Anal. Calcd for $C_3H_4FN_3O_5$: C, 19.91; H, 2.23; F, 10.49; N, 23.21. Found: C, 20.6, 20.5; H, 2.7, 2.6; F, 9.8, 10.1; N, 23.0, 23.0.

Registry No.—**1**, 18139-02-1; **2**, 17003-80-4; **4**, 33046-31-0; **5**, 33191-89-8; **6**, 33046-32-1; **7**, 33147-03-4; **8**, 33046-33-2; **9**, 33046-34-3; **10**, 33191-90-1; **12**, 33046-35-4; *N*-(2,2,2-fluorodinitroethyl)acetamide, 22691-71-0; *N*,*N*′-bis(2,2,2-fluorodinitroethyl)-4,4-dinitroheptanedioic amide, 33046-37-6; *N*,*N*′-di(*tert*-butyl)-*N*,*N*′-bis(2,2,2-fluorodinitroethyl)oxamide, 33046-38-7.

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Reactions of Nitromethane with Hexafluorobenzene at 550°

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Nitromethane reacts with hexafluorobenzene at 550° to give products that differ greatly in nature from those with benzene under the same conditions. Pentafluorotoluene and pentafluorophenol are the major products, together with varying amounts of pentafluoroanisole, pentafluorobenzaldehyde, and decafluorobiphenyl. With *p*-difluorobenzene, nitromethane gives *p*-fluorophenol as the only major product. The driving force in reactions of nitromethane with fluorinated aromatics may be the formation of nitrosyl and nitryl fluorides.

Nitromethane reacts with benzene at 500–550° to give aniline, *N*-methylaniline, and biphenyl as major products, together with minor amounts of toluene, anisole, phenol, and *N*-benzylideneaniline.[1] The deuterium content of products from labeled reagents indicated that *N*-methylaniline formed by insertion in benzene of methylnitrene from nitromethane, and aniline by subsequent loss of CH_2 from *N*-methylaniline.[2] Apart from biphenyl, a product derived entirely from benzene, nitrogen compounds comprised about 79% of the total products. It was of interest to find if nitromethane would give analogous products with substituted benzenes. We therefore allowed nitromethane to react with hexafluorobenzene at 550° and determined the products by mass spectrometry, gas chromatography, and directly coupled gas chromatography–mass spectrometry.

Experimental Section

Hexafluorobenzene was from Aldrich Chemical Company. It analyzed 98% hexafluorobenzene and 1% each of penta- and tetrafluorobenzenes. The pentafluoro derivatives of toluene, anisole, aniline, benzaldehyde, and decafluorobiphenyl were from Pierce Chemical Company. Nitromethane was Eastman Reagent Grade, distilled prior to use. The apparatus, procedure, and analytical methods are fully described in previous publications.[3]

In a typical experiment a mixture of 10.72 ml (0.2 mol) of nitromethane and 118 ml (1.0 mol) of hexafluorobenzene was pumped into a Vycor tube filled with Vycor chips at 550° in a stream of argon flowing at 20 ml/min. Liquid products were condensed in a bulb at 0°; gases were collected in gas bulbs for mass spectral analysis. Distillation of the liquid products recovered 171 g, almost all hexafluorobenzene, at 78–80°, and left 12.6 g of a higher boiling residue whose composition is shown in Table II, along with the composition of gases generated in the reaction.

Results and Discussion

Products from the reaction of nitromethane with hexafluorobenzene determined by gas chromatography are listed in Table I. These included various amounts of unknowns, whose molecular weights were determined by mass spectrometry; these are listed in Table II, along with the composition of gaseous products.

TABLE I

PRODUCTS FROM NITROMETHANE AND HEXAFLUOROBENZENE[a]

	Products[b]			
Nitromethane, mol	1	0.5	0.2	0.1
Weight of products boiling over 100°, g	26	27	12.6	7.0
Pentafluorotoluene	37.5	53.0	56.0	60.0
Pentafluorophenol	33.0	23.0	20.7	3.0
Pentafluoroanisole	5.9	9.8	9.9	12.7
Pentafluorobenzaldehyde	6.6	3.2	3.0	4.6
Decafluorobiphenyl	6.8	4.7	3.6	2.9
Unknowns	10.2	6.3	6.8	16.8

[a] Conditions: 1 mol hexafluorobenzene; 550°; contact time, 20 sec; argon, 20 ml/min. [b] Weight percent by gas chromatography.

