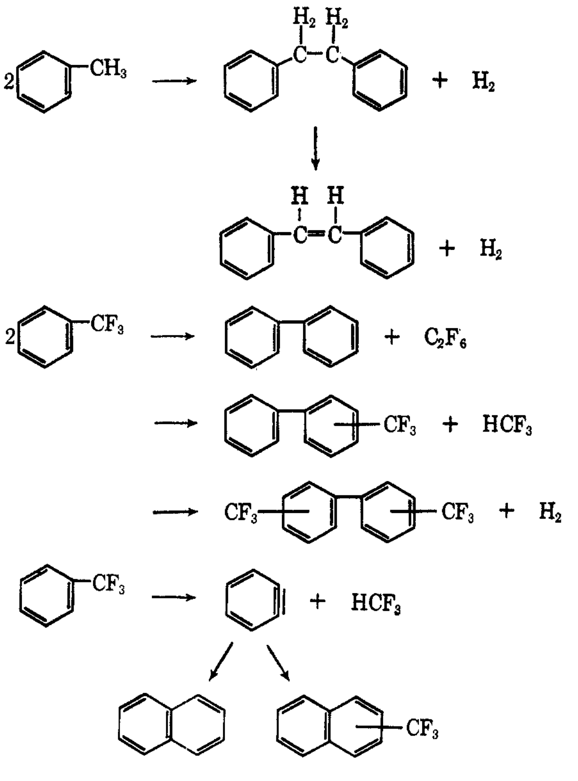


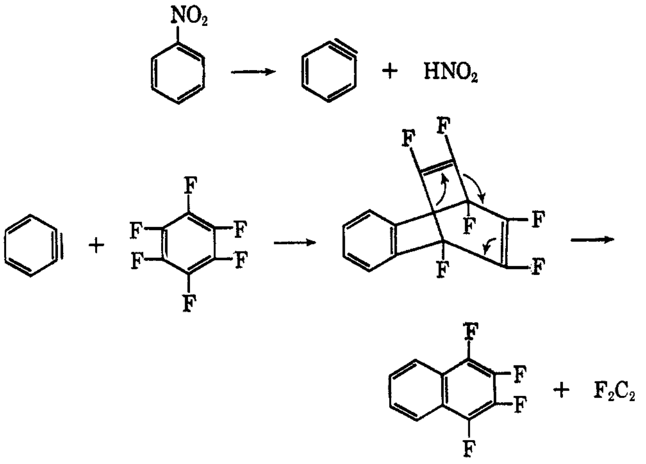
TABLE VIII

Bond	D, kcal/mole
$C_6H_5CH_2$–H	85[a]
$C_6H_5CH_2$–F	120[b]
C_6H_5–CH_3	87[b]
C_6H_5C–F_3	69[b]

[a] R. Walsh, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 650 (1966), and references cited therein. [b] See ref 6b, pp. 270–289.

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.[11] It most likely formed in the nitrobenzene reaction in the same way (Scheme II).

SCHEME II



The amount of tetrafluoronaphthalene formed in the reaction of nitrobenzene with hexafluorobenzene at 1:1.5 mole ratio 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 HNO_2 to give benzyne was strongly enhanced by the presence of hexafluorobenzene. Conceivably this effect may involve a charge-transfer complex. Hexafluorobenzene forms charge-transfer complexes with aromatic hydrocarbons,[12] but these are readily decomposed at much lower temperatures than those involved in this work. Moreover, both hexafluorobenzene and nitroaromatics are usually viewed as acceptor molecules and they would not be expected to form strong charge-transfer complexes with each other. How-

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

(12) C. R. Patrick and G. S. Prosser, *Nature*, **187**, 1021 (1960); E. McLaughlin and C. E. Messer, *J. Chem. Soc., Sect. A*, 1106 (1936); W. A. Duncan and F. L. Swinton, *Trans. Faraday Soc.*, **62**, 1082 (1966).

TABLE IX

SUBSTITUTED BIPHENYLS AND TERPHENYLS FROM REACTION OF NITROBENZENE WITH REAGENTS HEXAFLUOROBENZENE AND BENZENE-d_6[a]

	Relative concn[b]					
	Biphenyls			Terphenyls		
No. of substituent atoms (F or D)[b]	Hexafluorobenzene		Benzene-d_6	Hexafluorobenzene		Benzene-d_6
	1:5[c]	1:1.5[c]	1:5[c]	1:5[c]	1:1.5[c]	1:5[c]
0	...	...	4	...	...	2
1	2	...	7	...	...	3
2	1	...	9	...	...	5
3	3	...	9	...	...	8
4	12	37	24	3	23	13
5	100	100	100	4	27	31
6	92	37	9	4	...	42
7	32	...	47	3	...	40
8	8	...	32	3	...	44
9	12	10	8	12	20	70
10	52	27	15	60	27	91
11	...	...	...	36	...	65
12	...	...	...	8	...	38
13	...	...	...	...	...	43
14	...	...	...	...	...	53

