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Substituent effects of fluorine on chemical and physical properties in the naphthalene series

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SUBSTITUENT EFFECTS OF FLUORINE ON CHEMICAL AND PHYSICAL PROPERTIES IN THE NAPHTHALENE SERIES

by

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INTRODUCTION

A primary purpose of this work was to study the effect of fluorine as a substituent on the chemical and physical properties of the naphthalene nucleus. The reactions of fluorobenzene have been extensively studied by a number of workers, and these studies indicate that the strong electron withdrawing inductive effect of fluorine is partially opposed by an electron donating resonance if located in the positions ortho and para to the reaction site. There have been only few studies of the reactions of the fluronaphthalenes. The presence of the second ring, which allows the possibility of seven isomeric products from an electrophilic substitution reaction on fluoronaphthalene, and the attendant difficulties encountered in separating and identifying many of these products are important factors which have discouraged the quantitative study of the reactions of the fluoronaphthalenes, in particular, and substituted naphthalenes in general.

In this work the nitration of 1- and 2-fluoronaphthalene and the lithiation of 2-fluoronaphthalene were studied in detail. The nitrations were studied under a variety of conditions in order to determine from the product ratios information about the nature of the nitrating agent. The relative amounts of products formed gave an indication of the effect of the fluorine as a substituent. In order to

identify unambiguously the nitration products, it was necessary to synthesize all of the isomeric nitrofluoronaphthalenes, only three of which were known at the time this work was begun.

The lithiation of 2-fluoronaphthalene was carried out in order to gain information concerning the effect of the fluorine substituent on naphthalene in reactions in which a carbanion or carbanionoid is formed. This study also opened the door to the synthesis of a variety of the difficult to prepare 2,3-disubstituted naphthalenes.

The availability of the isomeric nitrofluoronaphthalenes prepared in this work allowed the study of the spectra of this series of compounds. The mass spectra were studied in order to gain an insight into the rearrangement observed in nitronaphthalenes in which a molecule of carbon monoxide is ejected from the molecule ion. The ^{19}F-nmr were studied in an effort to study the effect of the nitro group on the fluorine resonance from all the possible positions in the naphthalene nucleus. Study of the infrared spectra was undertaken to determine the effect of the fluorine upon the orientation of the nitro group by studying the change in the stretching frequencies of the nitro group.

LITERATURE REVIEW

Fluorine as a substituent in aromatic compounds has been found to form very stable bonds to carbon, 107 kcal/mole, and has the smallest van der Waals radius of the halogens, 1.35 Angstroms, which compares to a value of 1.1 Angstroms for hydrogen (1). Thus fluorine substituents are very close in size to the hydrogen and the steric effect of fluorine is the smallest among the halogens. Fluorine is the most electronegative element and shows the strongest inductive effect on those atoms adjacent to it. Acting in the opposite direction is the resonance effect which is stronger for fluorine than the other halogens. This effect acts on the π-electrons to increase electron density on the ortho- and para-positions (2). Thus the reactivity of the fluoroaromatic is

determined by the combination of the above effects and individual characteristics of the reagent.

These effects were also noted in the Hammet parameters for substituted benzenes which were tabulated by Taft (3), and are shown in Table 1. These parameters are indications

Table 1. Tabulated inductive σ_I and resonance σ_R parameters of substituents for para-substitution

	F	Cl	Br	I	NO_2	CH_3
σ_I	0.50	0.47	0.45	0.38	0.63	-0.05
σ_R	-0.44	-0.24	-0.22	-0.10	0.15	-0.13

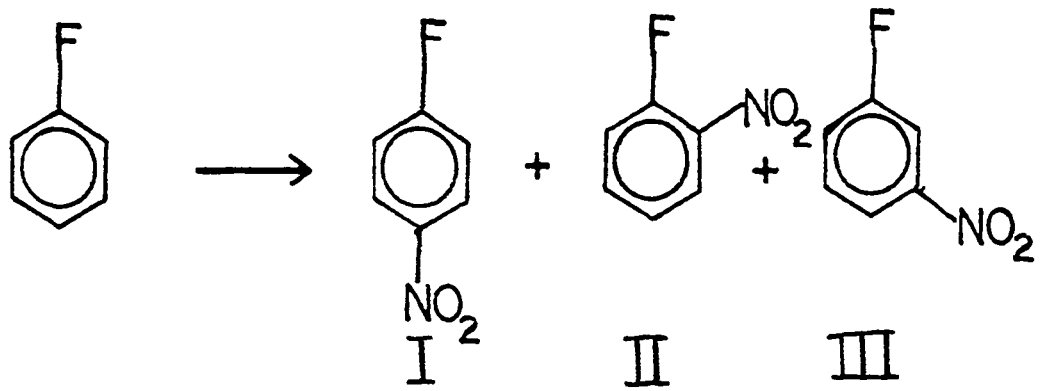
of the strong inductive withdrawal by the fluorine, and the strong resonance donation opposing it.

Electrophilic Substitution

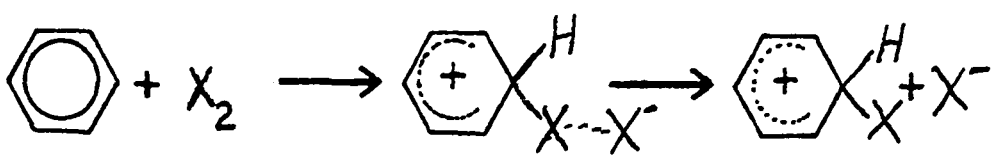
Fluorobenzene

The nitration of flurobenzene has been studied quantitatively with regard to isomer distribution and its reactivity relative to benzene (4, 5, 6, 7). The results indicated a decrease in reactivity compared to that of benzene toward nitration. The products obtained were predominantly para- (I), with a small amount of ortho- (II), and essentially no meta-nitrofluorobenzene (III).

The halogenation of fluorobenzene has been carried out under a variety of conditions with a variety of results. Chlorination of fluorobenzene with chlorine in acetic acid



yields approximately 90% para-chlorofluorobenzene (8). Under these conditions fluorobenzene was more reactive than benzene toward chlorination. However, the reverse order was noted by De la Mare and coworkers (9) in the chlorination with chlorine acetate in which $k_{C_6H_5F}/k_{C_6H_6}$ was 0.44. This was explained by the difference in the chlorinating agent. Chlorination with molecular chlorine in acetic acid has greater demand upon the electrons of the fluorobenzene than chlorination with chlorine acetate, which is a reaction of positive chlorine and more similar to nitration with nitronium ion than to the reaction with molecular halogen. Thus the



activating effect of the fluorine in molecular halogenation shows a greater call upon the resonance electron releasing effect in this reaction than in halogenation with positive halogen reagents. Whereas, in reaction with cationic reagents, the inductive effect is more important (9, 10, 11).

Studies on the bromination of halobenzenes in carbon disulfide in the presence of aluminum bromide exhibited an order of reactivity $C_6H_6 > C_6H_5F > C_6H_5Cl > C_6H_5Br$, with relative rates of approximately 1 : 0.04 : 0.2 : 0.1 (12). The order of the relative rates is consistent with the increased polarity of the reagent over molecular halogenation. The products obtained in the bromination of fluorobenzene were 10.7% ortho-, 0.2% meta-, and 89.1% para-bromofluorobenzene.

The above examples show the two opposing effects which contribute to the overall substituent effect of haloaromatic compounds. Inductive electron withdrawal tends to deactivate the compound toward electrophilic substitution, as noted by the general relative rate, $k_{C_6H_5X}/k_{C_6H_6}$, of less than 1.0. Since fluorine is the most electronegative element, this effect should be strongest in fluorine among the halogens, and it decreases in effect as one goes further away from the position bearing the fluorine. Thus it is strongest in the ortho- and weakest on the para-positions.

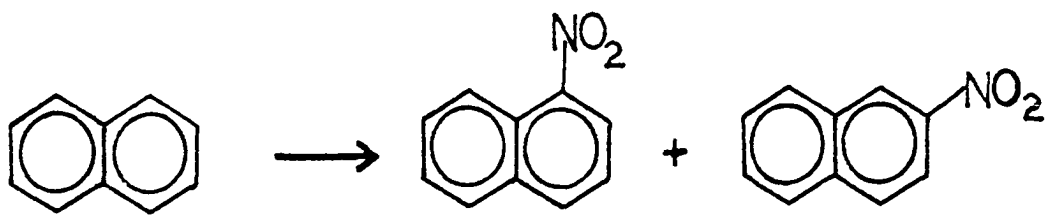
The opposing effect is a reasonance effect which results in the donation of electron density to the ortho- and

para-positions. This electron donation activates those positions towards electrophilic substitution and is strongest with fluorine among the halogens. The results of this effect can be seen in the nature of the products formed, for nearly all of the product is ortho- and para-substituted-fluorobenzene, with a negligible amount of the meta-product. In some reactions, such as chlorination with molecular chlorine, the resonance electron donation is more important than the inductive electron withdrawal, and causes the fluorocompound to be more reactive than the unsubstituted aromatic compound.

The steric effect of fluorine is not noticeable in these reactions, since any reduction in the amount of ortho-product due to steric effect would be masked by the reduction due to inductive electron withdrawal. However, the size of fluorine is not much greater than that of a hydrogen, so the steric effect is probably quite small or negligible.

Naphthalene compounds

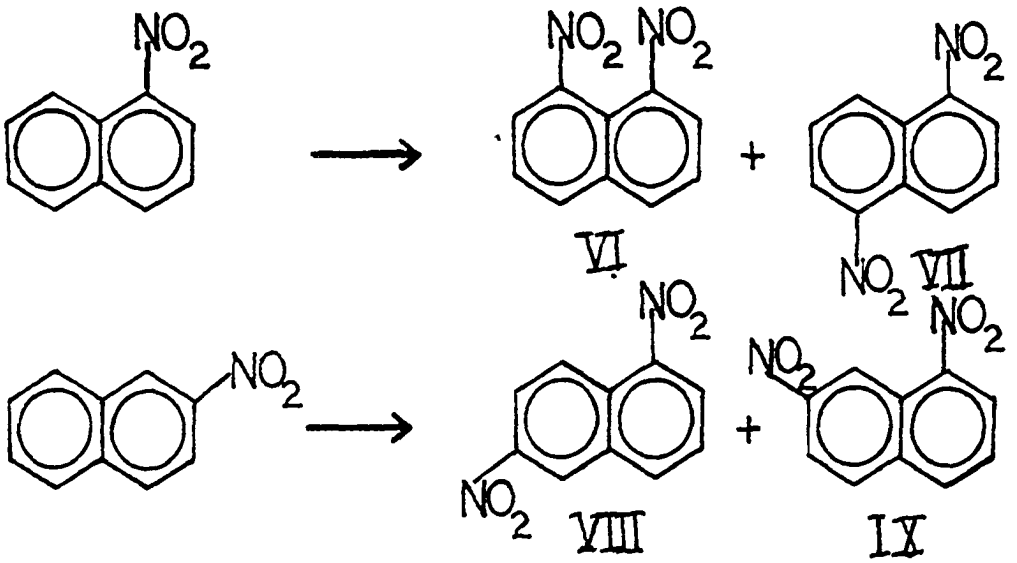
Nitration of naphthalene itself results in a mixture of α-(IV) and β-nitronaphthalene (V), with the α-isomer



IV V

predominating. The ratio of α/β-nitration varies considerably with the nitrating conditions and nitrating agents. Some examples of this product ratio are given in Table 2 (13).

Nitration of the nitronaphthalenes has been studied by Ward and Hawkins (14) and by Ward and coworkers (15). They found that nitration of 1-nitronaphthalene at 0° with nitric acid and sulphuric acid yielded 1,8- (VI) and 1,5-dinitronaphthalene (VII) in 66.5 and 33.5% yields respectively. Nitration of 2-nitronaphthalene at -5° yielded 1,6-(VIII) and 1,7-dinitronaphthalene (IX) in yields of 41 and 59% respectively.

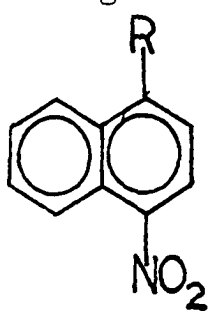


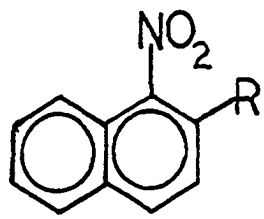
Nitration of the methyl- and methoxynaphthalenes were studied extensively by Alcorn and Wells (13, 16). Nitration of 1-methylnaphthalene gave a mixture of five isomers, the major product being 4-nitro-1-methylnaphthalene (X).

Table 2. The nitration of naphthalene

Medium	Temperature °C	k_α/k_β
HNO_3 in CH_3NO_2	25	28.5
HNO_3, H_2SO_4, HOAc, in HOAc	25	21.6
HNO_3 in Ac_2O	25	8.6
NO_2BF_4 in sulpholane	25	9.6

Nitration of 2-methylnaphthalene produced 1-nitro-2-methylnaphthalene (XI) as the major product among the isomers formed. Nitration of 1- and 2-methoxynaphthalene gave rise to three isomeric products in each case, with 4-nitro-1-methoxynaphthalene (XII) and 1-nitro-2-methoxy-naphthalene (XIII) predominating.

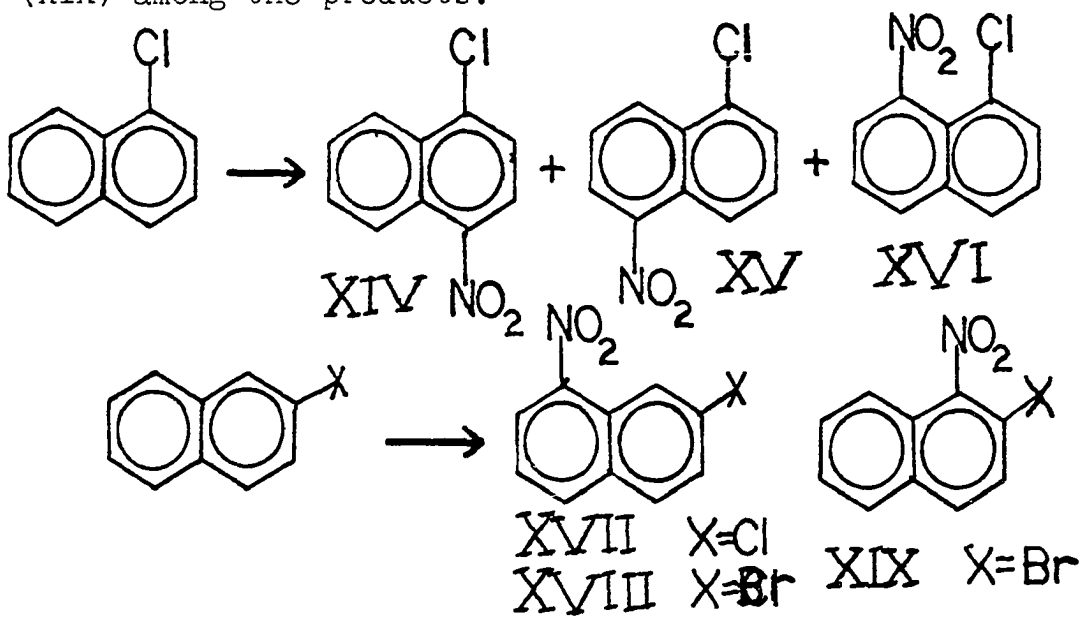




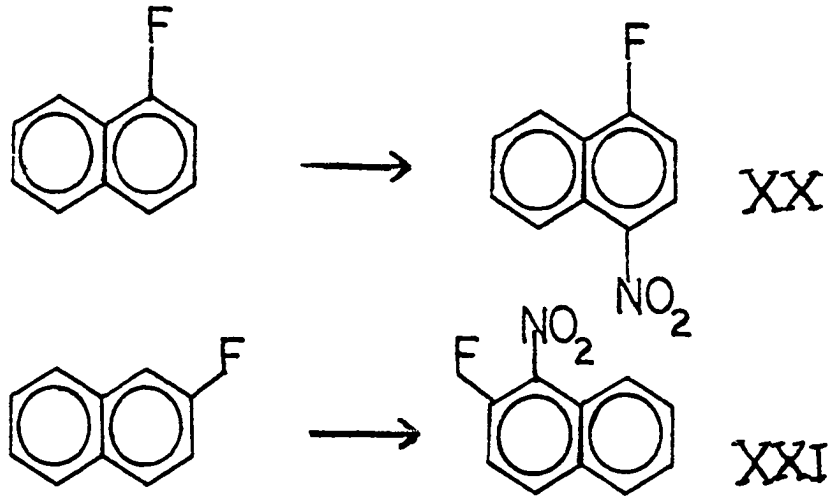
X R=CH_3 XI R=CH_3
XII R=OCH_3 XIII R OCH_3

Among the halonaphthalenes, nitration of 1-chloronaphthalene has been studied by Bassilios (17). He observed

formation of 4-(XIV), 5-(XV), and 8-nitro-1-chloronaphthalene (XVI) upon nitration with nitric acid in sulphuric acid at 35°. Scheid (18) observed formation of 8-nitro-2-chloronaphthalene (XVII) upon the nitration of 2-chloronaphthalene. Upon nitration of 2-bromonaphthalene, Zalkind and Filinov (19) identified 8-(XVIII) and 1-nitro-2-bromonaphthalene (XIX) among the products.



No quantitative studies have been reported using fluoronaphthalenes as substrates for nitration. Schiemann and coworkers (20), and later Bassilios and coworkers (21) have reported obtaining 4-nitro-1-fluoronaphthalene (XX) upon nitration of 1-fluoronaphthalene with fuming nitric acid in acetic acid. Schiemann and coworkers (20) reported that similar nitration of 2-fluoronaphthalene led to a mixture of nitro-2-fluoronaphthalenes, one isomer of which was 1-nitro-2-fluoronaphthalene (XXI). Kuhn and Olah (22)

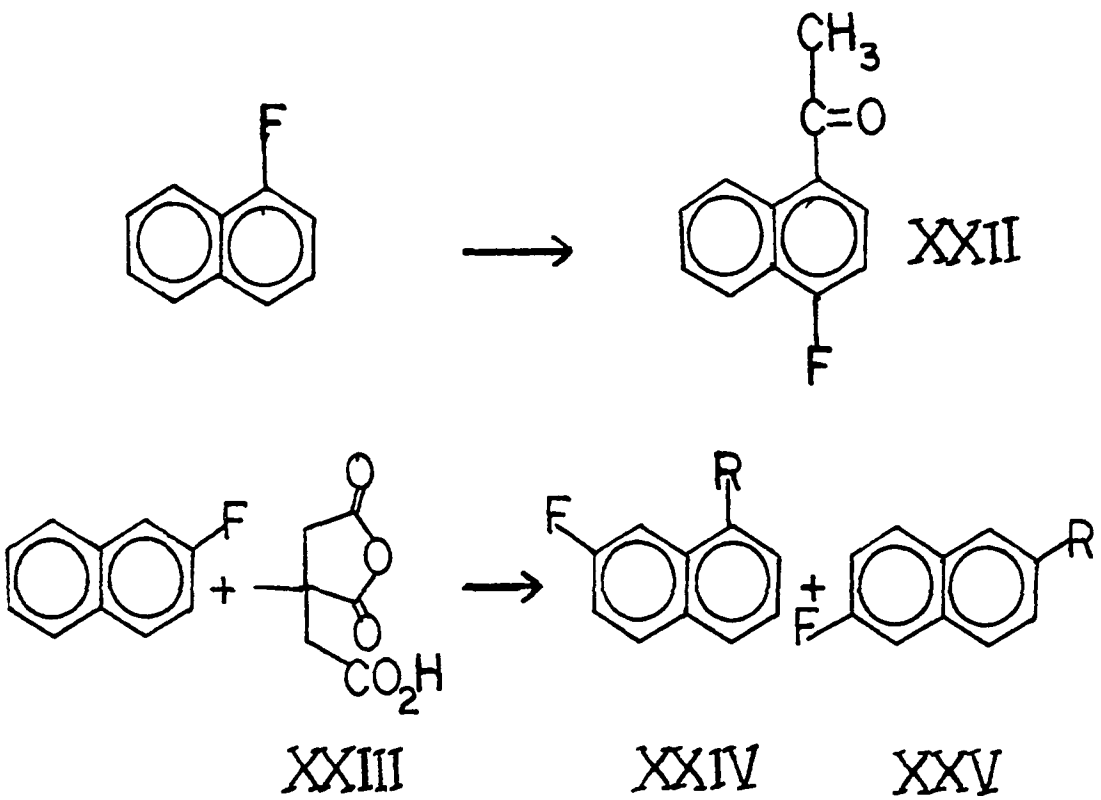


reported that the nitration of each fluoronaphthalene with nitronium fluoroborate in sulpholane produces approximately 75% yields of nitrofluoronaphthalenes; however, no indication of the nature or ratios of products was given.

Relative rates of halogenation of 1-halonaphthalenes have been studied by De la Mare and Robertson (23). They found that in chlorination and bromination with molecular chlorine and bromine in acetic acid the rates for 1-fluoronaphthalene relative to naphthalene ranged from 0.88 to 1.0, while the rates for the other 1-halonaphthalenes ranged from 0.02 to 0.07 relative to naphthalene. This is another indication of the strong activating resonance donation of the fluorine substituent.

Jacobs and coworkers (24) carried out the acylation of 1-fluoro-, 1-chloro-, and 1-bromonaphthalene with acetyl chloride and aluminum chloride in carbon disulfide. They

found the 4-halo-1-acetonaphthones as the major product in each case. The product from 1-fluoronaphthalene was greater than 95% 4-fluoro-1-acetonaphthone (XXII). Harnik and Jensen (25) observed that the acylation of 2-fluoronaphthalene with 3-methylcarballylic acid anyhydride (XXIII) and aluminum chloride resulted in a 2: 1 ratio of 8- (XXIV) to 6-substituted-2-fluoronaphthalenes (XXV).



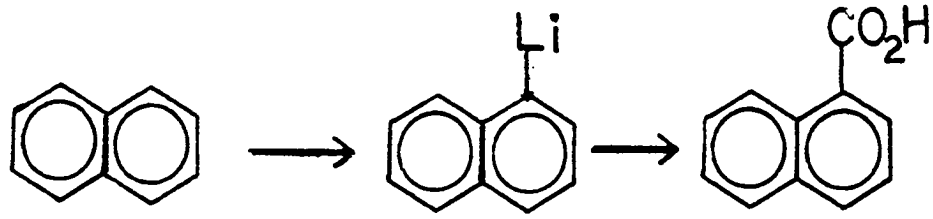
XXIII XXIV XXV

Lithiations

The reaction of naphthalene compounds with organometallic reagents have been studied and long used in synthesis.

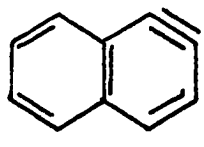
Three of the types of reactions which occur are halogen-metal exchange, elimination to form an aryne, and proton abstraction without elimination.

The topic of halogen-metal exchange has been reviewed by Jones and Gilman (26). As an example in the naphthalene series, Gilman and coworkers (27) found that treatment of 1-bromonaphthalene with n-butyllithium in petroleum ether at room temperature yielded 1-naphthoic acid (XXVI) in approximately 80% yield following treatment with carbon dioxide.