The two major products were pentafluorotoluene and pentafluorophenol, with pentafluoroanisole prominent among the less abundant ones. In addition, mass spectrometry showed a compound of molecular weight 180, corresponding to tetrafluoroanisole, tetrafluorobenzyl alcohol, or tetrafluorocresol. Its spectrum is compatible with the structure $CH_3C_6F_4OH$. A pair of peaks of about equal intensities at masses 179 and 180 resembles corresponding pairs in the spectra of $C_6F_5CH_3$[4,5] and $C_6F_4HCH_3$,[5] and thus suggests a methyl group on a fluorinated benzene ring. Masses of other fragments (probable derivations) follow: 161 ($M^+ - F$), 151 ($M^+ - CHO$), 150 ($[M^+ - H] -$

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[1] E. K. Fields and S. Meyerson, *Chem. Commun.*, 494 (1967).

[2] E. K. Fields and S. Meyerson, *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.*, **16**, No. 1, B96 (1971).

[3] E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969), and references cited therein.

[4] J. R. Majer, *Advan. Fluorine Chem.*, **2**, 55 (1961).

[5] L. D. Smithson, A. K. Bhattacharya, and C. Tamborski, *Org. Mass Spectrom.*, **4**, 1 (1970).

TABLE II

PRODUCTS FROM NITROMETHANE AND HEXAFLUOROBENZENE[a]

Liquids	Rel concn[b]
Compound of molecular weight 180	33
Pentafluorotoluene	100
Pentafluorophenol	55
Pentafluoroanisole	24
Pentafluorobenzaldehyde	3
Tetrafluoroxylene	10
Hexafluorotoluene	5
Methyl octafluorobiphenyl	4
Nonafluorobiphenyl[c]	3
Methyl nonafluorobiphenyl	4
Decafluorobiphenyl	6
Decafluoromethylbiphenyl	4
Gases	**Mol %[d]**
Nitric oxide	37.1
Carbon monoxide	30.6
Carbon dioxide	13.3
Silicon tetrafluoride	11.2
Nitrogen	3.5
Methane	2.6
Hydrogen cyanide	1.0
Ethylene	0.7

[a] Conditions: mole ratio, nitromethane to hexafluorobenzene, 1:5; 550°; contact time, 20 sec; argon, 20 ml/min. [b] Relative intensities in the low-voltage mass spectrum normalized to pentafluorotoluene = 100; identities confirmed by directly coupled gas chromatography–mass spectrometry. [c] This might arise, at least partly, from the pentafluorobenzene impurity in the hexafluorobenzene. [d] Determined by mass spectrometry.

TABLE III

COMPARISON OF PRODUCTS FROM NITROMETHANE WITH BENZENE AND WITH HEXAFLUOROBENZENE[a]

	C_6X_6, X	
	H	F
Liquids	Weight %[b]	
$C_6X_5CH_3$	0.5	56
$C_6X_5NH_2$	12.3	
C_6X_5OH	1.6	20.7
$C_6X_5OCH_3$	2.6	9.9
C_6X_5CHO	Trace	3.0
$C_6X_5NHCH_3$	5.5	
$C_6X_5C_6X_5$	69.7	3.6
$C_6X_5C_6X_4NH_2$	2.3	
$C_6X_5CH{=}NC_6X_5$	1.6	
Unidentified	3.9	6.8
Total weight of liquid products, g	5.2	12.6
Gases	Mol %[c]	
Nitric oxide	42.1	37.1
Carbon monoxide	24.3	30.6
Carbon dioxide	2.5	13.3
Silicon tetrafluoride		11.2
Nitrogen	12.9	3.5
Methane	14.2	2.6
Hydrogen cyanide	0.4	1.0
Ethylene	1.8	0.7
Hydrogen	1.8	

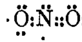
[a] Conditions: 0.2 mol of nitromethane, 1.0 mol C_6X_6; contact time, 20 sec; argon, 20 ml/min. [b] Determined by gas chromatography. [c] Determined by mass spectrometry.