[a] Isotopic composition of benzene-d_6 was 0.2% d_4, 5.7% d_5, 94.1% d_6. [b] From relative intensities in the low-voltage (7.5 v, uncorrected) mass spectra normalized to $X_5C_6C_6H_5$ = 100 (X is fluorine or deuterium). [c] Ratio of nitrobenzene/reagent.

ever, recently reported evidence for extensive charge delocalization into the *o*- and *p*-fluorine atoms of pentafluorophenylcarbonium ions[13] suggests that under some conditions hexafluorobenzene may function as the donor in charge-transfer complexes. The implied formation of fluoronium ions is supported by the mass spectra of fluoroalkanes[14] and the ^{19}F nmr spectra of phenyl- and diphenylfluorocarbonium ions.[15]

The contrast in results from hexafluorobenzene and *p*-difluorobenzene, the two reactants used in two different concentrations relative to nitrobenzene, is striking. With *p*-difluorobenzene, the products from nitrobenzene alone (phenol, biphenyl, and dibenzofuran) were formed in about the same ratios over a tenfold difference in original reactant concentrations. In the presence of hexafluorobenzene no products derived from nitrobenzene alone were formed in either of the two concentrations, although hexafluorobenzene would be expected to be the less reactive of the two fluorine compounds.

To investigate this phenomenon further, we are examining the behavior at high temperatures of other aromatic compounds in the presence of hexafluorobenzene, especially those that lose HX intramolecularly to form benzyne, such as chlorobenzene,[16] as well as benzotrifluoride.

Phenylation of Hexafluorobenzene and Hexadeuteriobenzene.—Table IX lists the fluorinated biphenyls and terphenyls formed in the reaction of nitrobenzene with hexafluorobenzene and, for comparison, the corresponding deuterated biphenyls and terphenyls from nitrobenzene and benzene-d_6. No unsubstituted biphenyl was formed in hexafluorobenzene even at the higher concentration of nitrobenzene and only very little in benzene-d_6. Dimerization of phenyl radical from nitrobenzene is almost completely absent in the presence of aromatic systems to which this highly energetic radical can add.[17,18]

Most striking is the much greater amount of hexafluorobiphenyl than of the corresponding hexadeuteriobiphenyl at the same concentration of nitrobenzene. Both probably arise by attack of phenyl radical on the hexasubstituted benzene; however, the greater strength of the C–F bond favors an allylic shift of a fluorine atom and loss of hydrogen.

For purpose of comparison, hexafluorobenzene was arylated by benzoyl peroxide in solution to give the products shown in Table II. The most striking difference between arylation by phenyl radicals in solution at a comparatively low temperature and that in the vapor phase at high temperatures is that between the almost complete absence of hexafluorobiphenyl among the products in the former case and the high yield in the latter. The intramolecular movement of hydrogen and fluorine atoms evidently has an appreciable energy of activation and requires the higher temperature. Tetrafluoroterphenyl was formed in about equal amounts in the two cases, whereas the benzoyl peroxide arylation gave more pentafluorobiphenyl than did nitrobenzene. Both probably arose from phenylation of pentafluorobiphenyl—phenyl radicals from benzoyl peroxide preferred to attack the unsub-

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(13) R. Filler, C.-S. Wang, M. A. McKinney, and F. N. Miller, *J. Am. Chem. Soc.*, **89**, 1026 (1967); G. A. Olah and M. B. Comisarow, *ibid.*, **89**, 1027 (1967).

(14) F. W. McLafferty, *Anal. Chem.*, **34**, 2 (1962); F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, p 111.

(15) G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 362 (1966).

(16) E. K. Fields and S. Meyerson, *ibid.*, 3388 (1966).

(17) Phenyl radical formed in a variety of ways in the presence of benzene, phenanthrene, and anthracene does not recombine to give biphenyl, but adds to the aromatic systems instead: J. D. Burr, J. M. Scarborough, J. D. Strong, R. I. Akawie, and R. A. Meyer, *Nucl. Sci. Eng.*, **11**, 218 (1961); G. W. Taylor, *Can. J. Chem.*, **35**, 739 (1957).

(18) The electron spin resonance of phenyl radical at 77°K indicates that the unpaired electron remains in the sp^2 orbital of the carbon atom at which scission occurs. The σ-type localized structure can account for the high reactivity of the phenyl radical [J. E. Bennett, B. Mile, and A. Thomas, *Chem. Commun.*, 265 (1965)]. In a different context, the difference between the ionization potential of the phenyl radical (9.20 ev) and that of benzene (9.50 ev) just barely exceeds the combined uncertainties of the measurements [I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Am. Chem. Soc.*, **86**, 2741 (1964)]. The near-equality of the two values constitutes further evidence that the odd electron is not coupled into the π system but remains highly localized. In contrast, the ionization potential of the resonance-stabilized benzyl radical (7.76 ev) [J. B. Farmer, I. H. S. Henderson, C. A. McDowell, and F. P. Lossing, *J. Chem. Phys.*, **22**, 1948 (1954)] is considerably lower than that of toluene (9.0 ev) [S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961)].

stituted benzene ring, whereas those from nitrobenzene were evidently more energetic and showed no discrimination. Arylation of benzenes containing chlorine and other substituent groups is being studied and the isomer ratios are being determined for comparison with those formed at low temperatures in solution.[19]

[19] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y. 1957, p 484.