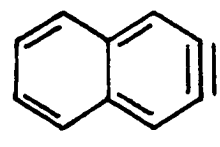


XXVI

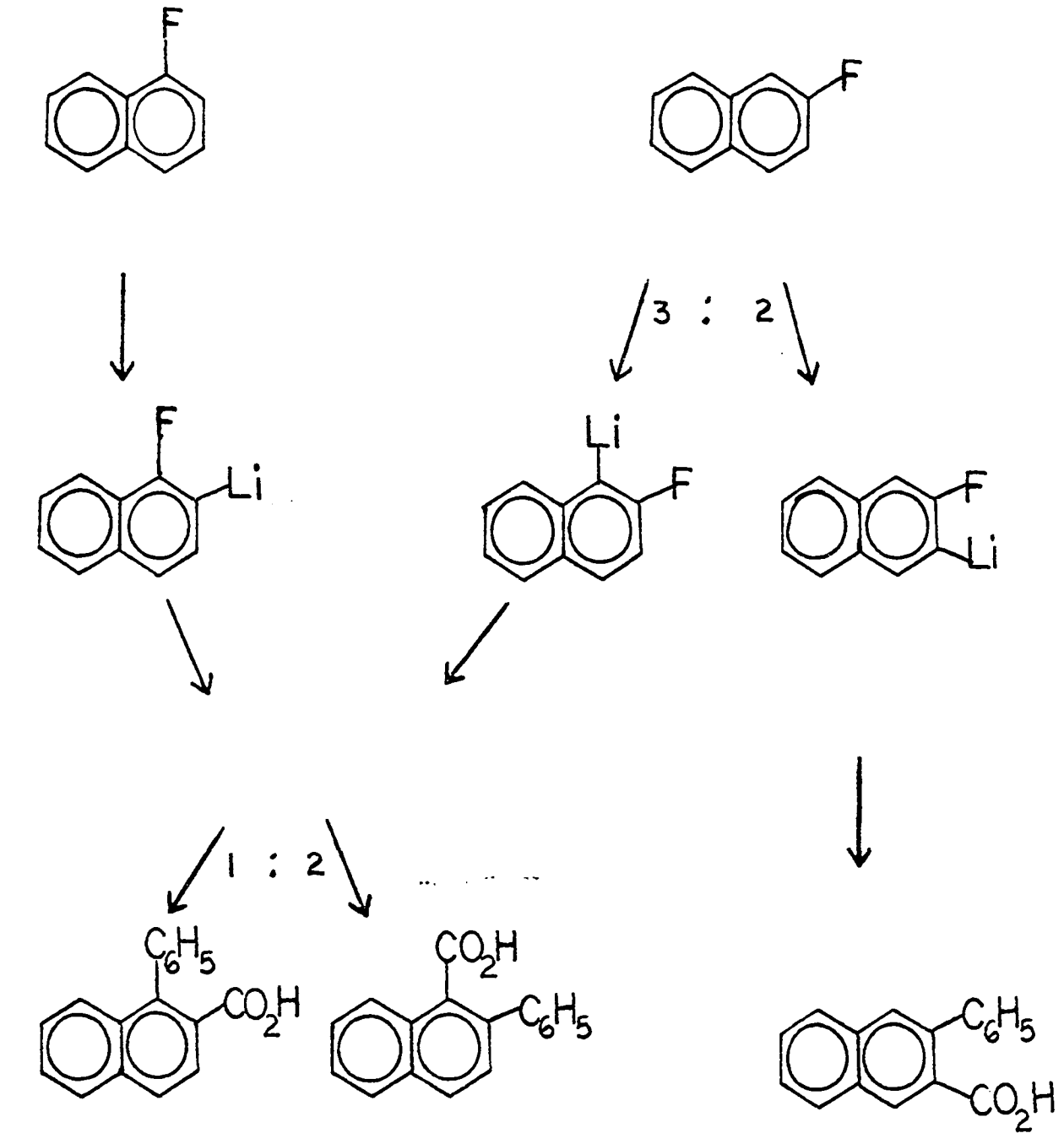
Huisgen and Rist (28) have investigated the lithiation of both fluoronaphthalenes in ether with phenyllithium at 18° and 35°. They observed the formation of three isomeric phenylnaphthoic acids, and proposed the scheme shown in Scheme 1 to explain their observations. Huisgen and Zirngibl (29) suggested that the "identical intermediate" was 1,2-naphthalyne (XXVII). This intermediate would be



XXVII



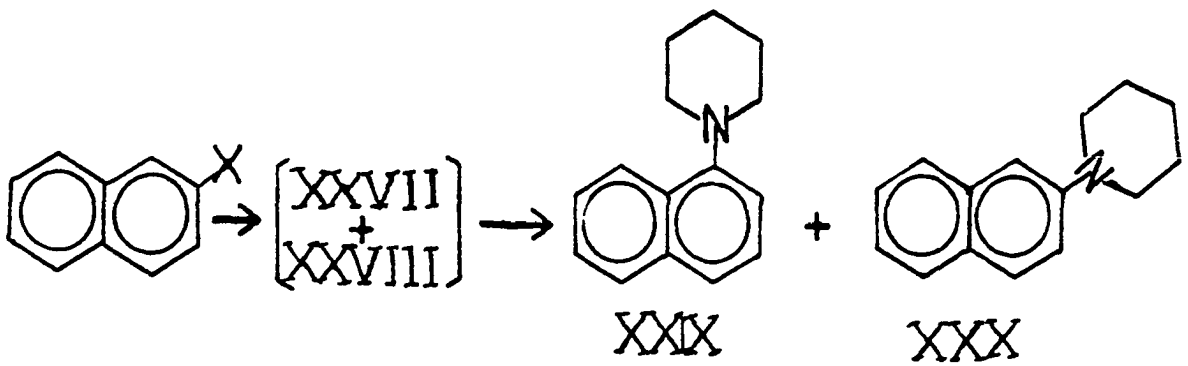
XXVIII



Scheme 1. Lithiation of 1- and 2-fluoronaphthalene by Huisgen and Rist (28)

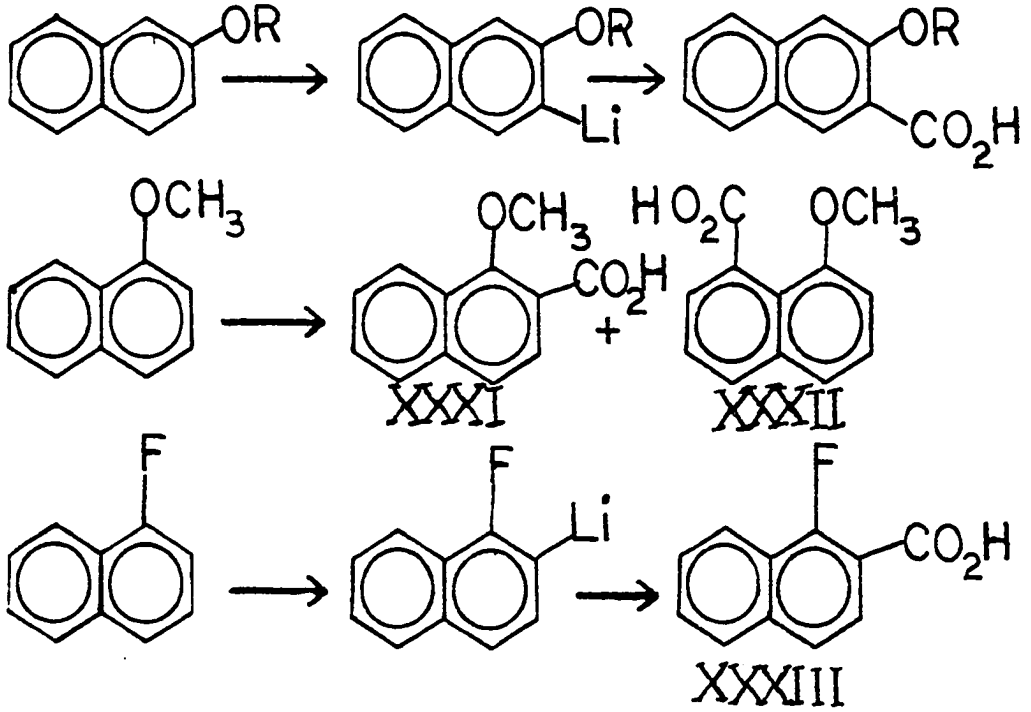
formed upon elimination of lithium fluoride from the lithioaromatic. They obtained the same ratio of 1,2-disubstituted compounds from reaction of 1-fluoronaphthalene with phenyl-, n-butyl-, or t-butyllithium in ether.

Bunnett and Brotherton (30) studied the reaction of the four 2-halonaphthalenes with sodamide and piperidine to yield a mixture of 1- and 2-piperidinonaphthalenes. They observed the same ratio of products, 26% 1- (XXIX) and 74% 2-piperidiononaphthalenes (XXX) in all cases, and explained the products on the basis of the same mixture of 1,2- (XXVII) and 2,3-napthalynes (XXVIII).



Gilman and Bebb (31) carried out the metalation of naphthalene with n-butyllithium in ether and obtained a mixture of 1- and 2- naphthoic acids in a ratio of about 2.5 : 1. The lithiation of 2-naphthol, 2-methoxy-, and 2-ethoxynaphthalene with butyllithium were carried out by Sunthankar and Gilman (32) and Gilman and coworkers (33). Proton abstraction formed the aryllithium which upon treatment with carbon dioxide led to formation of the 3-acids in all cases.

The metallation of 1-methoxynaphthalene with n-butyllithium was investigated by Graybill and Shirley (34). Attack at position 2 was favored, but they did observe a mixture of products following carbonation. They found 83% 1-methoxy-2-naphthoic acid (XXXI), and 17% 1-methoxy-8-naphthoic acid (XXXII).

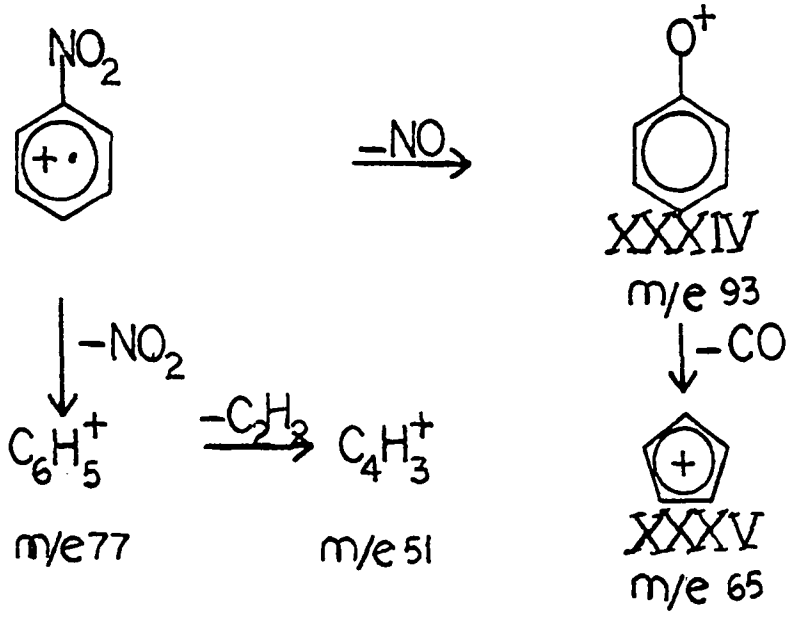


The lithiation of 1-fluoronaphthalene with n-butyllithium in tetrahydrofuran at -55° has been carried out by Gilman and Soddy (35). Under these conditions they were able to effect lithiation without the subsequent elimination that had been noted by the earlier workers. They obtained a 30% yield of 1-fluoro-2-naphthoic acid (XXXIII) following treatment with Dry Ice.

Spectra

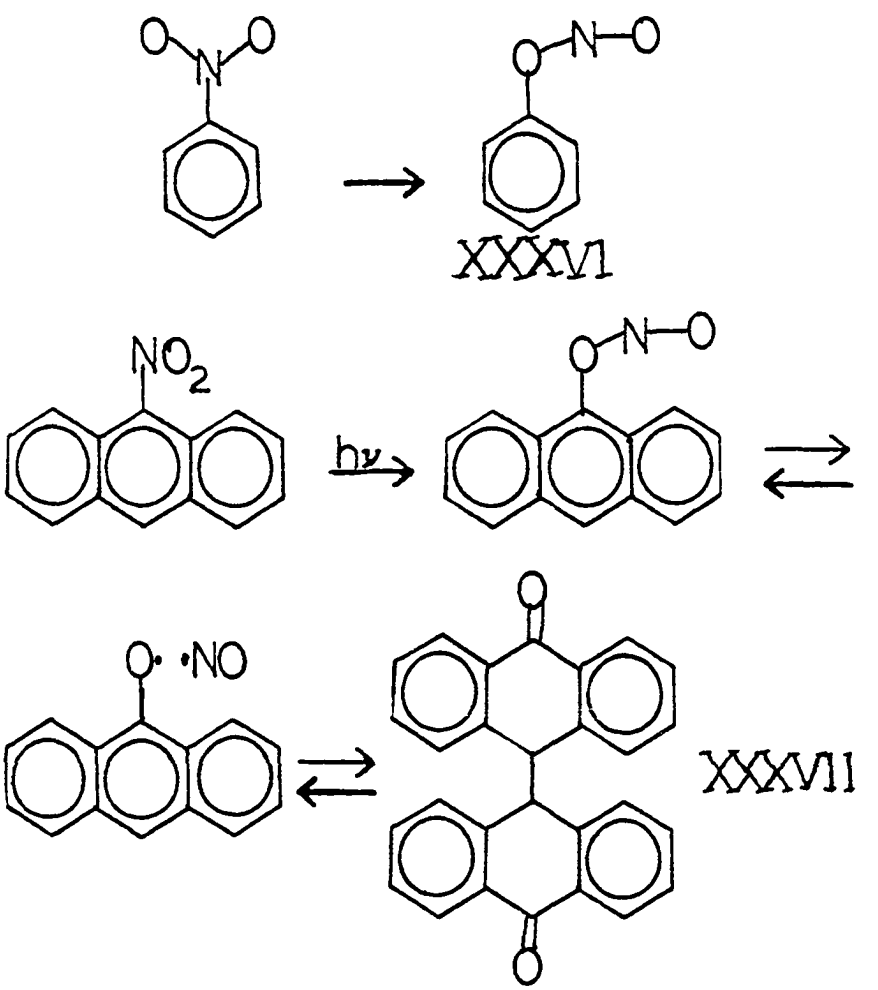
Mass spectra

The mass spectrum of nitrobenzene (36, 37) contains an intense molecule ion and the base peak (m/e 77) is that resulting from the loss of the nitro group. Also observed in the spectrum are a metastable loss of acetylene from the base peak to give the peak at m/e 51, and an ion at m/e 93 (XXXIV), which results from the loss of nitric oxide from the molecule ion. The ion at m/e 93 then loses carbon monoxide to yield the cyclopentadienyl ion at m/e 65 (XXXV).



The loss of nitric oxide from the molecule ion undoubtedly involves an initial rearrangement to the nitrite (XXXVI) prior to fragmentation. Similar rearrangements have

been noted for photochemical reactions by Chapman and coworkers (38) and by Meyerson and coworkers (39). Chapman and coworkers (38) observed the formation of 10,10-bianthrone (XXXVII) upon the irradiation of 9-nitroanthracene and postulated an initial nitro-nitrite rearrangement.

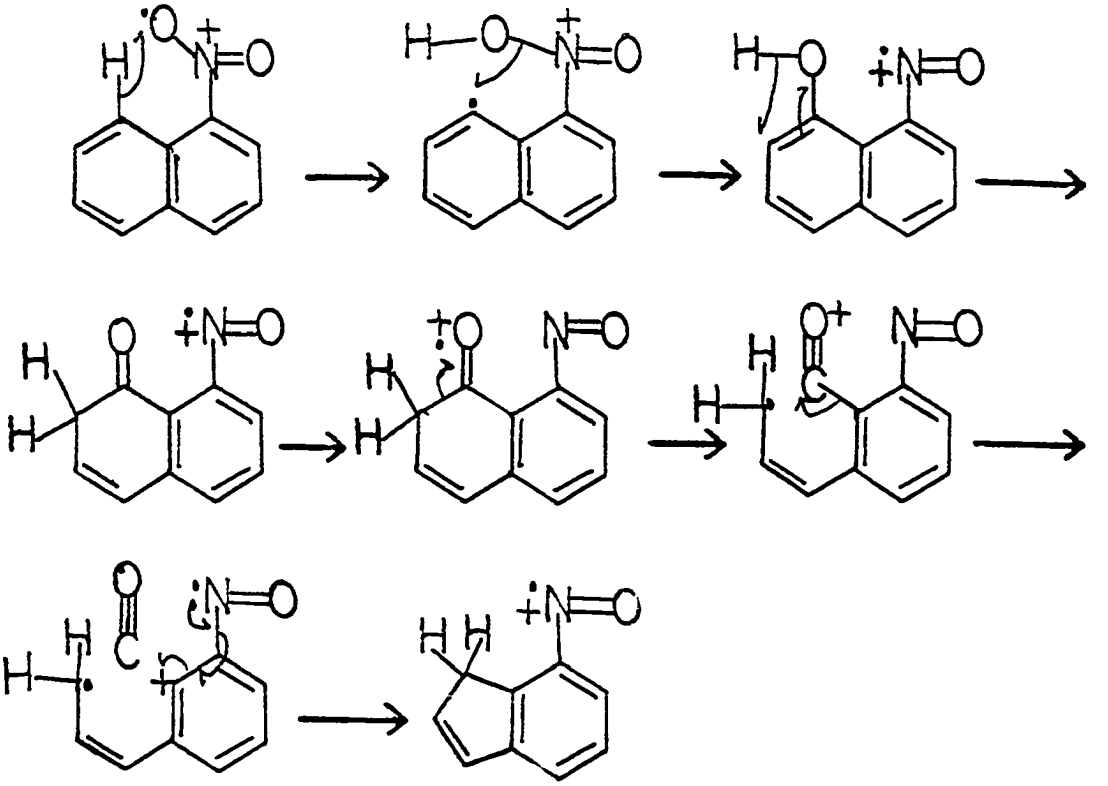


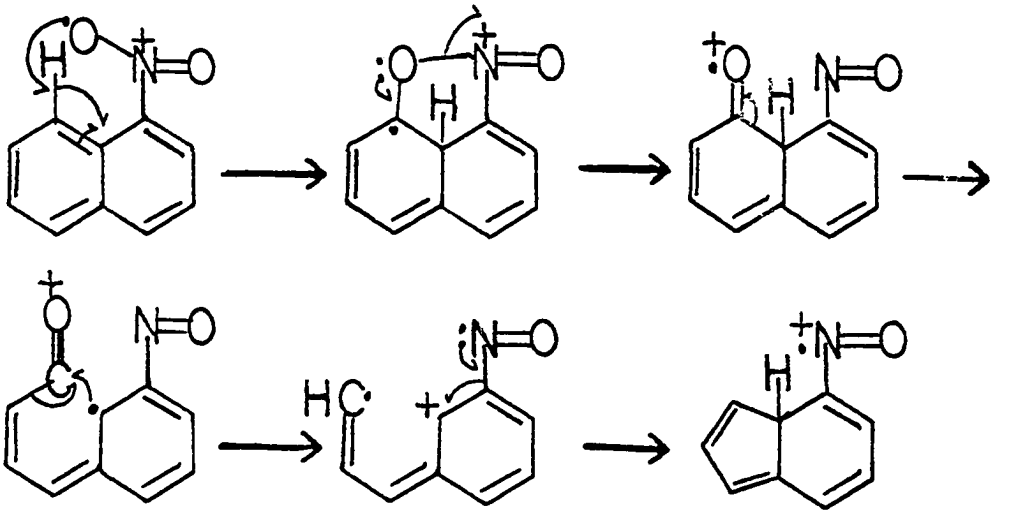
It was noted by Harley-Mason and coworkers (40), Beynon and coworkers (41), and Kinstle and coworkers (42) that the mass spectrum of 1-nitronaphthalene contains a peak

resulting from the loss of carbon monoxide from the molecule ion. However, no such ion was found in the spectrum of 2-nitronaphthalenes or in the nitrobenzenes. Since this loss of carbon monoxide does not occur in 2-nitronaphthalene, or in 8-amino-1-nitronaphthalene or 1,8-dinitronaphthalene (41), a mechanism was proposed which involved attack at the 8-position by one of the oxygen atoms of the nitro group, and eventual loss of C-8 in the carbon monoxide. This was shown to be the case by the work of Kinstle and coworkers (42), who studied this fragmentation using molecules containing ^{13}C in the 1- and 8-positions. Their results indicated, in fact, that the 8-carbon is lost in carbon monoxide.

Two mechanisms have been suggested for this process (40, 41, 42). They both involve transfer of the hydrogen from C-8 to different positions before the loss of carbon monoxide. These mechanisms are shown in Scheme 2. One involves an initial abstraction of the hydrogen by one of the oxygens of the nitro group followed by a hydroxyl transfer to position 8. The second involves a shift of the hydrogen on C-8 to the adjacent bridgehead carbon and attack of the oxygen on the carbon at C-8. Either of these species could then lose the molecule of carbon monoxide from C-8.

The loss of carbon monoxide was noted to be hindered by electron deficiency at the 8-position (41). For example, this loss was less for 4-amino-1-nitronaphthalene than for





Scheme 2. Mechanisms proposed for the loss of carbon monoxide from the molecule ion of nitronaphthalenes (40, 41, 42)

5-amino-1-nitronaphthalene, while it was not observed in 1,5-dinitronaphthalene where there would be a very strong withdrawal of electrons from the position peri to the nitro group, both by resonance and inductive effects of the second nitro group.

Aromatic compounds with a fluorine attached to the ring are characterized by the stability of the C-F bond. McLafferty (43) noted that the mass spectra of fluorobenzene and the fluoronaphthalenes contained only one significant peak, the molecule ion. In the fluoronaphthalenes no other ion exceeded 8% of the base peak. The peak at M-21, corresponding to the loss of H_2F was found to be about 6% of the base peak. The only fragment ion larger than that in the spectrum of the fluoronaphthalenes was the M-1 ion from loss of a hydrogen atom which is about 8% as intense as the base peak.

Bursey and coworkers (44) have used the para-fluorophenyl group as a label in the study of mass spectral reactions. They consider this group employable as a "dead" label as long as the entire aromatic group acts solely as a substituent on another reacting system. This is in agreement with the lack of significant fragmentation of fluorobenzene noted by McLafferty (43). However if the structure of the substituted ring is greatly altered during the

reaction, the para-fluoro substituent may exert a considerable electronic influence.

^{19}F-nmr

The range of chemical shift values which are observed for fluorine in ^{19}F-nmr is much greater than that observed in proton nmr. Thus the effects of a substituent upon the fluorine chemical shift are greatly magnified over the effects of the same substituent on the proton chemical shift. Taft and coworkers (45, 46) carried out extensive studies on the ^{19}F-nmr shielding in a large variety of meta- and para-substituted fluorobenzenes, and within the series of compounds they studied, they observed chemical shift ranges of over 7 ppm (400 Hz).

The substituent chemical shift (SCS) is the difference in chemical shift between the substituted compound and the unsubstituted parent compound. Taft and coworkers (45) were able to obtain a reasonable correlation between the SCS of the meta-substituted fluorobenzenes and the inductive substituent constant σ_I. They also observed a correlation between the SCS of the para-substituted fluorobenzenes and the reactivity resonance effect parameter σ_R^0 (46).

Fukui and coworkers (47) studied the ^{19}F-nmr of several compounds including 1- and 2-fluoronaphthalene and 4-nitro-1-fluoronaphthalene. They interpreted the chemical shift

difference between 1-fluoronaphthalene and 4-nitro-1-fluoronaphthalene on the basis of the π-conjugation decreasing the p-electron density of the fluorine which caused the shift to be negative.

Adcock and Dewar (48) studied the ^{19}F-nmr of a large number of substituted fluoronaphthalenes. They found that the effect of substituents on the chemical shifts of fluorine is different than that on conventional reactions. Thus attempts to correlate the ^{19}F-nmr chemical shifts with chemical reactions will not be successful.