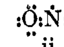
CHO), 136 ($M^+ - C_2FH$), 132 ($[M^+ - CHO] - F$ or $M^+ - CHOF$).

The identities of the two most abundant products, $C_6F_5CH_3$ and C_6F_5OH, in conjunction with a little tetrafluorophenol, furnish additional supporting evidence for ascribing the tetrafluorocresol structure to the product of molecular weight 180.

A striking contrast in the reactions of nitromethane with benzene and hexafluorobenzene is demonstrated in Table III. Aniline and biphenyl constituted 82% by weight of the liquid products in the nitromethane–benzene reaction; no pentafluoroaniline, and only 3.6% of decafluorobiphenyl formed in the nitromethane–hexafluorobenzene reaction. None of the liquid products from hexafluorobenzene contained nitrogen. Toluene and phenol constituted only 0.5 and 1.6% by weight, respectively, of the products from benzene, whereas the corresponding fluorinated toluene and phenol amounted to 56 and 20.7%, respectively, from hexafluorobenzene. Among the gases, methane constituted 14.2% from the benzene reaction, only 2.6% from the hexafluorobenzene reaction.

The sharply different product distributions can be rationalized in terms of the greater susceptibility of C_6F_6 than of C_6H_6 to nucleophilic attack,[6] even though the reactive intermediates in the gas phase are doubtless free radicals rather than ions. The electron-donating character of a methyl substituent, which might be translated into nucleophilicity of the methyl radical, would favor attack on C_6F_6 over that on C_6H_6. A measure of the extent of such preference is implied in the difference between the resultant bond-dissociation energies, $D(C_6F_5–CH_3) - D(C_6H_5–CH_3)$, which has been estimated at about 25 kcal/mol.[4] The high yield of pentafluorophenol, with no evidence for intermediate $C_6F_5NO_2$ formation, could be accounted for by NO_2 attack *via* an oxygen atom to form C_6F_5ONO as an intermediate, paralleling the formation of CH_3ONO in the photolysis of CH_3NO_2 by recombination of $CH_3\cdot$ and NO_2 through an oxygen atom.[7] The canonical structure i would appear to be a better nucleophile than


i


ii

ii. Support for this view can be drawn from the consistently lower ionization potentials of alkyl nitrites than of the isomeric nitroalkanes.[8]

Nitromethane at high temperature, alone or in the presence of benzene, decomposes to methyl radical and NO_2; the methyl radical abstracts hydrogen from nitromethane and goes to methane.[2]

$$CH_3NO_2 \longrightarrow CH_3\cdot + NO_2$$

$$CH_3\cdot + CH_3NO_2 \longrightarrow CH_4 + \cdot CH_2NO_2$$

The major overall reaction with hexafluorobenzene is

$$C_6F_6 + CH_3NO_2 \longrightarrow C_6F_5CH_3 + NO_2F$$

Apparently methyl radical is captured so rapidly by hexafluorobenzene that it cannot abstract hydrogen

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(6) J. A. Young, *J. Chem. Educ.*, **47**, 733 (1970); W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, Chapter 8.

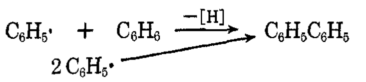
(7) G. C. Pimentel and G. Rollefson, "Formation and Trapping of Free Radicals," Academic Press, New York, N. Y., 1960, Chapter 4; R. E. Rebbert and N. Slagg, *Bull. Soc. Chim. Belg.*, **71**, 709 (1962); B. H. J. Bielski and R. B. Timmons, *J. Phys. Chem.*, **78**, 347 (1964).