Registry No.—Nitrobenzene, 98-95-3; fluorobenzene, 462-06-6; *p*-difluorobenzene, 540-36-3; benzotrifluoride, 98-08-8; hexafluorobenzene, 392-56-3; benzene-d_6, 1076-43-3; benzoyl peroxide, 94-36-0.

Acknowledgment.—The authors are indebted to D. K. Albert of the American Oil Co. for his assistance in gas chromatographic analyses.

Photochemistry of Some Dicyclopentadiene Derivatives

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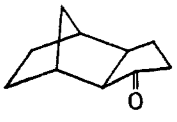
Photolysis of either *exo* or *endo* tricyclic ketones **1** or **2** led to β-(2-norbornenyl)propanal (**5**) as the major primary photoproduct. A secondary product was the *endo*-oxetane **6** formed *via* intramolecular photocycloaddition of **5**. Photorearrangement of epoxy ketone **11** yielded diketone **12** by hydrogen migration.

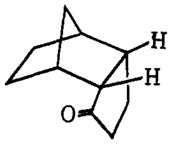
Photochemically induced reactions of ketones have been the subject of intensive investigations.[1] The unique synthetic possibilities in this area stimulated our interest in the examination of the behavior of some polycyclic ketones.[2] As a secondary consideration, it was anticipated that the rigid geometry inherent in these systems might provide information on the stereochemical requirements of some of the competing processes. This paper reports the results of studies with some derivatives of dicyclopentadiene. In particular, the *exo* and *endo* ketones **1** and **2** and the epoxy ketone **11** were investigated.[3]

Results

The required ketones **1** and **2** were prepared by catalytic reduction of the corresponding α,β-unsaturated systems **3** and **4**.[4]



1



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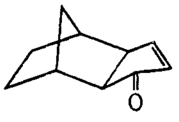

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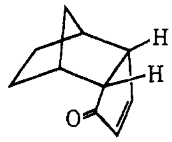

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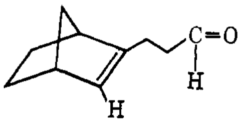
Solutions of **1** or **2** were irradiated (dioxane–water) through Pyrex filters with medium-pressure, mercury-vapor sources. Disappearance of starting ketones was accompanied by the formation of two new materials. As the reaction progressed, it was apparent that one of the photoproducts was formed from the other in a secondary reaction. Prolonged irradiation led to a single product at the expense of both the starting material and the primary photoproduct.

For isolation purposes, the reaction was discontinued when the ratio of the two new products was *ca.* 2:1. At this point most (>95%) of the starting material had been consumed.

The two components were isolated by gas chromatography and characterized as described below. The primary product displayed a strong carbonyl absorption band at 5.77 μ, double-bond absorptions at 6.15 and 11.53 μ, and an aldehyde C–H stretching vibration at 3.68 μ. The integrated nmr spectrum revealed one olefinic proton at τ 4.48 and an aldehyde proton at 0.34.

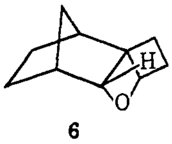
These data, and the fact that both **1** and **2** led to the same product, leave little doubt that the primary product has structure **5**.

1 or **2** $\xrightarrow{h\nu}$

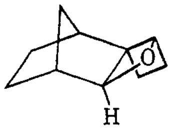


5

The nature of the secondary photoproduct was deduced from the absence of carbonyl absorption in the infrared spectrum and the presence of a strong absorption band at 10.06 μ.[5] These data and literature analogies[6] suggested an oxetane structure for this substance. The two most likely alternatives appeared to be **6** and **7**. A secondary carbinol was obtained on reduction of the oxetane with lithium aluminum hydride.[7] Of the four possible alcohols derivable from



6



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[1] For a general survey, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 5.

[2] An excellent bibliography may be found in R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., New York, N. Y., 1966, Chapter 3.

[3] Photolysis of the unsaturated ketone **4** in dilute solution led only to high-melting materials, presumably dimeric in nature. Unpublished observations of A. S.

[4] K. Alder and G. Stein, *Ann.*, **504**, 205 (1936). P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

[5] G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

[6] W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

[7] S. Searles, Jr., K. A. Pollart, and E. F. Lutz, *J. Am. Chem., Soc.* **79**, 948 (1957).