Adcock and Dewar (48) did, however, develop a treatment for determining substituent chemical shifts (SCS) which involves a combination of field and mesomeric effects. They approximated the mesomeric effect by using the charge densities induced at each carbon by a formyl group and multiplied this by a constant characteristic of the substituent. The field effect on the chemical shift of fluorine should be due to the polarization of the electrons forming the C-F bond, and should depend on the field along the axis of the bond. They estimated this field effect by using a point charge model where the vector potential along the C-F bond is given by $F_S Cos\theta/r_{ij}$. Together these effects give the following equation.

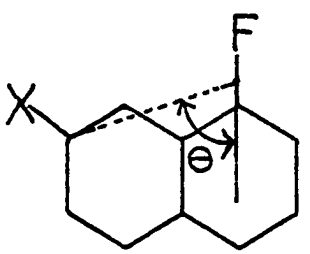
$$SCS = \frac{F_S \cos\theta}{r_{ij}} + M_S q_{ij}$$

where F_S and M_S are constants characteristic of the substituent

r_{ij} is the distance between atom i and the midpoint of the C-F bond

q_{ij} is the charge at atom j induced by formyl at position i

θ is the angle described below



The values they calculated for SCS for the substituents NO_2, CN, and COOH agreed well with the observed values of SCS for those compounds. They used seven isomeric substituted-fluoronaphthalenes for each substituent, but these did not include any in which the substituent was adjacent to the fluorine. It had been observed that in such cases, the chemical shift of fluorine is dependent on considerably different effects. With regard to this, Caldow (49) had noted that the van der Waals shift makes a considerable contribution to the total chemical shift in fluorine, particularly when the substituent is ortho to the fluorine.

Infrared

Several tools have been used for the study of the steric inhibition of resonance in aromatic nitro compounds. Among them have been the use of proton nmr by Wells and Alcorn (50). They observed that the 8-proton in 1-nitronaphthalene absorbs at 1.64τ, the α-protons in naphthalene absorb at 2.20τ, while in 1-nitro-2-methylnaphthalene the 8-proton absorbs at 2.32τ. They attribute this upfield shift in 1-nitro-2-methylnaphthalene to the twisting of the nitro group by the presence of the methyl group on the 2-position. Other studies using proton nmr have been carried out by Heidberg and coworkers (51), and Franck and Williamson (52) who studied the nmr of substituted benzenes.

Trotter (53) has shown by X-ray crystallography that the nitro groups in 1,5-dinitronaphthalene are twisted 49° from the plane of the rings about the C-N bond. Trotter (54) has also determined the structure of nitromesitylene and has shown that the nitro group is twisted 66° out of the plane of the aromatic ring in that compound. He studied the infrared spectra of nitromesitylene and a number of other nitro compounds with the aim of showing a correlation between the infrared absorption frequencies and the degree of twist of the nitro group. The nitro stretching frequencies of nitromesitylene were compared with 9-nitroanthracene and 9,10-dinitroanthracene. The values of these stretching

Table 3. Nitro group frequencies (cm^{-1}) and deviation from coplanarity in nitromesitylene and related compounds

Compound	NO_2 stretching		NO_2 twist in degrees
	Symmetrical	Antisymmetrical	
Non-conjugated	1377	1586	90.0
9-Nitroanthracene	1374	1530	84.7
Nitromesitylene	1362	1531	66.4
9,10-Dinitroanthracene	1367	1542	63.7
Conjugated	1349	1518	0

frequencies as obtained in the solid state are listed in Table 3. From the shift in the absorption to higher frequency in the hindered compounds, it can be seen that the resonance interaction of the aromatic π-electrons with the nitro group is reduced in all the compounds in comparison to the completely conjugated compound. The angle of twist of the nitro group out of the aromatic plane is also included in Table 3, and the correlation between the angle of twist and the reduction in resonance interaction can be observed.

Katrizky and Ridgewell (55) have observed the effect of the peri-hydrogen on an α-substituent in naphthalene. They observed the O-methyl absorption in the infrared spectra of

0.2M chloroform solutions of the methoxynaphthalenes. They found the α-O-methyl absorption at 1104 cm^{-1} and the β-O-methyl absorption at 1033 cm^{-1}. The normal range for monocyclic methoxy compounds is 1013 - 1048 cm^{-1}. They attributed the change to strong steric effects of the peri-hydrogen. This is comparable to the shift observed in 2,6- and 2,3-disubstituted anisoles.

RESULTS AND DISCUSSION

Nitrations of Fluoronaphthalenes

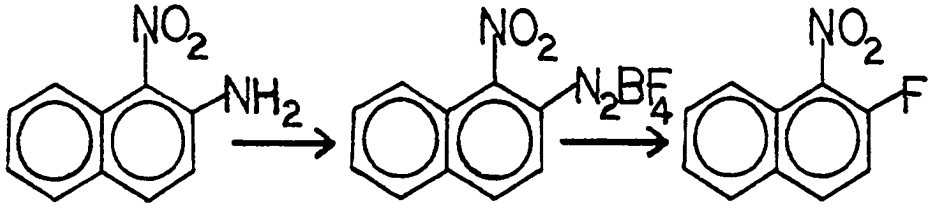
In order to study the effect of various substituents upon the mass spectral behavior of nitronaphthalenes, which was being carried out by other workers in these laboratories, it was desirable to obtain several fluoronitronaphthalenes. The fluoronaphthalenes were nitrated with the aim of isolating the major product in each case and using it for the mass spectral studies. However, upon nitration of 2-fluoronaphthalene a product was obtained which could not be purified to the point where a reasonable melting range could be obtained. This product was then injected into the gas chromatograph and it was found to give five peaks of fairly similar retention time which apparently could all be mononitrofluoronaphthalenes. This presents the problem of just what are these products, and what effect does the fluorine have as a substituent in the nitration of the fluoronaphthalenes. It was decided to pursue this reaction further, and in the course of the work many individual fluoronitronaphthalenes would become available for use in the mass spectral studies.

Synthesis and structure determination

Nitration of each fluoronaphthalene can give rise to seven possible isomeric mononitrofluoronaphthalenes. In order to identify unambigously the products of nitration,

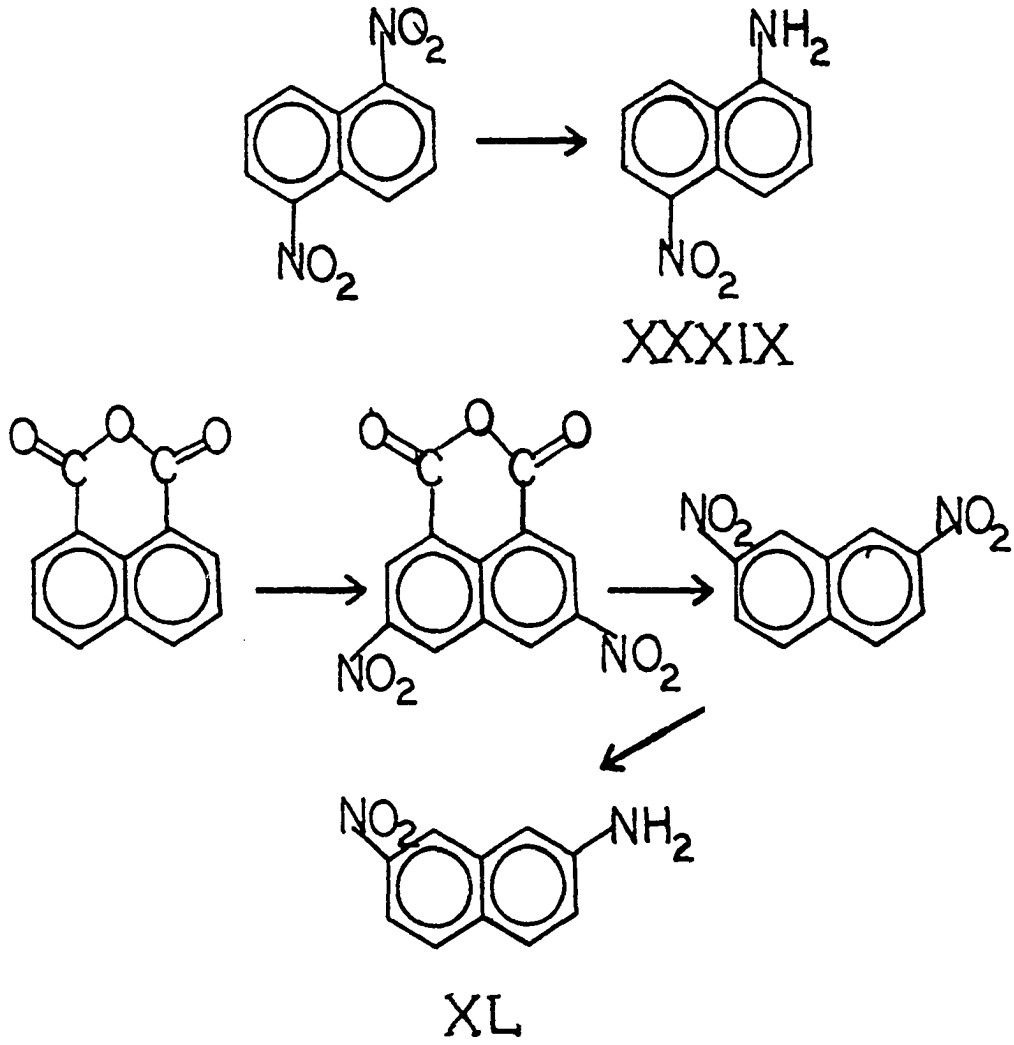
it was necessary to synthesize each of the possible products. Twelve of the fourteen nitrofluoronaphthalenes were prepared from the corresponding nitronaphthylamines via the diazonium fluoroborates. The normal preparation of the diazonium salt which involves diazotization in aqueous hydrochloric acid was found to be too messy, giving rise to much foaming and poor yields. The method used by Brill (56) was then employed with good results. According to this procedure the diazotization is carried out in a mixture of tetrahydrofuran and fluoboric acid at 0°. The diazonium salt then precipitates out as it is formed and may be filtered off and dried. The diazonium salt were then thermally decomposed to produce the desired nitrofluoronaphthalene in about 20 - 30% yield.

Only one of the nitronaphthylamines, 1-nitro-2-naphthylamine (XXXVIII) was obtained as a commercial sample. 1,5-Din-

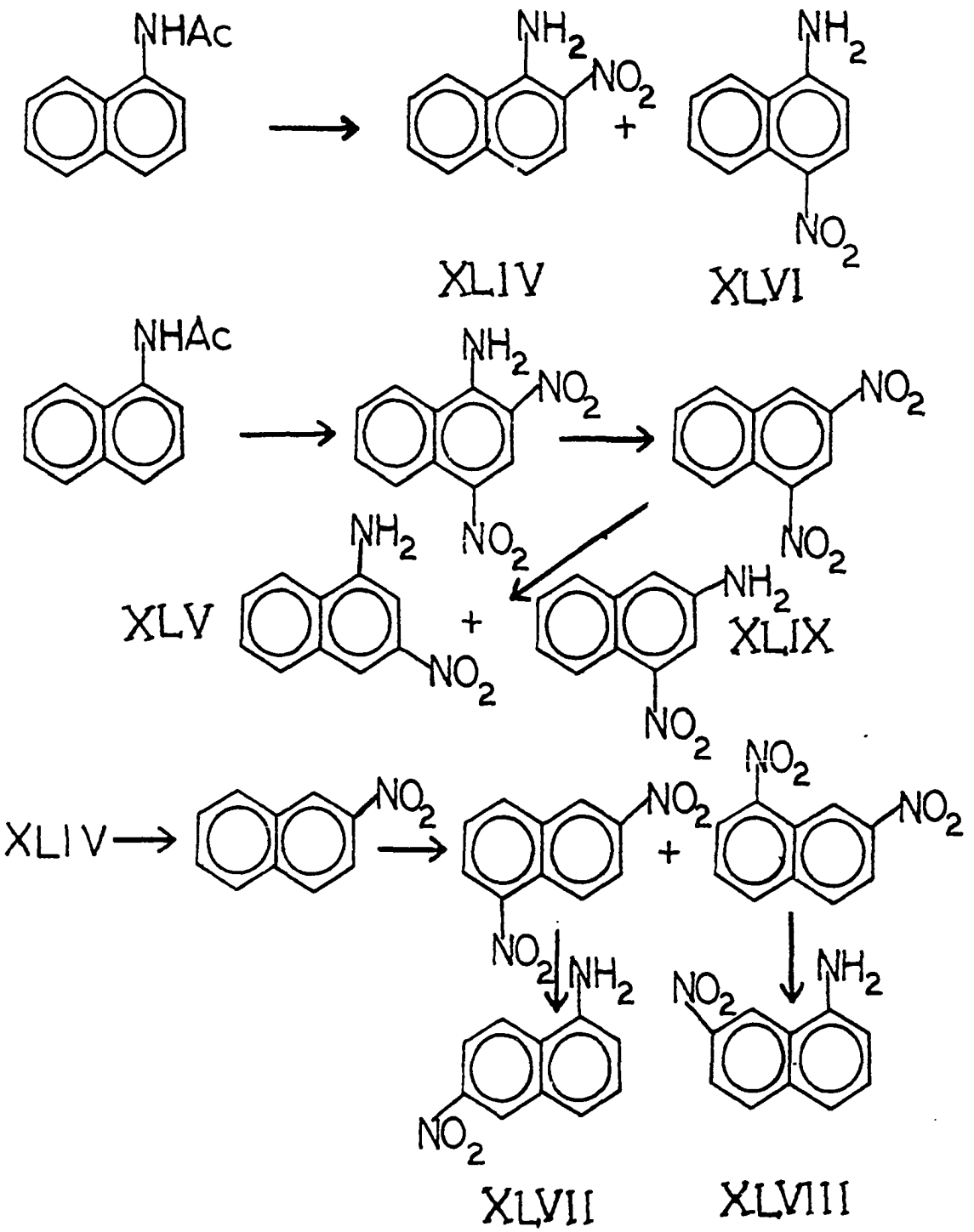


XXXVIII

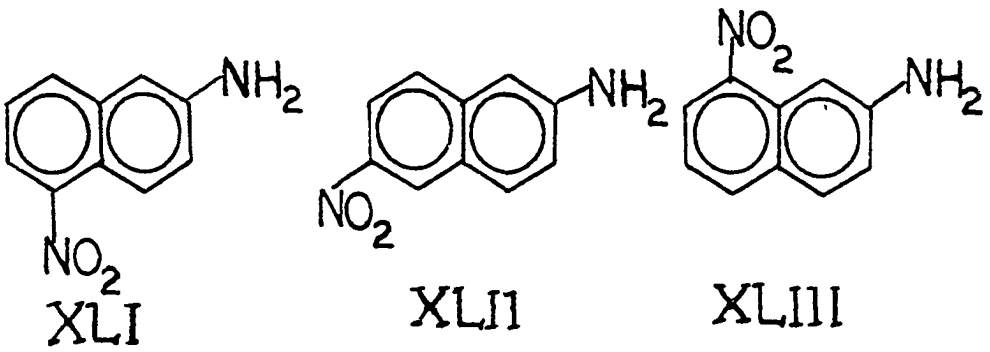
itronaphthalene was reduced to give 5-nitro-1-naphthylamine (XXXIX), while 7-nitro-2-naphthylamine (XL) was obtained from naphthalic anhydride by a series of reactions involving



nitration, decarboxylation, and reduction. Nitration of 2-naphthylamine gave rise to 5-, 6-, and 8-nitro-2-naphthylamines (XLI, XLII, and XLIII respectively). The remainder of the isomers 2-, 3-, 4-, 6-, and 7-nitro-1-naphthylamines (XLIV to XLVIII respectively), and 4-nitro-2-naphthylamine (XLIX) were prepared from 1-naphthylamine as shown in Scheme 3. However, the remaining two isomers 8-nitro-1-



Scheme 3. Nitronaphthylamines prepared from 1-naphthylamine

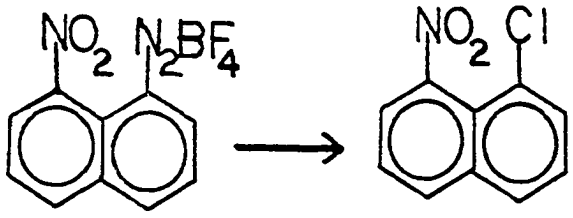


XLI XLII XLIII

fluoronaphthalene and 3-nitro-2-fluoronaphthalene could not be prepared by this method.

Preparation of 8-nitro-1-fluoronaphthalene was attempted by diazotization and decomposition of the corresponding amine, but this attempt failed when the salt decomposed in a flash yielding only a black residue from which no product could be isolated. This result was not unexpected since the same reaction had been carried out by Willstaedt and Scheiber (57) with similar results.

The decomposition was then attempted by the method of Bassilios and coworkers (21). They prepared 8-nitro-1-fluoronaphthalene by decomposition of the diazonium salt in acetone catalyzed by cuprous chloride. However use of this method failed to give any nitrofluoronaphthalenes, even though cuprous chloride from four different sources was used. In one case an excess of cuprous chloride was used and 8-nitro-1-chloronaphthalene (L) was obtained. The corresponding



L

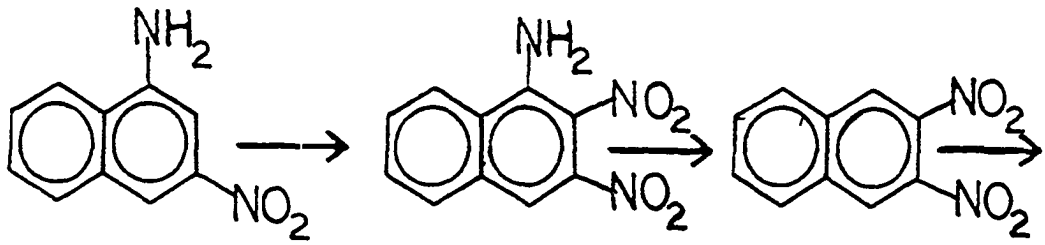
fluorocompound could not be prepared from 4-nitro-1-naphthylamine (XLVI) by this method either.

It was found that the product from nitration of 1-fluoronaphthalene which had the longest retention time on the gas chromatograph did not agree with the retention time of any of the six isomers already on hand, the 2-, 3-, 4-, 5-, 6-, and 7-nitro-1-fluoronaphthalenes. Collection of this product by gas chromatography yielded a yellow solid mp 77-79°. Analysis by mass spectrometry indicated that it was a mononitrofluoronaphthalene, and that the nitro group was on an α-position. Therefore it must be the other possible isomer, 8-nitro-1-fluoronaphthalene (mp lit. 84° (21)).

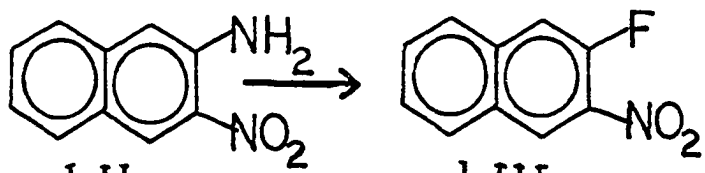
The preparation of the remaining isomer, 3-nitro-2-fluoronaphthalene, was the most difficult and several unsuccessful routes were attempted before success was achieved. The details of this work can be found in the Experimental Section.

The first method attempted involved the reduction of 2,3-dinitronaphthalene (LI) to 3-nitro-2-naphthylamine (LII)

and diazotization of the amine as before to yield 3-nitro-2-fluoronaphthalene (LIII). However it was found that the



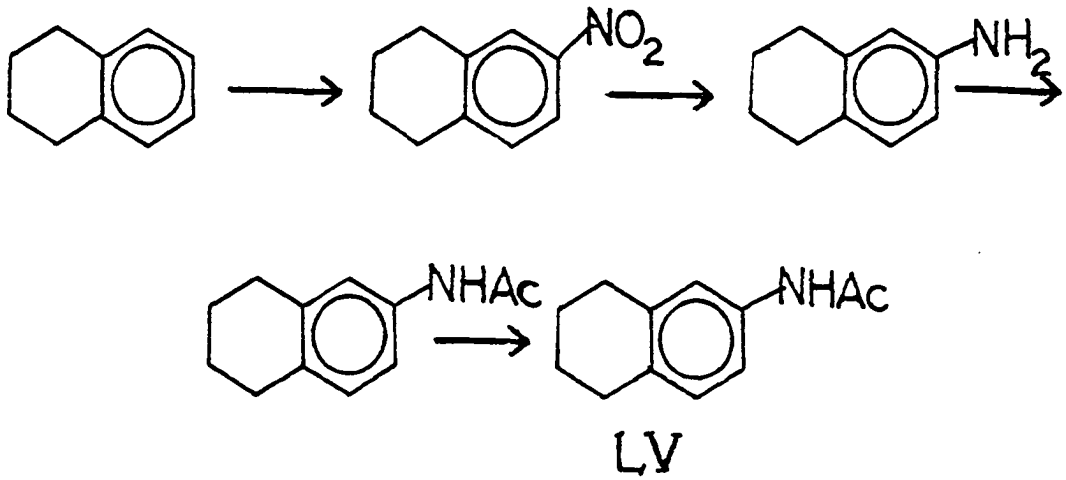
XLV LIV LI



LII LIII

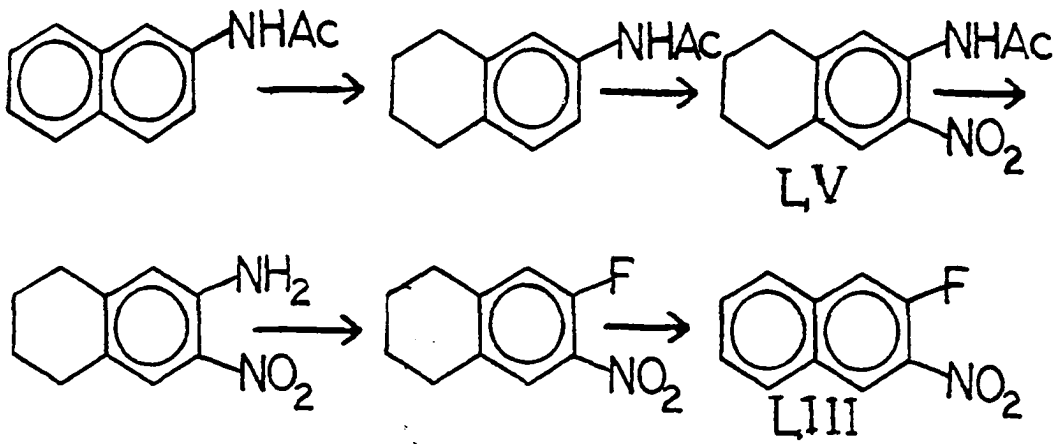
product formed upon nitration of 3-nitro-1-naphthylamine (XLV) was not 2,3-dinitro-1-naphthylamine (LIV), as reported by Hodgson and Turner (58), but was a mixture of compounds in which nitration had occurred in the nonsubstituted ring (59).

Nitration of tetralin to give 6-nitrotetralin, followed by reduction, acetylation, and nitration to yield N-acetyl-7-nitro-6-aminotetralin (LV) was the basis for another route in the attempted preparation of 3-nitro-2-fluoronaphthalene (LIII). However very poor yields in the preparation of LV caused dismissal of this route. It was found that reasonable quantities of LV could be obtained more easily starting with N-acetyl-2-naphthylamine (60). However upon attempted diazotization and introduction of fluorine the major product



LV

obtained was nitrotetralin; i.e., the diazonium group was replaced by hydrogen.