(8) The differences for the methyl, ethyl, *n*-propyl, and isopropyl compounds all fall in the range of 0.4 to 0.6 eV. For the ionization-potential data, see R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, Appendix IV; M. J. S. Dewar, M. Shanshal, and S. D. Worley, *J. Amer. Chem. Soc.*, **91**, 3590 (1969).

from nitromethane to give methane, as it does in the presence of benzene. Further, pentafluorotoluene is not attacked so readily by radicals as is toluene, at least in the presence of excess hexafluorobenzene.

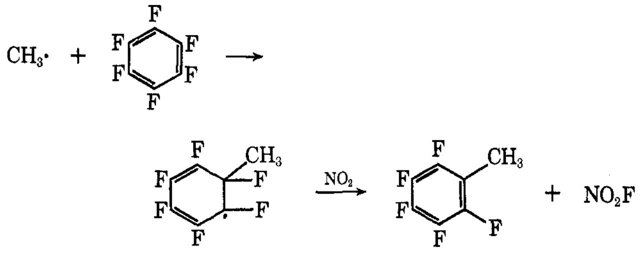
The role of NO_2 is also quite different in the two reactions. It abstracts a hydrogen from benzene to give phenyl radical, which forms biphenyl by arylating benzene or by dimerizing.

$$NO_2 + C_6H_6 \longrightarrow HNO_2 + C_6H_5\cdot$$



$$C_6H_5\cdot + C_6H_6 \xrightarrow{-[H]} C_6H_5C_6H_5 \qquad 2\,C_6H_5\cdot \longrightarrow C_6H_5C_6H_5$$

NO_2 does not readily abstract a fluorine atom from hexafluorobenzene, for there was little decafluorobiphenyl. Rather it appears to take a fluorine atom from the intermediate cyclohexadienyl free radical formed by addition of methyl radical to hexafluorobenzene.



Methoxyl radical, a possible contributing precursor of pentafluorophenol, may arise from a prior nitro–nitrite rearrangement

$$CH_3NO_2 \longrightarrow CH_3ONO \longrightarrow CH_3O\cdot + NO$$

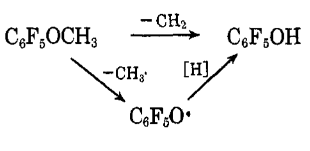
or dissociation and recombination, as in the known photochemical sequence[7]

$$CH_3NO_2 \longrightarrow CH_3\cdot + NO_2 \longrightarrow CH_3ONO \longrightarrow CH_3O\cdot + NO$$

followed by

$$CH_3O\cdot + C_6F_6 \xrightarrow{NO} CH_3OC_6F_5 + NOF$$

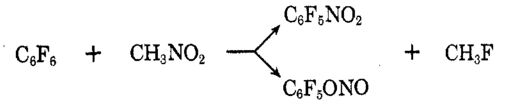
Such a nitro–nitrite rearrangement was strongly evident in the thermal decomposition of nitrobenzene, but took place to a much lesser extent in thermal decomposition of nitromethane and in its reaction with benzene. Pentafluorophenol may form from pentafluoroanisole by loss of either CH_2 or $CH_3\cdot$.



$$C_6F_5OCH_3 \xrightarrow{-CH_2} C_6F_5OH \qquad C_6F_5OCH_3 \xrightarrow{-CH_3\cdot} C_6F_5O\cdot \xrightarrow{[H]} C_6F_5OH$$

In reactions of anisole with nitrobenzene at 600°, as well as in the decomposition of anisole alone at that temperature, some of the products are most readily explained on the basis of carbene formation and insertion.[9]

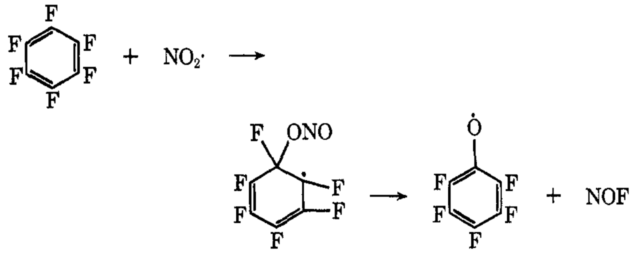
Aromatic nitro compounds give phenols upon decomposition at elevated temperatures.[3] However, the path to pentafluorophenol through formation of pentafluoronitrobenzene or perhaps pentafluorophenyl nitrite directly, not involving prior dissociation of nitromethane,