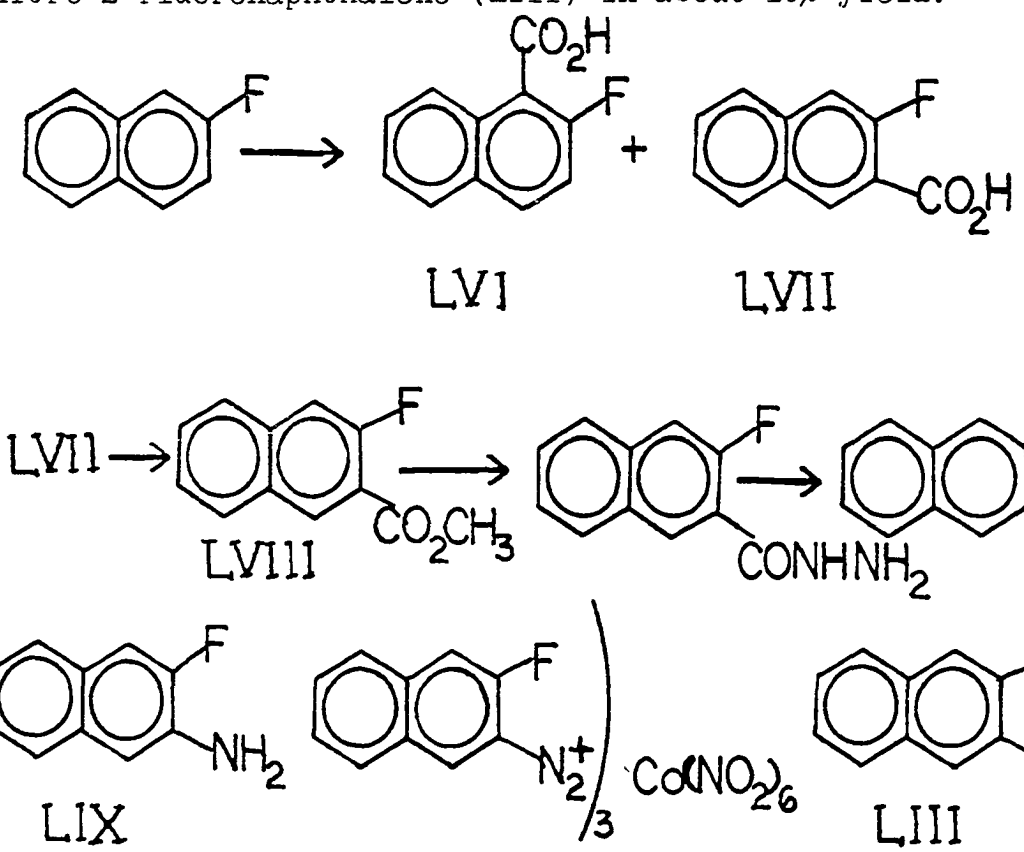


LV

LIII

The successful route involved initial lithiation of 2-fluoronaphthalene followed by carboxylation to give a 70% yield of a mixture of 1- and 3-carboxy-2-fluoronaphthalenes (LVI and LVII). This reaction has not been reported previously, and will be discussed further in the section on

lithiations. A mixture of the corresponding methyl esters was separated by preferential hydrolysis of 3-carbomethoxy-2-fluoronaphthalene (LVIII) using methanolic potassium hydroxide. 3-Carbomethoxy-2-fluoronaphthalene (LVIII) was converted to the hydrazide which was rearranged to form 3-amino-2-fluoronaphthalene (LIX). Diazotization of LIX and decomposition of the cobaltinitrite salt gave the desired 3-nitro-2-fluoronaphthalene (LIII) in about 10% yield.



Identification of the products of nitration of the fluoronaphthalenes was done primarily by comparison of the gas chromatographic retention times of the authentic isomeric nitrofluoronaphthalenes with the nitration mixtures. In

several cases two different isomers had identical retention times which corresponded to that of one peak in the nitration mixture; for example, 6- and 7-nitro-2-fluoronaphthalene were found to have identical retention times. However, these isomers could be separated using a column of Bentone 34 and SE-30 on Chromosorb P, and this data indicated that only the 6-isomer and none of the 7-isomer was present in the nitration mixture. No column was found that would separate 4- and 5-nitro-1-fluoronaphthalene. These two isomers combined make up approximately 80 to 90% of the nitration mixture from the nitration of 1-fluoronaphthalene. The ^{19}F-nmr chemical shift difference in these compounds allowed the determination of their relative amounts by integration of the areas of the peaks in the spectrum. The binary mixture was separated from the total reaction mixture by chromatography on alumina in order to remove the large excess of fluoronaphthalene before running the ^{19}F-nmr spectrum.

As a further check on the product assignments, ^{19}F-nmr spectra were obtained on the complete product mixtures from the nitrations of 1- and 2-fluoronaphthalene with nitric acid in acetic anhydride. The components and their relative amounts observed in the mixtures, as determined by ^{19}F-nmr in dimethylacetamide, are shown in Tables 4 and 5.

A very small peak was observed in the ^{19}F-nmr spectrum of the mixture from 2-fluoronaphthalene nitration at

Table 4. ^{19}F-nmr of the product of nitration of 1-fluoronaphthalene

Component	Hz from 1-fluoro-naphthalene	Per cent from nmr integration	Per cent from VPC
2-Nitro-1-fluoro-naphthalene	+64	3	4.5
1-Fluoronaphthalene	0	--	---
5- and 7-Nitro-1-fluoronaphthalene	-192	13	19.5
8-Nitro-1-fluoro-naphthalene	-468	7	9.5
4-Nitro-1-fluoro-naphthalene	-720	77	66.5

Table 5. ^{19}F-nmr of the product of nitration of 2-fluoro-naphthalene

Component	Hz from 2-fluoro-naphthalene	Per cent from nmr integration	Per cent from VPC
1-Nitro-2-fluoronaphthalene	+428	10	10.5
2-Fluoronaphthalene	0	--	---
4-Nitro-2-fluoronaphthalene	-32	--	1.5
5-Nitro-2-fluoronaphthalene	-152	30	30.0
6- and 8-Nitro-2-fluoronaphthalene	-402	62	58.0

approximately -32 Hz from 2-fluoronaphthelene. This peak could be due to 4-nitro-2-fluoronaphthalene which is present (from VPC analysis) as approximately 1.5% of the product mixture. The results of this study agree with the assignments made on the basis of the correlation of VPC retention times of the authentic isomers with the nitration mixtures.

Product studies

Nitrations were carried out in acetic acid (HOAc) according to the procedure of Schiemann and coworkers (20). Other conditions used for nitration were nitric acid in acetic anhydride (Ac_2O); nitric acid, sulfuric acid, and acetic acid in acetic acid (mixed); nitric acid in nitromethane (CH_3NO_2); and nitronium fluoroborate in sulpholane (NO_2BF_4). The product mixtures were analyzed using an F and M Model 500 gas chromatograph. The best separations were obtained using a LAC-446 column at 181°.

The results of the nitration of 1-fluoronaphthalene, 2-fluoronaphthalene, and naphthalene are shown in Tables 6, 7, and 8. Included in these results are the product ratios of the nitrofluoronaphthalenes and nitronaphthalenes and the relative rates $k_{F\text{-}NAPHTHALENE}/k_{NAPHTHALENE}$, as determined by gas chromotography.

Table 6. Products of nitration of 1-fluoronaphthalene (per cent)

Conditions	Temperature °C	2-NO_2	4-NO_2	5-NO_2	7-NO_2	8-NO_2	$\frac{k_F}{k_{NAPH}}$
Ac_2O	25	4.5	68.0	14.0	4.0	9.5	.31
Ac_2O	35	3.5	69.5	13.0	3.0	10.5	.16
Ac_2O	45	4.0	68.5	14.0	3.0	10.5	.17
CH_3NO_2	25	1.0	74.5	14.0	1.5	8.5	.13
CH_3NO_2	35	1.0	78.0	11.5	1.5	8.0	.14
CH_3NO_2	45	1.0	77.5	11.5	1.0	9.0	.15
Mixed	25	1.0	74.0	11.0	1.5	12.5	.16
NO_2BF_4	25	4.5	68.0	15.5	1.5	10.5	.46
HOAc	60	---	76.0	16.0	0.5	7.5	---

These product studies on the nitration of fluoronaphthalenes indicate that a greater variety of products are formed than were detected in previous studies (20, 21, 22).

Repetition of nitration of 1-fluoronaphthalene under the conditions of Schiemann and coworkers (20) (HOAc at 60°) yielded a mixture of products including 4-nitro-1-

Table 7. Products of nitration of 2-fluoronaphthalene (per cent)

Conditions	Temperature °C	1-NO_2	4-NO_2	5-NO_2	6-NO_2	8-NO_2	$\frac{k_F}{k_{NAPH}}$
Ac_2O	25	10.5	1.5	30.0	20.0	38.0	.25
Ac_2O	35	11.0	1.5	29.0	20.5	38.0	.15
Ac_2O	45	11.5	1.0	29.0	18.0	40.0	.13
CH_3NO_2	25	23.0	2.5	19.0	7.0	49.0	.05
CH_3NO_2	35	23.0	2.0	18.5	8.5	48.0	.04
CH_3NO_2	45	23.0	2.5	19.5	9.0	46.0	.04
Mixed	25	22.5	2.5	20.5	8.0	46.5	.12
NO_2BF_4	25	12.5	1.5	29.5	19.0	37.0	.46
HOAc	60	25	2	19	9	45	---

fluoronaphthalene, the only product reported by Schiemann and coworkers. Under these conditions, 4-nitro-1-fluoronaphthalene was found to make up 76% of the product mixture. Under other controlled conditions 4-nitro-1-fluoronaphthalene was formed in 68 to 78% yield. The product ratios and rates of nitration relative to naphthalene are listed in Table 6.

Table 8. Products of nitration of naphthalene

Conditions	Temperature °C	Per cent 1-NO_2	Per cent 2-NO_2	$\frac{k\alpha}{k\beta}$	$\frac{k\beta}{k\alpha}$
Ac_2O	25	90.9	9.1	10.0	.100
Ac_2O	35	91.3	8.7	10.5	.095
Ac_2O	45	91.7	8.3	11.0	.091
CH_3NO_2	25	97.1	2.9	33.5	.030
CH_3NO_2	35	96.8	3.2	30.2	.033
CH_3NO_2	45	96.4	3.6	26.8	.037
Mixed	25	96.0	4.0	24.0	.041
NO_2BF_4	25	91.0	9.0	10.1	.099

Repetition of the nitration of 2-fluoronaphthalene according to the procedure of Schiemann and coworkers (20) (HOAc at 60°) yielded a mixture of five components including only a 25% yield of 1-nitro-2-fluoronaphthalene, the only component identified by Schiemann and coworkers. Nitration of 2-fluoronaphthalene under other controlled conditions gave 10 to 23% yields of 1-nitro-2-fluoronaphthalene, while the major product in all cases was 8-nitro-fluoronaphthalene

(37 to 49% yield). The product ratios and relative rates are listed in Table 7.

The relative rate studies indicate that 2-fluoronaphthalene is somewhat less reactive toward nitration than is 1-fluoronaphthalene. The fluoronaphthalenes were found to be from 0.05 to 0.46 times as reactive as naphthalene, depending upon nitration conditions. This is in good agreement with the values of 0.15 for the rate relative to benzene for the nitration of fluorobenzene with acetyl nitrate (7), and to 0.45 for nitration with nitronium fluoroborate in sulpholane (6). Extension of the studies of relative rates using 1-chloro- and 1-bromonaphthalene again parallel the benzene series rather closely as shown in Table 9.

The decided deactivating electron withdrawing effect of the fluorine substituent on the naphthalene nucleus is readily apparent. However, it is also obvious that fluoronaphthalene is decidedly more reactive than chloronaphthalene. Consideration of only inductive electron withdrawal would predict the reverse order, so it is apparent that an electron donating resonance effect must be operating in the fluoronaphthalenes.

A convenient method of expressing the reactivity of a position in a substituted compound relative to a single position in an unsubstituted compound is the use of partial

Table 9. Relative rates for nitration with nitric acid in acetic anhydride

	Temperature	ArH	ArF	ArCl	ArBr	ArI
Ar = C_6H_5 [a]	18 °C	1	.15	.033	.030	.18
Ar = $C_{10}H_7$	25 °C	1	.31	.14	.12	---

[a]Values of Bird and Ingold (7).

rate factors. These factors give a good measure of the effect of a substituent on each position. The partial rate factors for the nitration of fluorobenzene with nitric acid in acetic anhydride at 0° were determined by Knowles and coworkers (5). The values from this

$$f_o(m) = \frac{6}{2} \times \frac{\%\ \text{ortho-(meta) product}}{100} \times \frac{k_{C_6H_5X}}{k_{C_6H_6}}$$

$$f_p = 6 \times \frac{\%\ \text{para-product}}{100} \times \frac{k_{C_6H_5X}}{k_{C_6H_6}}$$

work were 0.04 for the ortho-position and 0.77 for the para-position. No nitration was observed for the meta-position so the partial rate factor for that position was 0. This shows that the reactivity of the ortho-position is decreased by 25 times while the reactivity of the para-position is

decreased by 1.3 over its reactivity in benzene by the presence of the fluorine substituent. One also notes the decrease in the inductive influence when going from the ortho to the para-position, while both positions are activated by resonance relative to the meta-position where reaction is not observed.

In order to study the electronic effect of the fluorine at the various positions in the naphthalene nucleus, partial rate factors were determined for each position in fluoronaphthalene relative to a similar position in the naphthalene nucleus. Due to the two different types of positions in the naphthalene nucleus, more elaborate calculations are needed to determine the partial rate factors. They were determined as described by Alcorn and Wells (13, 16) in their studies on the nitration of the methyl- and methoxynaphthalenes. Their values are listed in Tables 10 to 13.

$$\frac{k_i}{k_\alpha} = \frac{i}{100} \times \frac{k_X}{k_N} \times 4\ 1 + \frac{k_\beta}{k_\alpha} \qquad \frac{k_j}{k_\beta} = \frac{j}{100} \times 4\ 1 + \frac{k_\alpha}{k_\beta}$$

Where $k_{i(j)}$ = specific rate constant for nitration at a particular $\alpha(\beta)$-position of the substituted naphthalene

$k_{\alpha(\beta)}$ = specific rate constant for nitration at an $\alpha(\beta)$-position of naphthalene itself

i (j) = percentage of the nitro isomer produced

k_X/k_N = rate of overall nitration of X relative to naphthalene

Table 10. Partial rate factors for nitration of 1-methylnaphthalene

Conditions	$2\text{-}NO_2$	$3\text{-}NO_2$	$4\text{-}NO_2$	$5\text{-}NO_2$	$8\text{-}NO_2$
Ac_2O	20	5.2	4.2	1.0	1.7
CH_3NO_2	161	26	56	8.5	5.3
Mixed	17	3.1	6.5	1.5	1.3
NO_2BF_4	22	0.7	27	4.0	7.4

Table 11. Partial rate factors for nitration of 1-methoxynaphthalene

Conditions	$2\text{-}NO_2$	$4\text{-}NO_2$	$5\text{-}NO_2$
Ac_2O	203	74.5	0.58
CH_3NO_2	14300	4600	18.9

In this work k_α/k_β was obtained by carrying out nitration of naphthalene, i(j) from nitrations of the fluoronaphthalenes, and k_X/k_N from competition reactions between fluoronaphthalene and naphthalene. All of these experiments were carried out under identical experimental conditions. The

Table 12. Partial rate factors for nitration of 2-methylnaphthalene

Conditions	1-NO_2	3-NO_2	4-NO_2	5-NO_2	6-NO_2	8-NO_2
Ac_2O	6.2	0.6	1.9	1.1	6.7	1.6
CH_3NO_2	51	4.4	7.7	5.1	37	11.6
Mixed	6.6	0.7	1.1	0.8	5.0	1.8
NO_2BF_4	5.4	0.5	1.7	0.6	2.8	1.4

Table 13. Partial rate factors for nitration of 2-methoxynaphthalene

Conditions	1-NO_2	6-NO_2	8-NO_2
Ac_2O	32.6	62.3	4.6
CH_3NO_2	1500	6010	270
Mixed	8.3	33.5	1.5

partial rate factors determined for the nitration of the fluoronaphthalenes are listed in Tables 14 and 15.

The positions at which nitration of the fluoronaphthalenes occurs substantiates the importance of electron

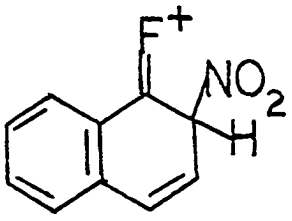
Table 14. Partial rate factors for the nitration of 1-fluoronaphthalene

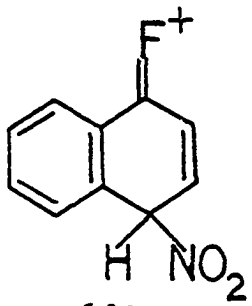
Conditions	Temperature	2-NO_2	4-NO_2	5-NO_2	7-NO_2	8-NO_2
Ac_2O	25	.614	.927	.191	.546	.130
Ac_2O	35	.258	.487	.091	.221	.073
Ac_2O	45	.326	.508	.104	.245	.078
CH_3NO_2	25	.179	.399	.074	.269	.046
CH_3NO_2	35	.175	.451	.066	.262	.046
CH_3NO_2	45	.167	.482	.072	.167	.056
Mixed	25	.160	.493	.073	.240	.083
NO_2BF_4	25	.919	1.374	.313	.306	.212

donation by resonance. One may study this better by looking at the partial rate factors for each position rather than by looking at the product ratios. In 1-fluoronaphthalene the positions that one would expect to be activated by resonance are the same ones in which substitution has predominantly occurred. The major products are 4-nitro-1-fluoronaphthalene followed by, in some cases, 2-nitro-1-fluoronaphthalene. These are the "quinoid" positions in the fluorine-bearing

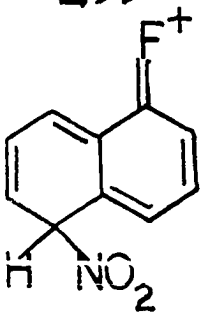
Table 15. Partial rate factors for the nitration of 2-fluoronaphthalene

Conditions	Temperature	1-NO_2	4-NO_2	5-NO_2	6-NO_2	8-NO_2
Ac_2O	25	.116	.017	.330	2.200	.418
Ac_2O	35	.072	.010	.191	1.415	.250
Ac_2O	45	.065	.006	.164	1.123	.227
CH_3NO_2	25	.047	.005	.049	.483	.101
CH_3NO_2	35	.038	.003	.030	.424	.079
CH_3NO_2	45	.038	.004	.032	.400	.076
Mixed	25	.113	.013	.103	.960	.233
NO_2BF_4	25	.248	.030	.585	3.880	.733

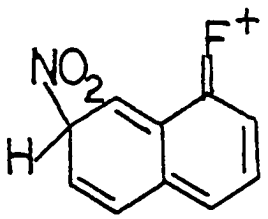




LX



LXI



ring, which are activated by resonance electron donation. Resonance structures in which the aromaticity of the non-substituted ring is not destroyed can be written for them, see LX and LXI. The predominance of 4-nitro-1-fluoro-naphthalene is in agreement with the fact that the 4-position is further removed from the fluorine atom and its strong electron withdrawing inductive effect. In the non-substituted ring, electron donation by resonance would favor nitration at the 5- and 7-positions, and these corresponding nitro compounds are formed.

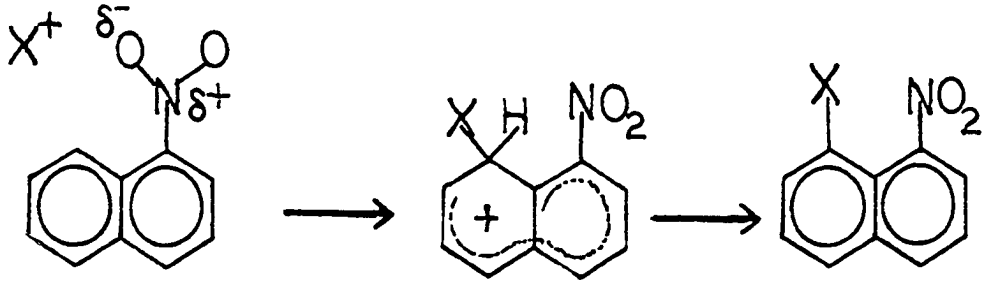
The other product found is 8-nitro-1-fluoronaphthalene This product would not be expected by normal consideration of resonance donation. However, since an α-position is more reactive in naphthalene than a β-position, the 8-position would be expected to be more reactive than the 3- or 6-positions. This higher reactivity of the α-position has been explained by Stock (61) in terms of the electrophilic localization energy L^+. The value of L^+ reflects the difference in delocalization energy of the π-electrons in the starting hydrocarbon and product ion, where

$$L^+ = \text{change in } \pi\text{-electron density} - 2\alpha$$

A smaller value of L^+ indicates less energy required for the reaction. Values of L^+ calculated were 2.54β for benzene, 2.30β for the 1-position of naphthalene, and 2.48β for the 2-position of naphthalene. This thus predicts that

naphthalene would undergo substitution predominantly in the 1-position, and both positions in naphthalene would be more reactive than benzene. Partial rate factors for the nitration of naphthalene are 470 and 50 for the α- and β-positions relative to benzene were determined from the data of Streitwieser and Fahey (62). The substituent effects of the fluorine are then added to this positional effect of naphthalene itself.

One may also argue that the attraction of the positive nitrating agent toward the negative fluorine atom makes attack at the position <u>peri</u> to the fluorine somewhat more favored. A similar explanation was given by Wells and Ward (63) for the large amount of 8-nitration in the nitration of the nitronaphthalenes. They postulated that the dipole of the nitro group may be responsible for results observed since its direction is such that the reagent approach to the 8-



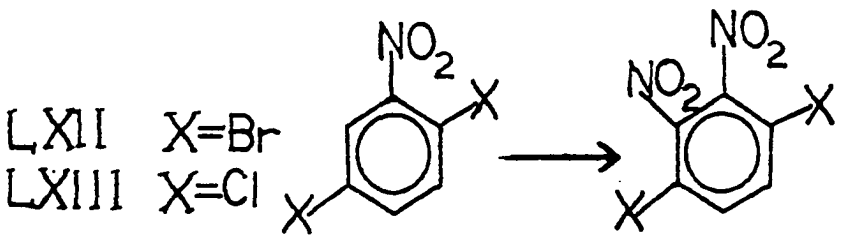
position is facilitated. This type of behavior would not be important for the NH_3^+ group, whose electrostatic field will be the same in all directions. It is only important when the

Table 16. Mononitration of the nitronaphthalenes and the naphthylammonium ions

Substituent	Ratio $\frac{5\text{-}NO_2}{8\text{-}NO_2}$	% Yield
$\alpha\text{-}NH_3^+$	1.8 : 1	94
$\alpha\text{-}NO_2$	1 : 2.0	98
$\beta\text{-}NH_3^+$	1.6 : 1	74
$\beta\text{-}NO_2$	1 : 1.4	99

reagent has a full charge and reagent repulsion or attraction is a rate determining factor. Their results for the nitration of the nitronaphthalenes and the naphthylammonium ions are listed in Table 16.

Hammond and coworkers (64) gave a similar explanation for their results in the nitration of 2,5-dibromo- (LXII) and 2,5-dichloro-nitrobenzene (XLIII). They observed nitration at the 6-position, which would otherwise seem to be the less likely product due to greater steric hindrance and strong deactivation of the position next to the nitro group. However their proposals applied only to planar non-linear substituents containing a dipole whose negative end may attract the attacking reagent.



At the remaining positions in 1-fluoronaphthalene, one would not expect to find significant nitration, since there would be no activation to counteract the inductive deactivation by the fluorine substituent. Assuming that the partial rate factors for the 3- and 6-positions were similar to that of the 8-position, the yield of the 3- and 6-nitro-1-fluoronaphthalenes would range from 0.2 to 1% of the nitration product. If they were present in such small amounts, detection and identification would be quite difficult.

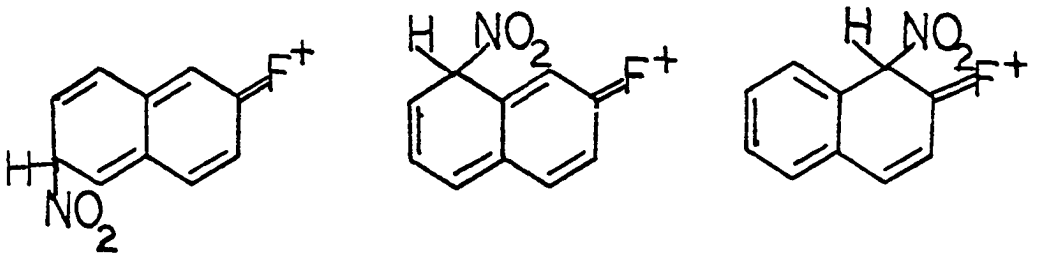
The three products formed in the greatest amounts in the nitration of 1-fluoronaphthalene are the result of nitration in the same positions as those found by Bassilios (17) in the nitration of 1-chloronaphthalene. However the order he observed was 4 > 8 > 5, while that observed in this work with 1-fluoronaphthalene was 4 > 5 > 8 > 2 = 7. This difference may be due to the decreased importance of the resonance effect in the case of the chlorine substituent, thus decreasing the activation of the 5-position over the 8-position. The decreased importance of the inductive effect of the halogen in

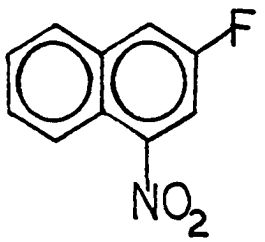
the case of chlorine would also favor 8-nitration in 1-chloronaphthalene over that in 1-fluoronaphthalene.

The nitration of 1-methoxynaphthalene, a very reactive substrate involving a substituent with a strong resonance electron donation, was studied by Alcorn and Wells (16). The positions of nitration have partial rate factors in the order of 2 > 4 > 5, as shown in Table 11. This shows the decrease of inductive electron withdrawal relative to the increase of electron donation by resonance in 1-methoxynaphthalene over 1-fluoronaphthalene.

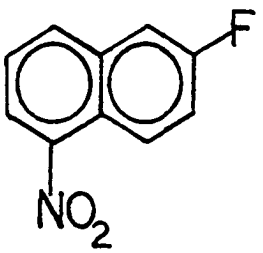
1-Methylnaphthalene is a substrate with reactivity much more similar to that of 1-fluoronaphthalene. In this compound the order of the partial rate factors is generally 2 > 4 > 3 > 5 > 8. Here both inductive and resonance effects favor nitration, and this readily explains the order with activation of positions 2, 4, and 5 by resonance donation and 2 > 3 > 4 by inductive donation.

Nitration of 2-fluoronaphthalene yields five mononitroproducts, the 1-, 4-, 5-, 6-, and 8-nitro-2-fluoronaphthalenes. By far the major amount of nitration occurs in the ring not bearing the fluorine which is evidence again for the strong inductive electron withdrawal by the fluorine. From the partial rate factors, listed in Table 7, it is seen that the predominant products are the 6- followed by 8-nitro-2-fluoronaphthalene, both positions activated by resonance.





LXIV



LXV

In two cases, the 6-position has a partial rate factor greater than 1.0 indicating that it is actually more reactive than a similar (β)-position on naphthalene. The third and fourth most reactive positions are the 1- and 5-positions, their order being dependent upon the conditions of nitration. The 1-position is activated by resonance donation, but since it is located next to the fluorine-bearing carbon it is very strongly deactivated by inductive withdrawal. The 5-position is an α-position in the non-substituted ring, which is located quite distant from the fluorine atom.

The last observed product is 4-nitro-2-fluoronaphthalene (LXIV), the result of nitration in the non-activated α-position in the fluorine-bearing ring. Here one can see the large difference in the inductive effect as one goes further

from the fluorine atom. There is a change of a factor of 8 or 20, depending upon conditions, as one moves from the 4- (LXIV) to the 5-position (LXV). This increase in rate occurs as one moves into the ring not bearing the fluorine atom, and goes two carbon atoms further away from the electronegative fluorine atom.

In agreement with these findings are those of Zalkind and Filinov (19) who were able to identify 8- and 1-nitro-2-bromonaphthalene among the products of nitration of 2-bromonaphthalene. Scheid (18) observed that nitration of 2-chloronaphthalene yields 8-nitro-2-chloronaphthalene.

The order of partial rate factors for the nitration of 2-methoxynaphthalene (16) was 6 > 1 > 8 while the order observed in the nitration of 2-fluoronaphthalene was generally 6 > 8 > 5 > 1 > 4 as listed in Table 15. The difference in reactivity of position 1 can be explained by the increased importance of the inductive effect in 2-fluoronaphthalene relative to that in 2-methoxynaphthalene.

The partial rate factors for nitration of 2-methylnaphthalene were generally in the order 1 > 6 > 8 > 4 > 5 > 3. The main difference in the order of activation between 2-fluoronaphthalene and 2-methylnaphthalene is the change in position 1. It is deactivated by inductive withdrawal by the adjacent fluorine but activated by inductive donation by the methyl group.

Mechanism

It is noted that nitration in nitromethane and with mixed acid gave lower values of $k_{F\text{-}NAPH}/k_{NAPH}$ for both 1- and 2-fluoronaphthalene than nitrations with nitronium fluoroborate and with nitric acid in acetic anhydride. In conjunction with this difference in relative rates, there is a striking difference in position selectivities (Tables 6 and 7), which is particularly noticeable in nitration of 2-fluoronaphthalene. There is a very close similarity in the product ratios of nitrations in acetic anhydride and with nitronium fluoroborate, and again between the nitrations in nitromethane and with mixed acid. This similarity seems to indicate a similarity in mechanism within each pair of nitration conditions and a noticeable difference in mechanism between the two pairs of nitration conditions.

The same relationship was shown for nitration of naphthalene as shown in this work in Table 8 and in the work of Alcorn and Wells (13) in Table 2. Similar, although not as striking, relationships were observed in the products and relative rates in nitration of the methylnaphthalenes in the work of Alcorn and Wells (13). Their results are listed in Tables 17 and 18.

The mechanisms and nitrating species in nitration have been discussed by Hughes and coworkers (65), Norman and Taylor (11), and many others. Olah and coworkers (66) have

Table 17. Nitration of 1-methylnaphthalene (per cent)

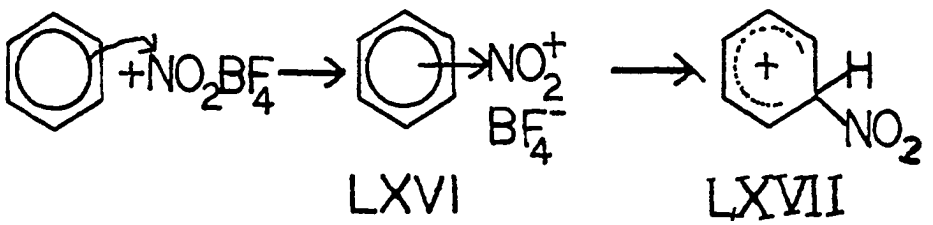
Conditions	2-NO_2	3-NO_2	4-NO_2	5-NO_2	8-NO_2
Ac_2O	23.3	6.1	43.0	10.1	17.5
CH_3NO_2	7.4	1.2	73.5	11.1	6.8
Mixed	9.5	1.0	68.8	9.4	11.2
NO_2BF_4	33.6	1.2	43.9	6.3	11.9

Table 18. Nitration of 2-methylnaphthalene (per cent)

Conditions	1-NO_2	3-NO_2	4-NO_2	5-NO_2	6-NO_2	8-NO_2
Ac_2O	52.7	0.6	17.1	9.0	6.6	13.7
CH_3NO_2	66.2	0.1	10.1	6.6	1.7	15.2
Mixed	63.6	0.3	10.0	7.4	2.2	17.4
NO_2BF_4	56.6	0.6	18.7	7.0	3.0	14.1

found that nitrations with nitronium fluoroborate in organic solvents cannot be considered as a reaction of the free nitronium ion, since their cryoscopic measurements of nitronium fluoroborate in sulpholane showed that it exists

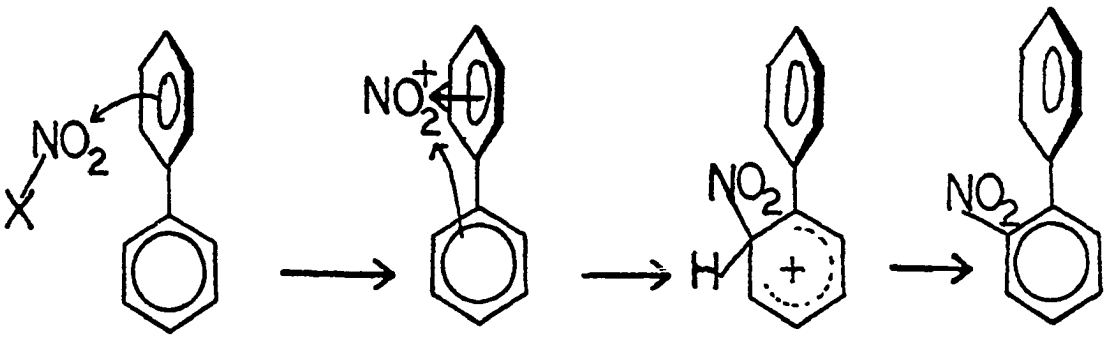
as an ion pair, not as the free nitronium ion. Olah and coworkers (67) have described the nitration with nitronium fluoroborate in sulpholane in terms of a π-complex formed by a nucleophilic displacement of the solvated nitronium fluoroborate by the π-electrons of the aromatic substrate. According to this proposal, formation of the π-complex (LXVI) is the rate determining step, and the π-complex then collapses to the σ-complex (LXVII) which then leads to the observed products.



LXVI LXVII

In nitration with nitric acid in acetic anhydride at 25°, Bordwell and Garbisch (68) have shown that the electrophilic reagent present is acetyl nitrate. Fischer and coworkers (69, 70) have suggested that protonated acetyl nitrate is the species responsible for nitration of toluene and ortho-xylene using nitric acid in acetic anhydride. Taylor (71, 72) in work published after we had obtained our preliminary results, observed that the nitration of biphenyl with dinitrogen pentoxide in acetonitrile, protonated acetyl nitrate, and nitronium fluoroborate in sulpholane gave similar high ortho/para ratios among the products. He explained this as arising

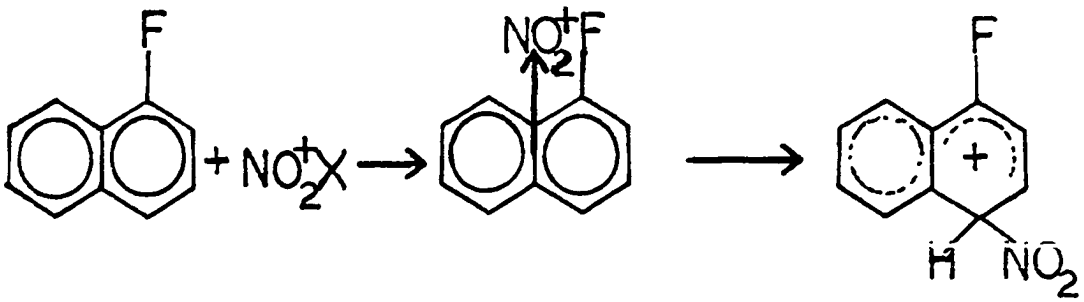
from a mode of nitration in which the π-electrons of the ultimately unsubstituted phenyl-ring carries out a nucleophilic displacement of X or X^- from NO_2^+X or NO_2X to give a



LXVIII LXIX

π-complex involving the nitronium ion. This π-complex (LXVIII) then goes on to form the most accessible σ-complex (LXIX), which is, because of the nonplanarity of the phenyl-rings, that formed at the ortho-position in the other ring.

In view of the close similarity of the products of the nitration of the fluoronaphthalenes with nitronium fluoroborate and with nitric acid in acetic anhydride, it would seem reasonable that nitration with both of these reagents proceeds via formation of a π-complex.



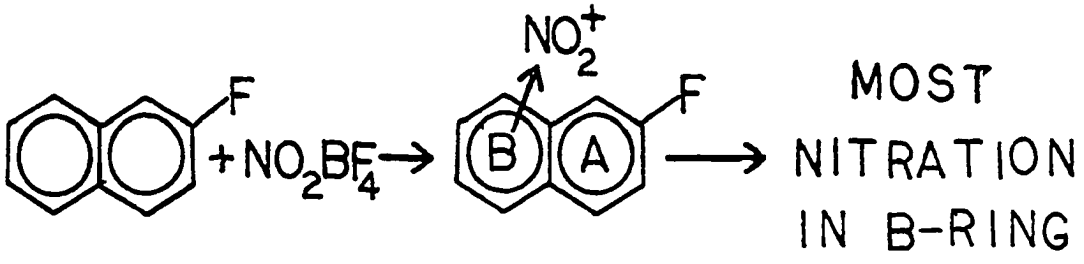
Nitrations with nitric acid in nitromethane and with nitric acid and sulfuric acid in acetic acid have been described as consistent with the rate determining step being heterolysis of the nitric acidium ion (11). The nitronium ion which is generated then reacts rapidly with the substrate.

$$H_2O^+ - NO_2 = H_2O + NO_2^+$$

The nitronium ion thus formed reacts directly to form the σ-complex which goes on to form products. It has been noted that a parallel between low selectivity nitration and Lewis basisity suggests rate controlling π-complex formation in one case (Ac_2O, NO_2BF_4), while a parallel between high selectivity nitration and other electrophilic substitution reactions suggests rate controlling σ-complex formation in the other cases (68).

In view of the difference in the type of complex originally formed, it is not surprising to find a difference in product ratios between the two sets of nitration conditions. In those nitrations leading directly to the σ-complex the product ratios are determined solely by a competition among the positions on the naphthalene nucleus with the solvated nitronium ion. However in the cases where the π-complex is originally formed, there is already an orientation of the nitronium ion in the complex, and this complex then collapses to the σ-complexes which lead to the observed

products. In view of the very strong electron withdrawal by the fluorine on the one ring, it seems reasonable that the nitronium ion in the complex may be located to greater degree over the ring not bearing the fluorine substituent. That ring would have a smaller deficiency of the electrons available for formation of the complex, since it is further away from the electron withdrawing fluorine substituent. The effect of such an orientation is particularly noticeable in 2-fluoronaphthalene, where 25% of the product is found in the fluorine-bearing ring in cases involving original σ-complex formation, while only 12% of the product is found in the fluorine-bearing ring when π-complex formation occurs.



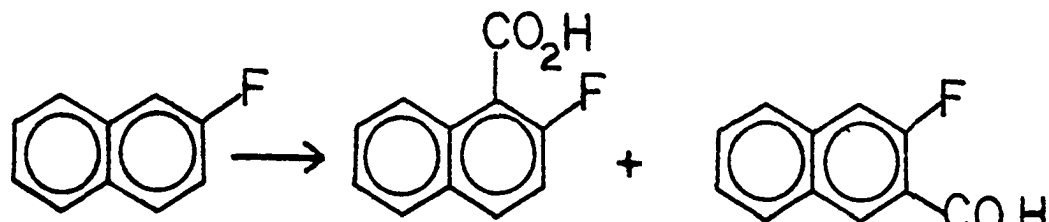
Extension of this idea of the π-complex with the nitronium ion oriented to a greater degree over one ring to the other naphthalene systems which have been extensively studied is not possible. With the methoxynaphthalenes, the resonance activation is so strong that the inductive effect doesn't differentiate the rings as it does with the fluoronaphthalenes. With the methylnaphthalenes, the inductive and resonance effects are both in the same direction (donation),

but not strong enough to cause such a large differentiation between the two mechanism as far as amount of nitration in each ring is concerned. Thus in these systems there is no indication that π-complex orientation is important.

Lithiations

The treatment of 2-fluoronaphthalene in tetrahydrofuran (THF) under nitrogen or argon at -65° with n-butyllithium in hexane, conditions similar to those of Gilman and Soddy (35), yielded greater than 70% of two acids along with recovered 2-fluoronaphthalene (total recovery near 95%). Repeated recrystallization resulted in the separation of two acids, mp's 151-153° and 196.5-198° respectively. Based on comparisons of the melting points of the 2-acids with melting points of a variety of naphthoic and 2-substituted naphthoic acids, it was most reasonable that the lower melting acid was 2-fluoro-1-naphthoic acid, since in general the 1-acids had lower melting points than the two acids. Proton nmr (dimethylacetamide) showed a downfield doublet at 520 Hz from TMS (J_{H-F} = 7 Hz) in the spectrum of the higher melting acid, while no such absorption was present in the spectrum of the other isomer. This one proton doublet was assigned to the 4-proton in 2-fluoro-3-naphthoic acid,

which was coupled to the fluorine and shifted downfield by the adjacent carboxyl group. A series of reactions which converted the higher melting acid to 3-nitro-2-fluoronaphthalene proved conclusively that the acid with mp 151-153° was 2-fluoro-1-naphthoic acid (LXX) and the acid with mp 196.5-198° was 2-fluoro-3-naphthoic acid (LXXI).



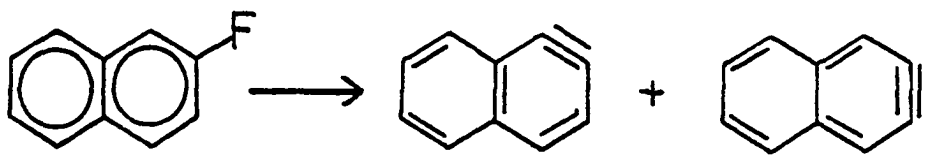
LXX LXXI

The carboxylation products were obtained in the ratio of approximately 54% 2-fluoro-1-naphthoic acid (LXX) to 46% 2-fluoro-3-naphthoic acid (LXXXI) when n-butyllithium was used for the lithiation. This product ratio is quite consistent with that observed by Huisgen and Rist (28). They observed 60% metallation at the 1-position and 40% at the 3-position by lithiating 2-fluoronaphthalene with phenyllithium in ether. However the products they obtained were the phenylnaphthoic acids formed as a result of elimination and naphthalyne formation, not the fluoronaphthoic acids.

The use of t-butyllithium changed the product ratio to 39% 2-fluoro-1-naphthoic acid and 61% 2-fluoro-3-naphthoic acid. The acids from the lithiation with t-butyllithium

were obtained in a total yield of approximately 55% along with approximately 30% recovered starting 2-fluoronaphthalene. This change in product ratio is in the direction expected due to increased steric hindrance of approach of the organolithium to the 1-position by the peri-hydrogen.

Steric effects in the metallating reagent were also postulated by Bunnett and Brotherton (73) to explain the difference between their data and that of Huisgen and Rist (28). Huisgen and Rist had observed 60% 1,2- and 40% 2,3-naphthalyne as intermediates in the lithiation of 2-fluoro-



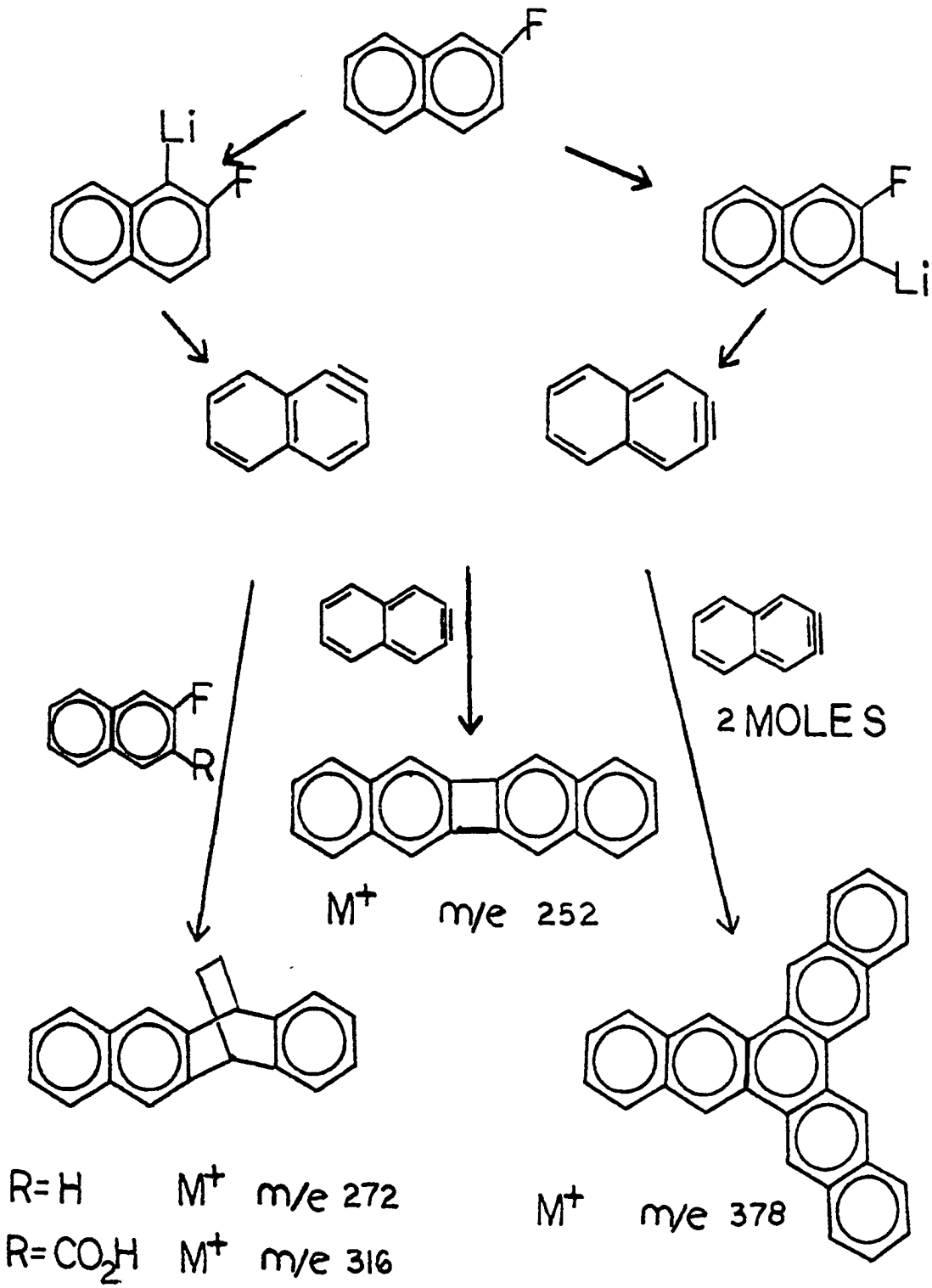
naphthalene with phenyllithium. Using the smaller reagent sodamide in piperidine, Bunnett and Brotherton (73) estimated formation of 81% 1,2- and 19% 2,3-naphthalyne from 2-fluoronaphthalene.