$$C_6F_6 + CH_3NO_2 \longrightarrow \begin{cases} C_6F_5NO_2 \\ C_6F_5ONO \end{cases} + CH_3F$$

$$C_6F_5NO_2 \longrightarrow C_6F_5ONO \xrightarrow{-NO} C_6F_5O\cdot \xrightarrow{[H]} C_6F_5OH$$

appears to be excluded by the absence of methyl fluoride from the products. An alternative mechanism for pentafluorophenol is addition of NO_2 through the oxygen atom to hexafluorobenzene, followed by loss of NOF.



Pentafluorophenoxy radical then abstracts a hydrogen from nitromethane to give pentafluorophenol.

Most of the gaseous products may be accounted for by these reactions.

$$NO_2F + CH_3NO_2 \longrightarrow HF + CH_2(NO_2)_2$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$CH_2(NO_2)_2 \longrightarrow CO + H_2O + 2NO$$

$$CH_2(NO_2)_2 \longrightarrow CO_2 + H_2O + {}^1/_2N_2 + NO$$

Nitryl fluoride is a good nitrating agent;[10] dinitromethane decomposes readily at temperatures around 100°,[11] though the products have not been described. The formation of less nitrogen than demanded by the equations above indicates that other paths to CO_2 may exist.[12]

Some HF and subsequently SiF_4, as well as pentafluorobenzaldehyde, may also arise by the following process.

$$C_6F_6 + CH_3NO_2 \longrightarrow C_6F_5CH_2NO_2 + HF$$

$$C_6F_5CH_2NO_2 \longrightarrow C_6F_5CHO + HNO$$

Although C_6F_6 is thermally stable, being recovered unchanged after 30 sec at 700°,[13] we found that it reacted readily at elevated temperatures with organic compounds containing hydrogen atoms, even aromatic hydrogen, such as in chlorobenzene.[9]

$$C_6F_6 + C_6H_5Cl \xrightarrow[20\ \text{sec}]{700^\circ} C_6F_5C_6H_4Cl + HF$$

Other products arose solely from chlorobenzene: biphenyl, chloro- and dichlorobiphenyl, and chloronaphthalene, the latter presumably derived from benzyne.[14] The driving force in these reactions of hexafluorobenzene apparently comes from the formation of HF.

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(9) E. K. Fields and S. Meyerson, unpublished results.

(10) S. J. Kuhn and G. A. Olah, *J. Amer. Chem. Soc.*, **83**, 4564 (1961).

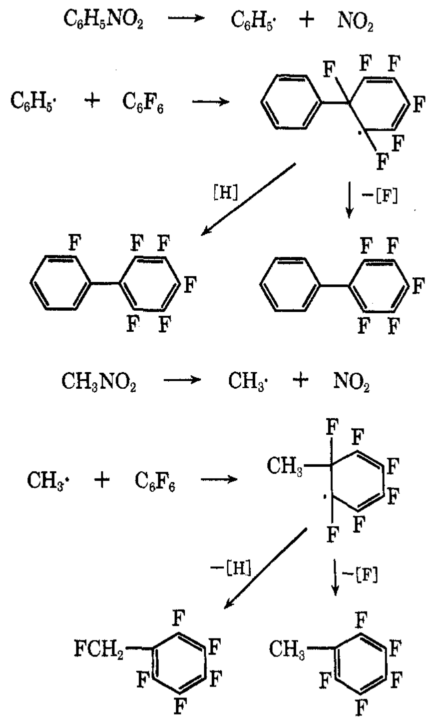
(11) P. Duden, *Ber.*, **26**, 3004 (1893).

(12) A referee has pointed out that both NO_2F and NOF attack glass readily to form SiF_4. In addition, NOF forms a white solid with glass, which may explain the formation of less nitrogen than demanded by the equations.