If lithiation of 2-fluoronaphthalene was carried out at -65° there was little tendency toward elimination and naphthalyne formation. If the temperature of the lithiation mixture was allowed to rise to approximately -30° elimination and naphthalyne formation became important. As the temperature of the mixture rose to near -30° an exothermic reaction occurred which caused the temperature to climb rapidly to

-15°. After again cooling to -30° for some time a portion of the mixture was quenched with Dry Ice in ether to produce a mixture of products including fluoronaphthalene and a variety of products whose molecular weights, determined by mass spectrometry, are listed in roughly decreasing order of quantitative importance: M^+ at m/e 378, 372, 190, 316, and in very minor amounts 252 and 184. Allowing the temperature of the lithiation mixture to rise to 0° before quenching yielded a similar mixture of products except that no acids at all are obtained. The compounds obtained at m/e 190 and 184 correspond to fluoronaphthoic acid and butylnaphthalene respectively. The formation of the higher molecular weight products can be explained as shown in Scheme 4.

As the reaction mixture warms to near -30°, elimination of lithium fluoride occurs to form isomeric naphthalynes which then react in a variety of ways. By the time the mixture is allowed to warm to 0°, all the lithio-naphthalene compounds have reacted and none are left to react with the carbon dioxide to form acids. All the compounds formed from a molecule of naphthalyne may be a mixture of isomers resulting from the reaction of either 1,2- or 2,3-naphthalyne.

Similar behavior was noted by Gilman and Soddy (35) in the lithiation of fluorobenzene in THF. They observed that upon allowing the temperature of the lithiation mixture to



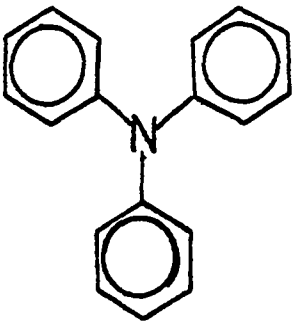
Scheme 4. Lithiation of 2-fluoronaphthalene

rise to -30° an exothermic reaction occurred. Triphenylene was found among the products of this reaction.

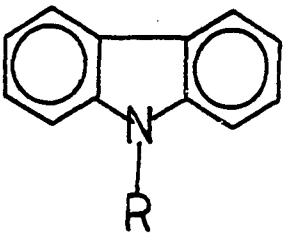
The presence of fluorine as a substituent in lithiation of 2-fluoronaphthalene has considerable effect upon the rate of the reaction. The lithiation of naphthalene in THF with n-butyllithium at 25° gives rise to only a 20% yield of a mixture of 1- and 2-naphthoic acids along with 80% recovery of naphthalene. Similar results were obtained by Gilman and Gray (74). The fluorine substituent allows the reaction to occur at -65° to give a 70% yield of fluoronaphthoic acids. The strong electron withdrawing inductive effect of the fluorine makes the adjacent hydrogen more acidic, and stabilizes the anions formed giving rise to faster reaction. This activating effect of fluorine is similar to that of other strong inductive electron withdrawing substituents such as amino and alkoxy groups. Lithiation of other halonaphthalenes generally gives rise to halogen-metal interchange or elimination, in contrast to the lithiation of the fluoronaphthalenes at -65°.

The fluorine limits the attack to the adjacent positions. Similar behavior is noted in the lithiation of aromatic ethers and amines. In the lithiation of various anilines, Gilman and coworkers (75) and Gilman and Spatz (76) observed lithiation only in the positions ortho to the amino group.

The exceptions they noted were triphenylamine (LXXII) and N-phenylcarbazole (LXXIII). In these cases they noted lithiation in the meta-positions. They explained this on the basis of steric hindrance due to the three phenyl groups, and found that replacement of one of the phenyl groups with a smaller group such as hydrogen of a methyl group (LXXIV) allows lithiation to occur in the ortho-position. In the naphthalene series, lithiation of the 1-ethers gave exchange at the 2- and 8-positions as noted by Graybill and Shirley



LXXII



LXXIII R = C_6H_5

LXXIV R = CH_3

(34), while lithiation of the 2-ethers was observed to give lithiation in the 3-position (32, 33).

The lithiation of 2-fluoronaphthalene with n-butyllithium gives a 54 to 46% ratio of 2-fluoro-1-naphthoic acid and 2-fluoro-3-naphthoic acid, which is the same as the α/β ratio obtained in the lithiation of naphthalene in this work, where the ratio of 1- to 2-naphthoic acids was also 54 to 46%.

Thus the fluorine does have a strong effect on determining the position and rate of lithiation, in so far as it causes attack to occur at the positions adjacent to the fluorine where the anion can be stabilized by the inductive withdrawal of the fluorine. However, as far as favoring attack at either the α- (1) position or β - (3) position to a greater extent than in naphthalene, there appears to be no directing effect. The steric effect of the fluorine upon the lithiation reaction thus appears to be negligible. The difference between the results obtained in the lithiation of 2-fluoronaphthalene and the 2-ethers (32, 33) in which attack was noted only in the 3-position may be due to increased steric hindrance from the alkoxy group of the ethers, which would have greater effect on the 1-position than on the 3-position due to the added hindrance by the peri-hydrogen. It may also be simply an experimental or analytical problem caused by lower yields and the possibility of the loss of a small amount of the 1-acids in the workup.

Spectra

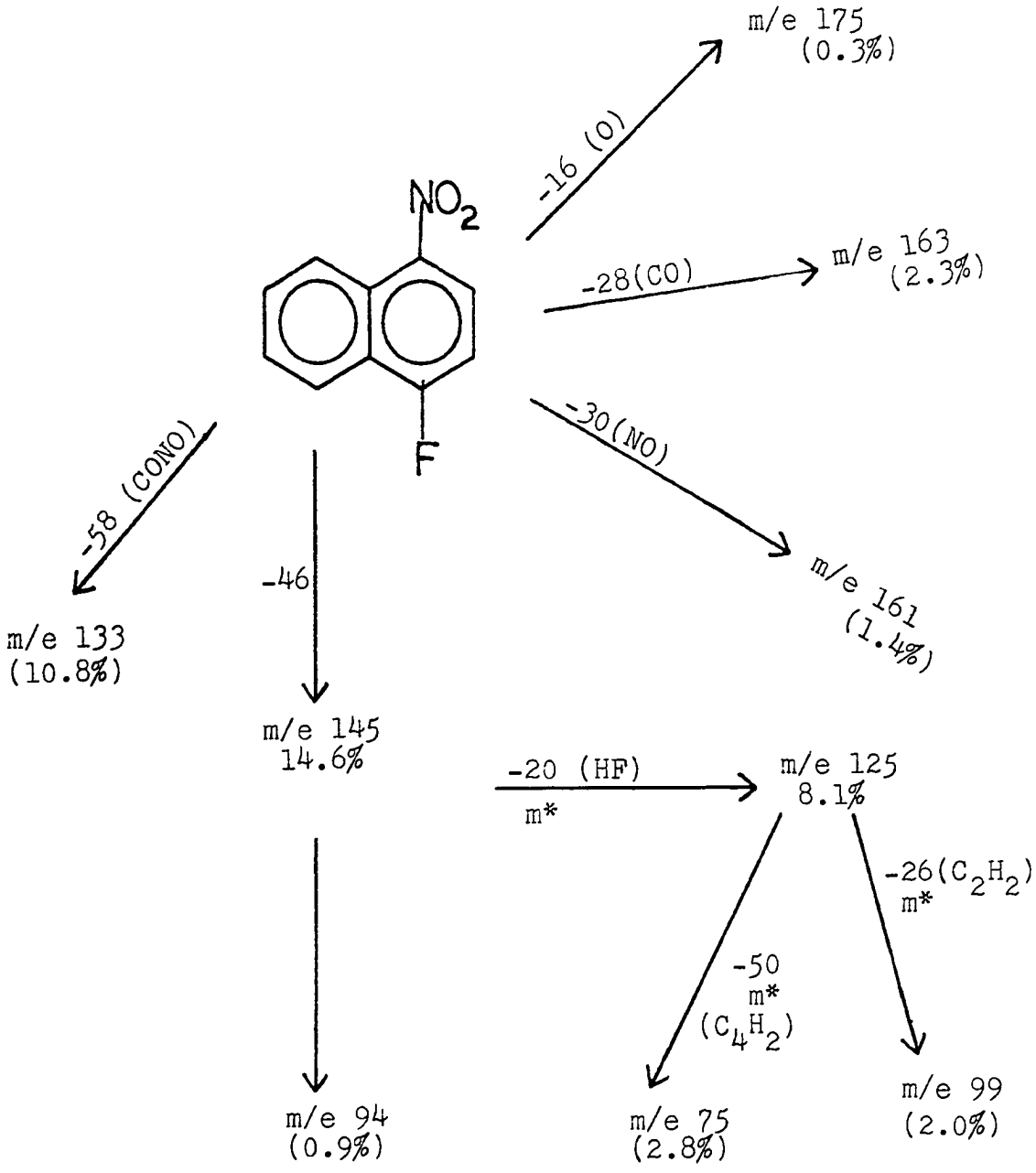
Mass spectra

Mass spectral analyses were carried out on the nitrofluoronaphthalenes and a number of other nitronaphthalenes

prepared during the course of this work. The fragmentation of particular interest in this study was the loss of carbon monoxide from the molecule ion of the substituted-α-nitronaphthalenes. This loss had been noted previously by a number of workers (40, 41, 42). Among the compounds studied were the fourteen isomeric nitrofluoronaphthalenes, several nitrochloronaphthalenes, and a number of nitronaphthylamines. The spectra of these compounds are summarized in Tables 19-24, and the spectra are tabulated in the Appendix. As was noted by the earlier workers, only those compounds which contained the nitro group on an α-position underwent significant loss of carbon monoxide from the molecule ion.

The normal fragmentation paths of the fluoro-1-nitronaphthalenes are shown using the example of 4-fluoro-1-nitronaphthalene (Scheme 5). The fragmentation pattern of the fluoro-2-nitronaphthalenes are very similar to those of the 1-nitro compounds, except that the loss of 28 mass units from the molecule ion is not observed.

The base peak in the spectra of all the fluoronitronaphthalenes except 6-fluoro-1-nitronaphthalene and 7-fluoro-2-nitronaphthalene was the parent ion. The other predominant ions were M-46, which corresponds to the loss of NO_2; M-58, which corresponds to the consecutive losses of CO and NO; and M-66, which corresponds to the losses of NO_2 and HF from the molecule ion.



Scheme 5. Major fragmentations of 4-fluoro-1-nitronaphthalene

Table 19. Mass spectra of fluoro-1-nitronaphthalenes (per cent of all ions with m/e greater than 70)

m/e	2-F	3-F	4-F	5-F	6-F	7-F	8-F
191 (M^+)	19.7	21.4	25.3	17.8	18.7	21.4	18.8
175 (M-16)	.3	.1	.3	.2	.3	.3	.3
171 (M-20)	---	---	---	.7	---	.2	---
163 (M-28)	4.2	3.5	2.3	3.3	1.0	1.5	.6
162 (M-29)	.2	.2	.3	.3	.4	.3	.9
161 (M-30)	1.0	1.3	1.4	1.5	.8	1.3	.9
145 (M-46)	11.4	15.1	14.6	14.9	20.6	18.3	16.3
133 (M-58)	14.7	14.4	10.8	16.3	16.4	9.9	9.1
125 (M-66)	8.2	8.6	8.1	8.5	9.4	8.9	8.4
99 (M-92)	1.9	2.3	2.0	2.2	2.7	2.4	2.4
94 (M-97)	.9	1.1	.9	1.0	1.3	1.2	1.1
75 (M-116)	3.3	3.1	2.8	3.4	3.2	3.0	3.2
Total	66.0	71.1	68.8	70.1	74.8	68.7	62.0

The loss of carbon monoxide from the molecule ion to give the ion at m/e 163 was found to make up 2.3 to 4.2% of the total ions when the fluorine was in positions 2 through 5; however, when the fluorine substituent was in positions 6, 7, or 8, the loss of carbon monoxide was reduced to 0.6

Table 20. Mass spectra of fluoro-2-nitronaphthalenes (per cent of all ions with m/e greater than 70)

m/e	1-F	3-F	4-F	5-F	6-F	7-F	8-F
191 (M^+)	30.4	27.7	30.6	26.8	29.7	18.6	27.7
175 (M-16)	.4	.4	.2	.3	.3	.3	.3
171 (M-20)	---	---	---	---	---	---	---
163 (M-28)	---	---	---	---	---	---	---
162 (M-29)	---	---	---	---	.1	---	---
161 (M-30)	2.8	1.1	.3	.1	1.0	.2	.2
145 (M-46)	23.7	20.8	24.6	25.9	25.5	35.0	24.8
133 (M-58)	11.6	8.2	8.5	7.2	7.6	9.5	7.3
125 (M-66)	8.2	8.0	9.4	8.8	7.5	9.0	7.6
99 (M-92)	2.8	1.9	2.0	2.3	2.0	2.5	2.1
94 (M-97)	1.0	1.0	1.0	1.1	1.1	1.3	1.1
75 (M-116)	4.3	2.3	3.1	3.1	2.5	3.0	2.7
Total	85.2	71.4	79.7	75.6	77.3	79.4	73.8

to 1.5% of the total ionization. This indicates that the fluorine substituent has an effect upon the loss of carbon monoxide when it is in the positions close to that from which the molecule of carbon monoxide is split out, i.e., the

Table 21. Mass spectra of amino-1-nitronaphthalenes (per cent of all ions with m/e greater than 70)

m/e	2-NH_2	3-NH_2	4-NH_2	5-NH_2	6-NH_2	7-NH_2
188 (M^+)	21.2	26.8	27.0	14.0	28.3	19.5
171 (M-17)	.4	---	---	---	---	1.8
160 (M-28)	1.0	.2	---	.6	---	---
159 (M-29)	1.1	.2	1.2	1.0	---	.6
158 (M-30)	2.9	.8	7.0	.8	.5	3.0
142 (M-46)	3.7	10.9	9.3	1.9	19.6	8.8
130 (M-58)	5.0	5.6	3.0	2.6	4.8	3.9
115 (M-73)	14.9	22.3	12.4	13.3	11.2	12.6
89 (M-99)	1.9	2.1	1.9	1.8	1.4	1.6
Total	52.1	68.9	61.8	36.0	65.8	51.8

8-position (42). This fragmentation is least important when the fluorine is in the 8-position, when it makes up only 0.6% of the total ionization. This is reasonable since the fluorine atom would have to migrate prior to the loss of carbon monoxide, and this migration is more difficult than that of a hydrogen atom as noted by Bryant (77). In terms of the mechanisms proposed earlier (40, 41, 42) it appears

Table 22. Mass spectra of amino-2-nitronaphthalenes (per cent of all ions with m/e greater than 70)

m/e	1-NH_2	4-NH_2	5-NH_2	6-NH_2	7-NH_2	8-NH_2
188 (M^+)	35.4	24.0	16.9	26.4	30.8	28.0
171 (M-17)	---	---	---	---	---	---
160 (M-28)	---	---	---	---	---	---
159 (M-29)	---	---	---	---	---	---
158 (M-30)	1.5	1.4	---	3.5	---	.6
142 (M-46)	8.5	17.0	6.8	16.0	15.9	4.8
130 (M-58)	1.8	2.8	1.6	3.5	1.6	1.9
115 (M-73)	13.8	12.8	12.8	9.7	6.7	27.3
89 (M-99)	1.0	1.7	1.2	1.4	.9	1.5
Total	62.0	59.7	39.3	60.5	55.9	64.1

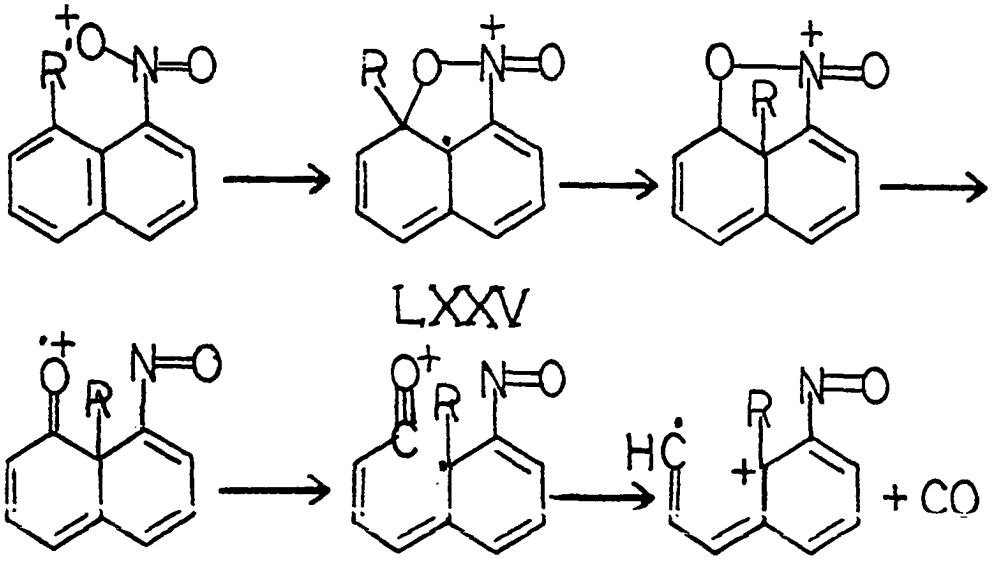


Table 23. Mass spectra of chloronitronaphthalenes (per cent of all ions with m/e greater than 70)

m/e	1-Cl 2-NO_2	4-Cl 1-NO_2	5-Cl 1-NO_2	8-Cl 1-NO_2
209 (M^+)	6.4	7.3	3.6	4.2
207 (M^+)	19.3	21.8	10.3	11.1
181 (M-28)	---	.8	1.5	.4
179 (M-28,30)	.3	2.6	4.6	1.3
177 (M-30)	.8	.9	1.5	.9
172 (M-35, 37)	.4	3.5	1.4	22.5
163 (M-46)	3.8	2.4	2.4	3.4
161 (M-46)	12.0	7.1	6.2	8.3
151 (M-58)	2.9	3.5	4.2	2.3
149 (M-58)	9.2	7.3	11.3	7.0
126 (M-81, 83)	14.9	10.1	12.9	12.9
125 (M-82, 84)	3.5	2.7	3.7	4.8
99 (M-108, 110)	2.2	1.6	3.0	2.9
75 (M-132, 134)	3.0	2.0	4.0	4.6
Total	78.7	73.6	70.6	86.6

Table 24. Mass spectra of miscellaneous nitronaphthalenes (per cent of all ions with m/e greater than 70)

m/e	1-Nitro-naphthalene	2-Nitro-naphthalene	m/e	4-Cyano-1-nitro-naphthalene
173 (M^+)	3.1	33.9	198 (M^+)	18.5
157 (M-16)	.1	.3	182 (M-16)	---
145 (M-28)	4.7	---	170 (M-28)	3.2
144 (M-29)	.4	.2	169 (M-29)	.5
143 (M-30)	4.2	.4	168 (M-30)	.8
127 (M-46)	17.7	25.3	152 (M-46)	12.9
115 (M-58)	22.2	6.1	142 (M-56)	3.0
101 (M-72)	3.4	2.4	140 (M-58)	14.4
			125 (M-73)	5.4
			99 (M-99)	1.9
			94 (M-104)	---
			75 (M-123)	3.5
Total	55.8	68.7		64.1

that the mechanism involving the transfer of the substituent on position 8 to the adjacent bridgehead is involved, since the transfer of fluorine to oxygen is not observed, even in more favorable situations (77).

The presence of the fluorine atom in the 8-position or even in the nearby 7- and 6-positions reduces formation of ion LXXV due to the strong electron withdrawing inductive effect of the fluorine from the 8-position. In a similar manner the loss of carbon monoxide occurs, but to a reduced degree in 8-chloro-1-nitronaphthalene. It is also observed that the loss of carbon monoxide is much larger for 5-fluoro-1-nitronaphthalene than for 4-fluoro-1-nitronaphthalene. This may be due to the more direct resonance electron donation in the case of the 5-fluoro-compound.

The effect of fluorine as a substituent in mass spectrometry is quite noticeable in this series of compounds. It indeed has an effect upon the loss of carbon monoxide from the molecule ion. Its effect on the molecule ion stability is also very noticeable, as it greatly increases the stability of the molecule ion relative to fragment ions, particularly in the series with the nitro group on the 1-position. In these compounds the molecule ion increases from 3% of the total ionization in 1-nitronaphthalene to about 20% of the total ionization in the fluoro-1-nitronaphthalenes.

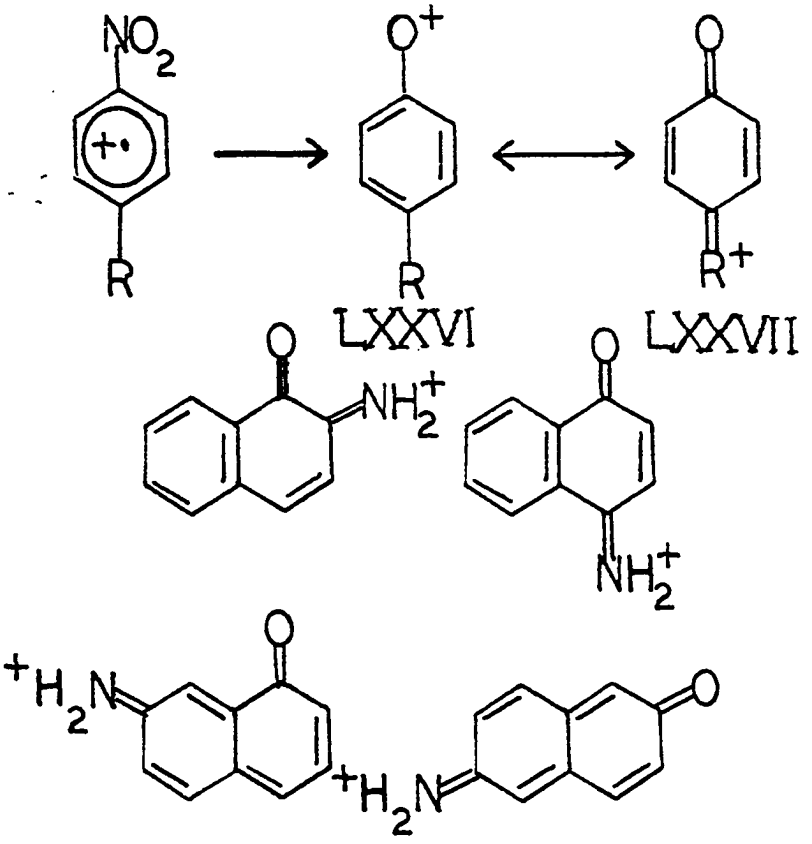
This data indeed shows the importance of the warning of Bursey and coworkers (44) that the fluorine-label technique may be used only when the entire aromatic group acts solely as a substituent on another reacting system. In this study

the fluorine is on the aromatic system undergoing reaction and does exert considerable electronic effect on the mass spectral fragmentation of the fluoronaphthalenes.

It is noted that the loss of carbon monoxide from the molecule ion of 5-chloro-1-nitronaphthalene is greater than that observed in 4-chloro-1-nitronaphthalene. This may be explained in the same manner as the similar relationship observed in 4- and 5-fluoro-1-nitronaphthalene. Even though the chloro group is not as strong a resonance donating group as the fluoro group, it is still strong enough that the direct conjugation from the 5- to the 8-position is more important than that from the 4-position in the other ring.

Bursey and McLafferty (78) carried out a study of the loss of NO from the molecule ion of substituted nitrobenzenes. They observed that para-substituents which can donate electrons by resonance favor this loss of NO. Their data pointed to a specially stabilized structure for the product ion (LXXVI), for which they were able to draw the resonance structure LXXVII. Among the groups for which they noted this stabilization from the para-position and thus increased amounts of the M-30 ion were amino, hydroxyl, methoxy, and the halogens.

In the aminonitronaphthalenes the M-30 ion is found to be much more intense in 2-, 7-, and particularly 4-amino-1-nitronaphthalenes than in the other isomers. This corresponds



to the positions from which the amino group can donate electrons by resonance to the positions which originally bore the nitro groups to stabilize the product ion. The M-30 ion is also more intense in 6-amino-2-nitronaphthalene. This compound also has the amino group on a position where it can donate electrons by resonance to the position where the nitro group was originally, but it is far enough removed from that position that its inductive effect is not

opposing the resonance effect as much as in the positions on the nitro-bearing ring.

In 5-amino-1-nitronaphthalene the loss of the nitro group is reduced to only 1.9% of the total ionization. In this compound another mode of fragmentation becomes more important. The second largest fragment ion is that at m/e 122 resulting from the loss of the amino-bearing ring. This shows that the position of charge localization and subsequent fragmentation is moved away from the nitro group.

^{19}F-nmr

^{19}F-nmr were obtained on twelve of the fourteen isomeric nitrofluoronaphthalenes prepared in this work. Many of the spectra were obtained prior to the publication of the paper of Adcock and Dewar (48) and five of the isomers studied in this work were included in their work. The two remaining isomers of which there was not enough for the ^{19}F-nmr spectra were among the seven studied by Adocock and Dewar.

A study was made of the chemical shift values and they were generally in agreement with what would be predicted on the basis of the nitro group being an electron withdrawing species. However those isomers in which the nitro group was on a carbon adjacent to the fluorine-bearing carbon were the exceptions. In those cases the ^{19}F-nmr resonances were

observed upfield from that of the unsubstituted fluoronaphthalenes. In the other isomers, the chemical shift was shifted downfield from the positions observed in the unsubstituted fluoronaphthalenes by the strong electron withdrawing effect of the nitro group. A similar effect was noted in the nitrofluorobenzenes. The ^{19}F-nmr resonance of ortho-fluoronitrobenzene is observed to be upfield from fluorobenzene while those of meta- and para-nitrofluorobenzene are observed to be downfield. The values are listed in Table 25.

This behavior of the compounds with the nitro group adjacent to the fluorine is in the opposite direction of that noted in the proton-nmr of the nitronaphthalenes. Wells and Alcorn (50) determined that the 2- and 8-protons were in the low field (1.6-1.8τ) region in the spectrum of 1-nitronaphthalene. The 1-proton in 2-nitronaphthalene was the low field proton at 1.05τ and the 3-proton was in the mid field region (1.7-1.8τ). These values compare to values of 2.06 and 2.47τ for the α- and β-protons in the spectrum of naphthalene. The above spectra were obtained by Wells and Alcorn using dimethylacetamide as solvent.

The results obtained in this work on the nitrofluoronaphthalenes agree with those of Adcock and Dewar (48) for those compounds in which the nitro group is not adjacent to the fluorine. A rough calculation of the substituent

Table 25. ^{19}F-nmr chemical shift of nitrofluorobenzenes

Compound	Chemical shift Hz from $CFCl_3$	Chemical shift Hz from fluorobenzene
Fluorobenzene	6404	0
ortho-Nitrofluorobenzene	6732	+328
meta-Nitrofluorobenzene	6204	-200
para-Nitrofluorobenzene	----	-660[a]

[a]Value of Taft and coworkers (46).

chemical shift (SCS) of the isomers prepared in this work using the method of Adcock and Dewar (48) agree with the observed values as well as those of Adcock and Dewar, except for those compounds with the nitro group adjacent to the fluorine. This extends the validity of the calculations of Adcock and Dewar to the rest of the nonadjacent positions in the naphthalene nucleus. The observed and calculated values of SCS for the nitrofluoronaphthalenes are listed in Tables 26 and 27.

The remaining four isomers with the fluoro and nitro groups on adjacent positions not only do not agree with the calculated value for SCS, but are all in the opposite direction. This shows the decided increase in the importance of other effects on the fluorine chemical shift which become

Table 26. ^{19}F-nmr chemical shifts and SCS for nitro-1-fluoronaphthalenes

Compound	Chemical shift Hz from $CFCl_3$	SCS Hz	SCS observed in ppm	SCS calculated in ppm
1-Fluoronaphthalene	6992	---	---	---
2-Nitro-1-fluoronaphthalene	7068	+76	+1.35	-12.34
3-Nitro-1-fluoronaphthalene	6716	-276	-4.90 (-4.87)[a]	-3.64[a]
4-Nitro-1-fluoronaphthalene	6272	-720	-12.73 (-12.77)[a]	-11.61[a]
5-Nitro-1-fluoronaphthalene	6796	-196	-3.47	-4.99
6-Nitro-1-fluoronaphthalene	6876	-116	-2.04 (-2.08)[a]	-1.81[a]
7-Nitro-1-fluoronaphthalene	6804	-188	-3.33 (-3.39)[a]	-2.48[a]
8-Nitro-1-fluoronaphthalene	6546	-446	-7.90	+1.28

[a]Values of Adcock and Dewar (48).

Table 27. ^{19}F-nmr chemical shifts and SCS for nitro-2-fluoronaphthalenes

Compound	Chemical shift Hz from $CFCl_3$	SCS Hz	SCS observed in ppm	SCS calculated in ppm
2-Fluoronaphthalene	6484	---	---	---
1-Nitro-2-fluoronaphthalene	6920	+436	+7.74	-21.33
3-Nitro-2-fluoronaphthalene	7064	+580	+10.03	-14.94
4-Nitro-2-fluoronaphthalene	---	---	-0.79[a]	-1.97[a]
5-Nitro-2-fluoronaphthalene	6352	-132	-2.34	-3.19
6-Nitro-2-fluoronaphthalene	6120	-364	-6.45 (-6.54)[a]	-5.13[a]
7-Nitro-2-fluoronaphthalene	6308	-176	-3.13	-3.37
8-Nitro-2-fluoronaphthalene	---	---	-6.76[a]	-6.70[a]

[a]Values of Adcock and Dewar (48).

particularly important when the substituent is adjacent to the fluorine. Part of the effect seems to be dependent upon the orientation of the nitro group on the adjacent carbon, since the direction of the chemical shift change is different in the compound in which the orientation of the nitro group is different. In 8-fluoro-1-nitronaphthalene in which the nitro group is twisted out of the plane of the ring the observed SCS is downfield from the calculated value, while in the other three isomers in which the orientation of the nitro group should be about the same they are all shifted upfield from the calculated values.

Infrared

Infrared studies were made on the isomeric fluoronitronaphthalenes and a number of other halonitronaphthalenes prepared in this work. The spectra were all obtained in the solid state as potassium bromide disks. Of particular interest was the determination of the nitro stretching frequencies as a key to gain information concerning the orientation of the nitro group and the effect of the fluorine substituent upon that orientation. The values obtained are listed in Table 28.

The most noticeable change is observed in the compounds in which the halogen is *peri* to the nitro group. The change

Table 28. Infrared nitro stretching frequencies of nitronaphthalenes

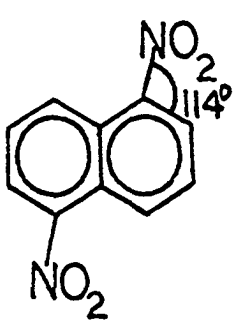
Compound	Stretching frequencies cm^{-1}	
	Symmetrical	Antisymmetrical
1-Nitronaphthalene	1333	1512
2-Fluoro-1-nitronaphthalene	1342	1532, 1513
3-Fluoro-1-nitronaphthalene	1338	1522
4-Fluoro-1-nitronaphthalene	1323	1524
5-Fluoro-1-nitronpahthalene	1328	1516
6-Fluoro-1-nitronaphthalene	1332	1513
7-Fluoro-1-nitronaphthalene	1328	1520
8-Fluoro-1-nitronaphthalene	1370	1530
4,8-Difluoro-1-nitronaphthalene	1362	1537
4-Chloro-1-nitronaphthalene	1330	1516
5-Chloro-1-nitronaphthalene	1333	1519
8-Chloro-1-nitronaphthalene	1361	1530
2-Nitronaphthalene	1330, 1342	1520
1-Fluoro-2-nitronaphthalene	1346	1537
3-Fluoro-2-nitronaphthalene	1340	1527
4-Fluoro-2-nitronaphthalene	1334	1526
5-Fluoro-2-nitronaphthalene	1332	1535
6-Fluoro-2-nitronaphthalene	1343	1538
7-Fluoro-2-nitronaphthalene	1340	1535
8-Fluoro-2-nitronaphthalene	1332	1538
1-Chloro-2-nitronaphthalene	1348	1528
1,5-Dinitronaphthalene	1348	1518
1,8-Dinitronaphthalene	1350	1524

is better seen in the symmetrical stretching frequency. This stretching frequency is shifted from about 1330 cm^{-1} in the majority of the compounds to 1360 to 1370 cm^{-1} in the three compounds in which the halogen is peri to the nitro group.

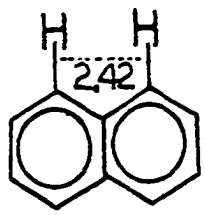
Trotter (54) had noted that compounds in which the nitro group was twisted out of the plane of the ring exhibited a considerable shift of the symmetrical stretching frequency. In the compounds he studied, the symmetrical stretching frequency was shifted to about 1360 to 1375 cm^{-1} for those compounds in which the nitro group was twisted at angles greater than 60°.

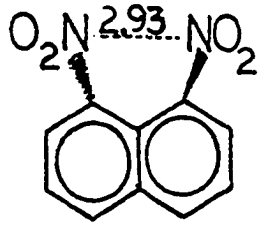
However, in the nitronaphthalenes there is more than one way in which the nitro group could reduce steric hindrance, and thereby reducing conjugation. Trotter (53) has shown by X-ray crystallography that the nitro groups in 1,5-dinitronaphthalene were twisted 49° from the plane of the nucleus about the C-N bond and is also displaced in the plane of the ring away from the peri-hydrogen. This increases the distance between the nitro group and the peri-hydrogen and reduces the exocyclic N-C-C angle to 114° as shown (exaggerated) in structure LXXVIII. Similarly Akopyan and Struchkov (79) determined the structure of 1,8-dinitronaphthalene (LXXIX) and observed that the nitro groups were twisted 45° from the plane, the C-N bonds splayed apart to increase the N---N distance from 2.42 Å to 2.93 Å, the C-N bonds deviated from

the aromatic plane by 0.37 Å in opposite directions, and the carbon atoms bearing the nitro groups were forced out of the plane of the molecule in the direction of the substituents.



LXXVIII





LXXIX

The infrared results for the halonitronaphthalenes indicate a decided decrease in conjugation for the peri-substituted compounds over the other isomers. However whether this increase is due solely to the rotation of the nitro group, or partially to other changes in the position of the nitro group cannot be stated with certainty. However in agreement with the correlation between the stretching frequency and the angle of twist are the values observed that 1,8-dinotronaphthalene with an angle of twist of 45° had a stretching frequency of 1350 cm^{-1} and 1,5-dinitronaphthalene with an angle of twist of 49° had a stretching frequency of 1348 cm^{-1}. This work does indeed show the decided effect of a fluorine atom on the peri-position over that of a hydrogen, even though there is only an increase of about 0.2 Å in

the van der Waals radius in going from hydrogen to fluorine.

There is not such a significant change in the nitro stretching frequencies of the compounds which have the fluoro and nitro groups on adjacent but not peri-positions. This is in agreement with the work of McDaniel and Brown (80) who studied the steric inhibition of resonance of substituted pyridines and substituted benzoic acids by studying the pKa of the compounds. They found that the ortho-effect in the halobenzoic acids involved some steric inhibition of resonance. The effect was in the order of increasing steric size I > Br > Cl > F with fluorine showing no effect within their experimental error.

As noted in this work the steric effect of fluorine on an adjacent position on the same aromatic ring is quite negligible, but a fluorine peri to a bulky substituent has considerable steric effect on the substituent's orientation.

EXPERIMENTAL

Reagents

Inorganic salts were commercial materials and were used without further purification. Nitronium fluoroborate was obtained from Alfa Inorganics. Fluoboric acid was obtained from Matheson, Coleman, and Bell as a 48% aqueous solution. Nitric acid, 90% minimum, obtained from Mallinckrodt Chemical Company, was twice distilled under vacuum at 32° from twice its volume of concentrated sulfuric acid. Tetramethylene sulphone (sulpholane), obtained from Shell, was distilled before use. Tetrahydrofuran (THF) was dried according to the procedure of Gilman and Soddy (35) before use. 1-Fluoronaphthalene, obtained from Pierce Chemical Company, was distilled before use and found to be pure by gas chromatography. 2-Fluoronaphthalene was obtained from Pierce Chemical Company, Aldrich Chemical Company, and Columbia Organic Chemicals, and was recrystallized from ethanol to mp 59-60° (lit 61° (20)) before use. Gas chromatography and mass spectrometry indicated that this 2-fluoronpahthalene contained approximately 2% chloronaphthalene was its only contaminate. n-Butyllithium was obtained from Foote Mineral Company as a 1.6M solution in hexane, and t-butyllithium was also obtained from Foote Mineral Company as a 1.24M solution in pentane. Other organic chemicals were obtained commercially and used without further treatment.

General Procedure

Mass spectra were obtained on an Atlas CH-4 mass spectrometer. ^{19}F-nmr were obtained on a Varian HA-60 spectrometer using dimethylformamide (DMF) as solvent and trichlorofluoromethane ($CFCl_3$) as internal reference. Proton nmr were obtained on a Varian A-60 spectrometer using dimethylacetamide as solvent and tetramethylsilane (TMS) as internal reference. Infrared spectra were determined on a Perkin Elmer Model 21 spectrometer as KBr pellets. Melting points were taken on a Thomas, Kofler micro hot stage. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona.

Synthesis

2-Nitro-1-naphthylamine and 4-nitro-1-naphthylamine

1-Napthylamine was acetylated and nitrated and the mixture of 2- and 4-nitro-1-naphthylamines separated according to a modification of the procedure of Hodgson and Walker (81). 1-Naphthylamine (60 g) was heated for 30 minutes on a hot water bath with 55 ml of acetic anhydride and 400 ml of acetic acid. The solution was cooled and 10 ml of nitric acid was added in one portion at 22° with a further 19 ml added gradually during 15 minutes at 15-20°. Continued stirring produced crystallization within 1 hour. After 7

hours the mixture was filtered to give 95 g of yellow solid. The 95 g of yellow solid was heated under reflux with a solution of 250 ml of ethanol and 250 ml of 50% sulfuric acid for 11 hours. The solution was then cooled and 500 ml of water was added to give 80 g of an orange mixture of 2- and 4-nitro-1-naphthylamines. This mixture was shaken for 10 minutes with 650 ml of acetic acid and 60 ml of hydrochloric acid and filtered. The filtrate was diluted with 500 ml of water, filtered, and the solid recrystallized from ethanol to give 20 g of 2-nitro-1-naphthylamine as orange needles, mp 140-144° (lit. 143-144° (81)). The mass spectrum included peaks at m/e 188 (base), 142, and 115.

The solid residue was added to 1 liter of water, filtered, and then recrystallized from ethanol to give 50 g of 4-nitro-1-naphthylamine as yellow needles, mp 190-193° (lit. 193-194° (81)). The mass spectrum included peaks at m/e 188 (base), 142, and 115.

2-Nitro-1-fluoronaphthalene

2-Nitro-1-naphthylamine (9.4 g) was dissolved in 100 ml of THF. To this solution was added 100 ml of 49% aqueous fluoboric acid, and after cooling to 0°, diazotization was brought about according to the procedure of Brill (56) by the addition of 4.2 g of sodium nitrite in 10 ml of water. After

stirring for 1 hour at 0° the mixture was filtered, washed with 50 ml of 5% fluoboric acid, 50 ml of methanol, and ether (2 X 50 ml) in that order. The diazonium salt was then dried in vacuum. The dried diazonium salt was mixed with about 5 times its weight of sand and decomposed with a free flame in a one-necked flask fitted with a distilling head from which a water cooled condensor led to a tray of water to collect the gases given off during the decomposition. Heating was maintained intermittently until the amount of fumes given off decreased. After cooling, the apparatus was washed with ether, the sand residue extracted with ether, and the ether residues then dried with anhydrous magnesium sulfate, decolorized with charcoal, filtered, and the ether removed to give a mixture of 80% 2-nitro-1-fluoronaphthalene and 20% 2-nitronaphthalene, mp 93.5-99° (lit. 96-96.5(56)). The ^{19}F-nmr (DMF) showed a doublet of doublets at 7068 Hz from $CFCl_3$ (J_{F-H} = 6.0 and 2.0 Hz). The infrared spectrum had bands at 1537, 1342, and 1330 cm^{-1}. The mass spectrum included peaks at 191 (base), 145, 133, and 125.

2,4-Dinitro-1-naphthylamine

1-Naphthylamine was acetylated and then nitrated by a combination of the methods of Hodgson and Walker (81) and Morgan and Evans (82). 1-Naphthylamine (75 g) was added to 400 ml of glacial acetic acid and to this was added 70 ml

of acetic anhydride. The solution was heated on a hot water bath for 20 minutes and then cooled to 70°. With the temperature kept below 70°, a mixture of 52 ml of acetic acid and 52 ml of 90% nitric acid was added gradually. Upon completion of this addition the temperature was raised to 96° until a solid began to separate. The mixture was then cooled in an ice bath and filtered to give N-acetyl-2,4-dinitro-1-naphthylamine in 80% yield. The amide (65 g) was hydrolyzed by dissolving in a mixture of 60 ml of water and 400 ml of concentrated sulfuric acid at room temperature and heating the solution to 70° for 10 minutes. After cooling for 15 minutes the solution was poured into 800 ml of ice-water. Filtration followed by recrystallization from acetic acid yielded 2,4-dinitro-1-naphthylamine as yellow needles, mp 245° (lit. 242° (82)), in 70% yield.

3-Nitro-1-naphthylamine and 4-nitro-2-naphthylamine

2,4-Dinitro-1-naphthylamine was diazotized and treated with cuprous oxide according to the procedure of Hodgson and Birtwell (83) to give 1,3-dinitronaphthalene, mp 149-151° (lit. 148°(84)), in 45% yield. 1,3-Dinitronaphthalene was reduced with sodium sulfide according to the procedure of Hodgson and coworkers (85). To 24 g of 1,3-dinitronaphthalene in 200 ml of refluxing methanol was added over 1 hour a

preheated solution of 42 g of sodium sulfide and 14 g of sodium bicarbonate in 100 ml of water. After cooling to 0°, the mixture was filtered, the solid dissolved in methanol, and filtered to remove sodium carbonate. Charcoal was added to the filtrate, the solution was filtered, and then crystallized by cooling to give orange needles of 3-nitro-1-naphthylamine, mp 136-138° (lit. 137° (85)), in 30% yield. The mass spectrum included peaks at m/e 188 (base), 142, and 115.

The original filtrate was added to 1500 ml of ice-water to give 7 g of a red solid mixture of 3-nitro-1-naphthylamine and 4-nitro-2-naphthylamine.

3-Nitro-1-fluoronaphthalene

3-Nitro-1-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 3-nitro-1-fluoronaphthalene in 25% yield. Recrystallization from ethanol yielded yellow needles, mp 93.5-95° (lit. 93-94° (86)). The ^{19}F-nmr (DMF) showed a doublet of doublets at 6716 Hz from $CFCl_3$ (J_{F-H} = 10.6 and 1.1 Hz). The infrared spectrum (KBr) had bands at 1526 and 1334 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

4-Nitro-1-fluoronaphthalene

4-Nitro-1-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 4-nitro-1-fluoronaphthalene in 35% yield. Recrystallization from ethanol yielded yellow needles, mp 79.5-80° (lit. 80° (20, 21)). The ^{19}F-nmr (DMF) showed a doublet of doublets of doublets at 6772 Hz from $CFCl_3$ (J_{F-H} = 9.8, 4.7, and 1.8 Hz). The infrared spectrum (KBr) had bands at 1524 and 1323 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

5-Nitro-1-fluoronaphthalene

1,5-Dinitronaphthalene was reduced with aqueous sodium sulfide according to the procedure of Hodgson and Kilner (87) to give 5-nitro-1-naphthylamine in 35% yield. The amine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 5-nitro-1-fluoronaphthalene in 20%. Recrystallization from ethanol yielded yellow needles, mp 70-71° (lit. 72°(21)). The ^{19}F-nmr (DMF) showed a doublet of doublets at 6796 Hz from $CFCl_3$ (J_{F-H} = 10.3 and 5.8 Hz). The infrared spectrum (KBr) had bands at 1516 and 1328 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

2-Nitronaphthalene

2-Nitro-1-naphthylamine prepared as previously described was diazotized and treated with cuprous oxide according to the procedure of Hodgson and coworkers (83) to give 2-nitronaphthalene in 20% yield. Recrystallization from ethanol gave yellow needles, mp 79-80.5° (lit. 78.7°(88)). The infrared spectrum (KBr) had bands at 1520, 1342, and 1330 cm^{-1}. The mass spectrum included peaks at m/e 173 (base), 127, and 115.

1,6-Dinitronaphthalene and 1,7-dinitronaphthalene

2-Nitronaphthalene was nitrated according to the procedure of Ward and Hawkins (14) to give a mixture of 1,6- and 1,7-dinitronaphthalenes in 74% yield. To 20 g of 2-nitronaphthalene dissolved in 160 ml of concentrated sulfuric acid was added slowly at -5° a mixture of 7.5 ml of nitric acid and 30 ml of sulfuric acid. The reaction was stirred vigorously until the dark red solution turned yellow. The solution was then poured into 1 liter of ice-water. The mixture was filtered and dried to give 22.5 g of crude product. The crude product was dissolved in benzene, added to an alumina column, and eluted with benzene. The order of elution was 2-nitronaphthalene, 1,6-dinitronaphthalene, and 1,7-dinitronaphthalene. Based on the amount of 2-nitronaphthalene not recovered, the dinitronaphthalenes were obtained in 74%

yield. They were in the ratio of 44% 1,6-dinitronaphthalene to 56% 1,7-dinitronaphthalene. Recrystallization from benzene gave colorless needles, mp 168-169° (lit. 166.5° (89)). The mass spectrum included peaks at m/e 218 (base), 172, and 126.

Recrystallization of 1,7-dinitronaphthalene from benzene gave yellow needles, mp 160-162° (lit. 156° (90)). The mass spectrum included peaks at 218 (base), 172, and 126.

6-Nitro-1-naphthylamine

1,6-Dinitronaphthalene was reduced with stannous chloride according to the procedure of Hodgson and Turner (91). Stannous chloride crystals (64 g) were added to 140 ml of acetic acid and heated to boiling. A current of hydrogen chloride gas was passed through the solution as it was cooled to 0°. To 100 ml of acetic acid was added 12 g of 1,6-dinitronaphthalene. The mixture was heated and cooled quickly to 30° to give a suspension to which was added over a period of 45 minutes, with stirring at below 30°, the stannous chloride solution. Stirring was then continued for 2 hours. To the mixture was added 20 ml of water, the mixture was heated to 65°, and distilled under reduced pressure to remove most of the acetic acid. The flask was washed out with 150 ml of water, basified with 400 ml of 20% sodium hydroxide, filtered, and the residue washed with water

and dried. The solid was extracted with 700 ml of 10% hydrochloric acid, the filtrate cooled to 0°, and neutralized to give upon filtration a reddish orange paste of 6-nitro-1-naphthylamine. About half of the starting 1,6-dinitronaphthalene was recovered upon the extraction with acid and the reduction was repeated on the recovered 1,6-dinitronaphthalene. A total yield of 2.3 g (20%) of 6-nitro-1-naphthylamine was obtained. Recrystallization from ethanol yielded red needles, mp 165-168° (lit. 167.5° (91)). The mass spectrum included peaks at m/e 188 (base), 142, and 115.