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

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

Hexafluorotoluene listed in Table II could form by carbene insertion, or by exchange of fluorine and hydrogen atoms in the intermediate cyclohexadienyl free radical, paralleling that in the reaction of phenyl radical derived from nitrobenzene with hexafluorobenzene.[13]



Decafluoromethylbiphenyl may form in a similar fashion.

Pentafluorotoluene has been made from hexafluorobenzene with methyllithium in 16% yield.[15] Pentafluorophenol has been prepared in 20% yield, along with dihydroxytetrafluorobenzenes, by the reaction of hexafluorobenzene with aqueous potassium hydroxide at 175° under pressure.[16] Pentafluorophenol has also been made by the reaction of pentafluorophenyllithium with trimethyl borate and oxidation of the dimethyl pentafluorophenyl borate with hydrogen peroxide. The overall yield was 39%.[17]

Our reaction of nitromethane with hexafluorobenzene provides a useful preparative method for pentafluorotoluene and pentafluorophenol. By varying the mole ratio of the two reactants from 0.1:1 up to 1:1, the reaction can give pentafluorotoluene with little pentafluorophenol, or about equal amounts of the two products, in a one-step reaction.

As shown in Table III, the nature of the products and relative amounts of analogous products in the reactions of nitromethane with benzene and hexafluorobenzene differed sharply. We therefore examined the reaction of nitromethane with a compound containing both hydrogen and fluorine atoms, *p*-difluorobenzene. The products of the reaction are listed in Table IV.

TABLE IV

PRODUCTS FROM NITROMETHANE AND *p*-DIFLUOROBENZENE[a]

Product	Rel concn[b]
Fluorotoluene	2
Fluorophenol	100
N-Methylfluoroaniline	1
Fluoroanisole	8
Difluorotoluene	3
Difluorophenol	3
N-Methyldifluoroaniline	4
Difluorobiphenyl	3
Trifluorobiphenyl	15
Tetrafluorobiphenyl	13

[a] Conditions: 1 mol of *p*-difluorobenzene, 0.2 mol of nitromethane; 550°; contact time, 20 sec; N_2, 20 ml/min. Total weight of products boiling above 95°, 17.7 g. [b] Relative intensities in the low-voltage (7.5 V nominal) mass spectrum, normalized to fluorophenol = 100.

The major product by far is fluorophenol; the ratio of its concentration to that of fluoroanisole, 12:1, suggests that the fluoroanisole arose from methylation of fluorophenol, rather than fluorophenol from fluoroanisole by loss of CH_2. Little fluorotoluene or difluorotoluene formed, in contrast to the reaction of nitromethane and hexafluorobenzene in identical mole ratios, which gave 2.8 times as much pentafluorotoluene as pentafluorophenol.

Displacement of a fluorine atom was preferred over that of a hydrogen atom by a ratio of 33:1, even though *p*-difluorobenzene has twice as many hydrogen as fluorine atoms. The driving force may be formation of NOF rather than NOH in the overall reaction

$$C_6H_4F_2 + CH_3NO_2 \longrightarrow C_6H_4FOH + NOF + CH_2$$

The behavior of nitromethane at 550° seems to be strongly influenced by the nature of added reagents. We are presently examining its reactions at different concentrations with a variety of benzene derivatives, as well as with pyridine and thiophene.

Registry No.—Nitromethane, 75-52-5; hexafluorobenzene, 392-56-3; benzene, 71-43-2; *p*-difluorobenzene, 540-36-3.

Acknowledgment.—The authors are happy to acknowledge the assistance of Dr. D. K. Albert of American Oil with gas chromatographic analyses.

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[15] British Patent 887,691, to National Polychemicals, Inc. (Jan 24, 1962); M. W. Buxton and J. C. Tatlow to Imperial Smelting Corp., British Patent 977,961, (Dec 16, 1964).

[16] W. J. Pummer and L. A. Wall, *J. Res. Nat. Bur. Stand.*, **A68**, (3), 277 (1964).

[17] G. M. Brooke, B. S. Furniso, W. K. R. Musgrave, and M. A. Zuasem, *Tetrahedron Lett.*, 2991 (1965).