6-Nitro-1-fluoronaphthalene

6-Nitro-1-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 6-nitro-1-fluoronaphthalene in 20% yield. Recrystallization from ethanol gave yellow needles, mp 113-114° (lit. 110° (21)). The ^{19}F-nmr (DMF) showed a doublet of doublets of doublets at 6876 Hz from $CFCl_3$ (J_{F-H} = 11.5, 6.0 and 2.1 Hz). The infrared spectrum (KBr) had bands at 1535 and 1332 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

7-Nitro-1-naphthylamine

1,7-Dinitronaphthalene was reduced with stannous chloride according to the procedure of Vesely and Dvorak (90).

1,7-Dinitronaphthalene (11 g) was dissolved in 40 ml of acetic acid saturated with hydrogen chloride. After cooling, 68 ml of a solution of stannous chloride (150 g $SnCl_2.2H_2O$ in 250 ml of absolute ethanol) saturated with hydrogen chloride was added dropwise with stirring at 15°. Stirring was continued for one hour and the mixture was then allowed to stand overnight. The mixture was distilled under reduced pressure at 50° and the residue poured into 350 ml of 20% sodium hydroxide. The mixture was filtered, the solid extracted with ether, and through the ether extracts was bubbled hydrogen chloride to precipitate the hydrogen chloride salt of the amine. The salt was then added to water to give 2.5 g of crude 7-nitro-1-naphthylamine (30% yield). Recrystallization from ethanol-water gave red needles, mp 130-133° (lit. 133-134° (92)). The mass spectrum included peaks at m/e 188 (base), 142, and 115.

7-Nitro-1-fluoronaphthalene

7-Nitro-1-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 7-nitro-1-fluoronaphthalene in 35% yield. Recrystallization from ethanol yielded yellow needles, mp 83.5-84.5° (lit. 83.5-84.4° (86)). The ^{19}F-nmr (DMF) showed a doublet of doublets split further at 6804 Hz from $CFCl_3$ (J_{F-H} = 10.4, 4.9, and 2.5 Hz). The infrared spectrum (KBr) had bands at

1538 and 1332 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

8-Nitro-1-fluoronaphthlane

1-Fluoronaphthalene (10 g) was dissolved in 80 ml of sulpholane and to the solution was added, over 20 minutes at 25°, 5 g of nitronium fluoroborate in 80 ml of sulpholane. Stirring was maintained for 1 hour and the solution was then poured into 1 liter of water. The mixture was neutralized with potassium carbonate and extracted with ether. The ether was removed to leave the crude reaction mixture. The product mixture was chromatographed on alumina, eluting with pentane then pentane-benzene. The progress of the separation was followed by VPC, and the last fraction collected was found to contain predominantly one isomer, the one which corresponded in retention time to the last product of the nitration mixture. This was collected by VPC from the last fraction to give 8-nitro-1-fluoronaphthalene, mp 77-79° (lit. 84° (21)). The ^{19}F-nmr (DMF) shows a complex multiplet at 6546 Hz from $CFCl_3$. The infrared spectrum (KBr) had bands at 1537 and 1362 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

1-Nitro-2-fluoronaphthalene

1-Nitro-2-naphthalene was diazotized by the method used for 2-nitro-1-naphthylamine. The salt was mixed with sand and decomposed by adding the mixture in small portions to a flask maintained at 160-165°. After cooling the flask was washed with ether and the ether removed to give 1-nitro-2-fluoronaphthalene in 10% yield. Recrystallization from ethanol gave yellow needles, mp 67-68° (lit. 64-64.5° (56)). The ^{19}F-nmr (DMF) showed a doublet of doublets at 6920 Hz from $CFCl_3$ (J_{F-H} = 9.7 and 5.3 Hz). The infrared spectrum (KBr) had bands at 1532, 1513, and 1342 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

N-Acetyl-3-nitro-1-naphthylamine

3-Nitro-1-naphthylamine was acetylated according to the procedure of Hodgson and Turner (58). To 130 ml of acetic acid containing 14 g of 3-nitro-1-naphthylamine was added 15 ml of acetic anhydride. The solution was heated to boiling and maintained at boiling for 3 minutes. Upon cooling, greenish brown crystals formed. They were filtered and washed with acetic acid to give 9.6 g (55% yield) of N-acetyl-3-nitro-1-naphthylamine, mp 264-266° (lit. 259° (85)).

Nitration of N-acetyl-3-nitro-1-naphthylamine

N-Acetyl-3-nitro-1-naphthylamine was nitrated according

to the procedure of Hodgson and Turner (58). N-Acetyl-3-nitro-1-naphthylamine (9.6 g) was stirred gradually into nitric acid (60 ml, d 1.5) below -6° for 90 minutes. The mixture was then poured into 300 g of ice and filtered. Recrystallization from acetic acid gave 8.3 g of yellow orange solid, mp 190-230°. The yellow orange solid (8 g) was heated under reflux for 2 hours with 26 ml of 50% sulfuric acid and 35 ml of ethanol. The mixture was then poured into 300 ml ice-water to give a reddish precipitate, which upon filtration and drying gave a reddish solid, mp 150-175°. The mass spectrum of this material indicated the presence of some dinitronaphthalenes and dinitronaphthylamine. Thin layer chromatography of this material on alumina using chloroform indicated three spots. The fastest moving material was yellow and the mass spectrum indicated M^+ at m/e 233, a dinitronaphthylamine. Other peaks observed were M-18 and M-28, these ions indicated that the compound probably contained an α-nitro group which was adjacent to the amino group. The second material consisted of a solid which gave red needles, mp 224-226°, which had M^+ at m/e 233, a dinitronaphthylamine. A peak was also observed at M-28 which indicated that the compound contains an α-nitro group. Further literature search indicated that the results of Hodgson and Turner (58) were incorrect, and the

dinitronaphthylamine from this reaction was not 2,3-dinitro-1-naphthylamine but a mixture of 3,8 and 3,5-dinitro-1-naphthylamines (59).

Nitration of tetralin

Tetralin was nitrated according to the procedure of Cumming and Howie (93). To 200 ml of tetralin maintained at 15-20° was added dropwise a mixture of 104 ml of nitric acid (d 1.4) and 208 ml of sulfuric acid. Stirring was maintained for 1 hour at 20° and then poured into water. The water mixture was shaken with carbon tetrachloride (3 X 300 ml). The carbon tetrachloride extracts were shaken with dilute sodium hydroxide, decolorized with charcoal, dried with magnesium sulfate, and filtered. Most of the carbon tetrachloride was removed on the rotovac. A sample was run on the VPC and indicated two major products in approximately equal amounts. Mass spectra of the products indicated that they were both nitrotetralins. The resulting liquid (250 ml) was then vacuum distilled. Six fractions were taken and the orangish liquid was distilling at 152° when the flask blew up. The temperature at the bottom of the column began to rise rapidly from approximately 170° to over 190° when the consistency of the material coming over changed radically and the distilling flask blew apart. The fractions collected were checked by VPC, and they contained: 1, tetralin; 2,

tetralin; 3, primarily 1-nitrotetralin; 4, approximately equal amounts of 1-and 2-nitrotetralin; 5, more 2- than 1-nitrotetralin; and 6, primarily 2-nitrotetralin.

Reduction of 2-nitrotetralin

The material from fractions 5 and 6 collected above containing mostly 2-nitrotetralin was reduced with tin and hydrochloric acid. To 32.4 g of 2-nitrotetralin and 40 g of tin metal was added 85 ml of concentrated hydrochloric acid. The temperature was allowed to rise to 75° and was kept near that temperature until no metal remained. The flask was then cooled and to the solution was added sodium hydroxide solution until the solution was basic. The solution was extracted with ether, the ether extracts were dried, charcoal added, filtered, and the ether removed to give 16 g of aminotetralin (60% yield). The amine was heated with 40 ml of acetic anhydride for 30 minutes and then poured into water. After several hours a white solid formed which was filtered and dried to give 10 g of N-acetyl-2-aminotetralin, mp 100-110° (lit. 107° (94)).

N-Acetyl-2-naphthylamine

2-Naphthylamine was acetylated according to the procedure of Hodgson and Kilner (87) to give N-acetyl-2-naphthylamine in

95% yield. Recrystallization from ethanol gave colorless leaflets, mp 131-133° (lit. 132° (95)).

N-Acetyl-2-aminotetralin

N-Acetyl-2-naphthylamine was reduced according to the procedure of Curtis and Viswanth (60) to give N-acetyl-2-aminotetralin in 25% yield. To 150 g of N-acetyl-2-naphthylamine suspended in 250 ml of decalin (distilled from Raney nickel) was added 15 g of Raney nickel (W2) in decalin suspension. The mixture was hydrogenated with stirring at 800 lb/in^2. The reaction vessel was heated to 200°, maintained at that temperature for 30 minutes, and allowed to cool. The product was filtered with filter aid and steam distilled to remove the decalin. The residue, 100 ml of hydrochloric acid, and 25 ml of ethanol were heated under reflux for 18 hours, cooled, and made alkaline with 25% sodium hydroxide. After further cooling an oily layer separated and was collected. Distillation of the oil gave 29 g of 2-aminotetralin, mp 35° (lit. 38-39° (96)). 2-Aminotetralin (32 g) and 50 ml of acetic anhydride were heated on a steam bath for 1 hour, 50 ml of water was added, and the solution was cooled in ice. N-Acetyl-2-aminotetralin (37 g) solidified as a white solid, mp 95-105° (lit. 107° (94)).

N-Acetyl-3-nitro-2-aminotetralin

N-Acetyl-2-aminotetralin was nitrated according to the procedure of Schroeter (96). To 37 g of N-acetyl-2-aminotetralin in 150 ml of acetic acid was added dropwise a mixture of 17.5 ml of nitric acid (d 1.4) and 12.5 ml of sulfuric acid. The temperature climbed slowly to 40° and then quickly rose to 70° before the solution could be cooled by an ice bath. The temperature was maintained at 40° for one half hour and the solution was poured into ice-water, filtered, and air dried. The product was purified by chromatography on alumina using chloroform as elutent to give 12.4 g (27% yield) of N-acetyl-3-nitro-2-aminotetralin, mp 137.5-138° (lit. 134-135.5° (96)).

3-Nitro-2-aminotetralin

N-Acetyl-3-nitro-2-aminotetralin was hydrolyzed to the free amine according to the procedure of Schroeter (96). N-Acetyl-3-nitro-2-aminotetralin (12.4 g) was heated on a steam bath for 20 minutes with 50 ml of ethanol and 30 ml of hydrochloric acid. The solution was then poured into water to give an orange solid. Recrystallization from ethanol gave 9.8 g (95% yield) of orange needles of 3-nitro-2-aminotetralin, mp 130-130.5° (lit. 125-127° (96)). The mass spectrum included peaks at m/e 192 (base), 164, and 146.

Diazotization of 3-nitro-2-aminotetralin

To 5 ml of sulfuric acid and 5 ml of water was added 1.9 g of 3-nitro-2-aminotetralin. The solution was cooled to 0° and to the solution was added slowly 1 g of sodium nitrite in 3 ml of water. Stirring was maintained for 10 minutes and then 1.0 g of sodium fluoroborate in 5 ml of water was added. Stirring was continued for 1 hour, the mixture was filtered, washed with methanol, washed with ether, and dried. The solid was decomposed thermally as described for 2-nitro-1-naphthylamine. The product obtained gave two peaks on the VPC. These products were collected by VPC and mass spectra were obtained on them. The first product was primarily a nitrotetralin (M^+ at m/e 177) with a small amount of fluoronitrotetralin (M^+ at m/e/ 195). The second product was primarily nitronaphthalene (M^+ at m/e 173) and a small amount of fluoronitrotetralin (M^+ at m/e 195) and fluoronitronaphthalene (M^+ at m/e 191).

2-Fluoro-3-naphthoic acid

2-Fluoronaphthalene was lithiated by a modification of the method of Gilman and Soddy (35), to be described later, give a mixture of 2-fluoro-1-naphthoic acid and 2-fluoro-3-naphthoic acid in 70% yield. The isomers were obtained in a ratio of 54% 1-acid to 46% 3-acid. The acid mixture (15 g)

was heated under reflux with 150 ml of methanol containing 3 ml of sulfuric acid for 18 hours. After cooling the solution was poured into 400 ml of water and made basic with potassium hydroxide. The mixture was extracted with ether and from the ether extracts was obtained 70% yield of the methyl esters in a ratio of about 33% 1-ester and 67% 3-ester. Acidification of the basic layer followed by extraction with ether gave 30% of the starting acid which was found to be nearly completely 2-fluoro-1-naphthoic acid. The mixture of methyl esters (12 g) was heated on the steam bath for 10 minutes with 50 ml of 20% methanolic potassium hydroxide. The mixture was poured into 200 ml of water, an additional 5 g of potassium hydroxide added, and extracted with ether. The ester recovered from the ether was predominantly methyl 2-fluoro-1-naphthoate. The basic solution was acidified with hydrochloric acid to give a white solid and was extracted with ether. The ether was removed to give 5 g of 2-fluoro-3-naphthoic acid. Recrystallization from ethanol yielded colorless needles, mp 196.5-198°. The proton-nmr (DMF) showed a multiplet at 444-500 Hz (integrated for 5 hydrogen), doublet at 520 Hz (integrated for 1 hydrogen, J_{H-F} = 7 Hz), and a broad singlet at approximately 750 Hz (integrated for 1 hydrogen). The infrared spectrum (KBr) included bands at 3400, 1690, and 1283 cm^{-1}. The mass spectrum included peaks at m/e 190 (base), 173, 145, and 125.

Anal. Calculated for $C_{11}H_7FO_2$: C, 69.47; H, 3.71.
Found: C, 69.54; H, 3.59.

Methyl 2-fluoro-3-naphthoate

2-Fluoro-3-naphthoic acid (34 g) was heated under reflux with a mixture of 500 ml of methanol and 8 ml of concentrated sulfuric acid for 18 hours. The solution was cooled, poured into 1 liter of water, made basic with potassium hydroxide, and extracted with ether. The ether extracts were dried and the ether removed to give 29 g of methyl 2-fluoro-3-naphthoate (80% yield). Recrystallization from ethanol yielded colorless needles, mp 90-91°. The ^{19}F-nmr (DMF) showed 4 peaks at 6543 Hz from $CFCl_3$. The proton nmr ($CDCl_3$) showed a singlet at 238 Hz (integrated for 3 hydrogen), a multiplet at 436-480 Hz (integrated for 5 hydrogen), and a doublet (J_{H-F} = 7 Hz) at 508 Hz (integrated for 1 hydrogen). The infrared spectrum (KBr) included bands at 1725, 1287, and 1205 cm^{-1}. The mass spectrum included peaks at m/e 204 (base), 145, and 125.
Anal. Calculated for $C_{12}H_9FO_2$: C, 70.58; H, 4.44.
Found: C, 70.64; H, 4.43.

2-Fluoro-3-naphthoylhydrazide

To 27 g of methyl 2-fluoro-3-naphthoate in 80 ml of absolute ethanol was added 30 ml of hydrazine hydrate. The

solution was heated under reflux for 3 hours, cooled, and filtered. The filtrate was diluted with water and after evaporating some of the ethanol was cooled and filtered again. A total of 26 g of 2-fluoro-3-naphthoylhydrazide (95% yield) was obtained. Recrystallization from ethanol gave colorless plates, mp 134-135.5°. The mass spectrum included peaks at m/e 204, 173 (base), 145, and 125.
Anal. Calculated for $C_{11}H_9FN_2O$: C, 64.70; H, 4.44; N, 13.72.
Found: C, 64.46; H, 4.44; N, 13.85.

2-Fluoro-3-naphthoylazide

2-Fluoro-3-naphthoylazide was prepared from 2-fluoro-3-naphthoylhydrazide by combination and modification of the methods of Goldstein and Cornamusaz (97) and Goldstein and Stern (98). To 17 g of 2-fluoro-3-naphthoylhydrazide in 80 ml of concentrated sulfuric acid, 160 ml of water, and 300 ml of acetic acid at 0° was added an aqueous solution of sodium nitrite followed by an additional 16 g of sodium nitrite. Stirring was maintained for 1 hour, the mixture was then filtered, washed with water, and dried to give 18 g (quantitative yield) of 2-fluoro-3-naphthoylazide which decomposed at approximately 70°. The infrared spectrum (KBr) had bands at 2250, 2150, and 1690 cm^{-1}. The mass spectrum included peaks at m/e 215, 187 (base), 173, 158, 145, 132, and 125.

2-Fluoro-3-naphthylamine

2-Fluoro-3-naphthoylazide (6.7 g) was decomposed by addition in small portions to 50 ml of concentrated sulfuric acid according to the method of Goldstein and Cornamusaz (97). The solution was stirred for a total of 1 hour and was then poured into 1 liter of ice-water. The mixture was neutralized with potassium carbonate and extracted with ether. Removal of the ether gave 2.35 g (50% yield) of 2-fluoro-3-naphthylamine. Recrystallization from ethanol gave colorless plates, mp 141-142°. The ^{19}F-nmr (DMF) showed a doublet of doublets at 7480 Hz from $CFCl_3$. The mass spectrum included peaks at m/e 161 (base), 140, and 133.

Anal. Calculated for $C_{10}H_8FN$: C, 74.52; H, 5.03; N, 8.69. Found: C, 74.37; H, 5.03; N, 8.56.

3-Nitro-2-fluoronaphthalene

2-Fluoro-3-naphthylamine was diazotized and the diazonium cobaltinitrite decomposed by the method of Hodgson and Marsden (99). 2-Fluoro-3-naphthylamine (9 g) was added to 20 ml of hydrochloric acid and 20 ml of water, and to the solution at 0° was added dropwise 4 g of sodium nitrite in 15 ml of water. Stirring was maintained for 30 minutes and the mixture was then neutralized with calcium carbonate, filtered, and to the filtrate was added 10 g of sodium cobaltinitrite. An orange precipitate formed, and after

15 minutes stirring the mixture was filtered, washed with water, air dried, and then vacuum dried. The diazonium salt (14 g) was added in portions to 90 ml of water containing 14 g of sodium nitrite, 14 g of cupric sulfate, and 6 g of cuprous oxide. Stirring was maintained for 90 minutes and the mixture was then extracted with ether. The ether extracts were dried, charcoal added, and the ether removed to yield a red oil which solidified upon setting. Chromatography on alumina, eluting with pentane and pentane-benzene mixtures yielded a yellow-orange solid. Recrystallization from ethanol-water gave yellow needles of 3-nitro-2-fluoronaphthalene, mp 74-75.5°. The ^{19}F-nmr (DMF) shows a doublet of doublets at 7064 Hz from $CFCl_3$. The infrared spectrum (KBr) had bands at 1527 and 1340 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125. Anal. Calculated for $C_{10}H_6FNO_2$: C, 62.83; H,3.16; N, 7.33. Found: C, 62.99; H, 3.02; N, 7.36.

4-Nitro-2-fluoronaphthalene

A mixture of 4-nitro-2-naphthylamine and 3-nitro-1-naphthylamine, prepared as described earlier, was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine. Recrystallization of the product mixture from ethanol gave predominantly 3-nitro-1-fluoronaphthalene. The mother liquor contained predominantly

4-nitro-2-fluoronaphthalene. Gas chromatographic collection of the 4-nitro-2-fluoronaphthalene from the mother liquor gave yellow needles, mp 66-70° (lit. 71.5-73° (86)). The infrared spectrum (KBr) had bands at 1522 and 1338 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

5-Nitro-2-naphthylamine

2-Naphthylamine was nitrated according to the procedure of Cohen and coworkers (100) to give 5-nitro-2-naphthylamine in 18% yield. 2-Naphthylamine (141 g) was added to a boiling solution of 2.5 g of urea in 1 liter of water and 75 ml of nitric acid (d 1.4). Upon cooling the nitrate precipitated as light gray flakes. The solid was filtered off, dried, powdered, and gradually added during 4 hours to 1.3 liters of well stirred sulfuric acid at -5°. The solution was poured into 10 liters of water, boiled, and filtered. The filtrate was cooled and treated with 10% boiling aqueous ammonia. After cooling to room temperature, the solution was filtered to give 27 g of crude 5-nitro-2-naphthylamine. Recrystallization from ethanol gave red needles, mp 144-145° (lit. 143-144° (101)). The mass spectrum included peaks at m/e 188 (base), 142, 130, and 115.

5-Nitro-2-fluoronaphthalene

5-Nitro-2-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 5-nitro-2-fluoronaphthalene in 15% yield. Recrystallization from ethanol gave yellow needles, mp 74.5-76°. The ^{19}F-nmr (DMF) showed a 6 peak pattern at 6352 Hz from $CFCl_3$ (J_{F-H} = 9.2 and 5.6 Hz). The infrared spectrum (KBr) had bands at 1513 and 1332 cm^{-1}.

Anal. Calculated for $C_{10}H_6FNO_2$: C, 62.83; H, 3.16; N, 7.33. Found: C, 62.97; H, 3.19; N, 7.31.

6-Nitro-2-naphthylamine and 8-nitro-2-naphthylamine

N-Acetyl-2-naphthylamine was nitrated according to the procedure of Hartman and Smith (102) to yield a mixture of 1-, 6-, and 8-nitro-2-naphthylamines. To 240 g of N-acetyl-2-naphthylamine in 400 ml of acetic acid was added dropwise over 45 minutes 115 ml of nitric acid (d 1.4). The temperature was kept below 40°, and stirring was continued for 10 minutes after completion of the addition of the nitric acid. The solution was then cooled in ice and the product separated in the form of a reddish yellow paste. This material was filtered, washed with 200 ml of 50% acetic acid, 400 ml of ether, and dried. The crude dry product (120 g) is a mixture of 1-, 6-, and 8-nitro-aceto-2-naphthalides.

This mixture was separated according to the procedure of Hodgson and Ratcliffe (103). The mixture of amides (120

g) was heated under reflux for 20 minutes in 500 ml of benzene. The solution was cooled and filtered. This precipitate (57 g) was heated under reflux for 90 minutes with a solution of ethanol (200 ml) and hydrochloric acid (50 ml) and filtered while hot to give a residue A. When cooled, the filtrate from A gave a small deposit B which was collected by filtration. Water was added to the filtrate from B, which when filtered gave precipitate C. The filtrate from C was made basic with ammonia and gave a precipitate D. Residues A, B, and D were extracted with 4 liters of cold dilute hydrochloric acid (1 ml of concentrated hydrochloric acid/100 ml of water). The combined filtrates were made basic with ammonia at 0° to give 2 g of a red solid. Recrystallization from ethanol gave 8-nitro-2-naphthylamine as dark red needles, mp 102.5-103.5° (lit. 104.5-105° (103)). The mass spectrum included peaks at m/e 188 (base), 142, 130, and 115.

The residue from A, B, and C were extracted with boiling ethanol, cooled, and filtered. Removal of most of the ethanol on the rotovac gave a brownish-yellow solid. This material when dissolved in acetone gave a dark precipitate which crystallized from ethanol as yellow-orange plates of 6-nitro-2-naphthylamine (3.3 g), mp 205° (lit. 207-207.5° (103)). The mass spectrum included peaks at m/e 188 (base), 142, 130, and 115.

6-Nitro-2-fluoronaphthalene

6-Nitro-2-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 6-nitro-2-fluoronaphthalene in 15% yield. Recrystallization from ethanol gave yellow needles, mp 109° (lit. 109.5-110.5° (86)). The ^{19}F-nmr (DMF) showed a doublet of doublets of doublets at 6120 Hz from $CFCl_3$ (J_{F-H} = 9.4, 8.4, and 5.5 Hz). The infrared spectrum (KBr) had bands at 1538 and 1343 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

2,7-Dinitronaphthalene

2,7-Dinitronaphthalene was prepared by the nitration of naphthalic anhydride and decarboxylation with copper in boiling quinoline according to the procedure of Hodgson and Ward (104). A solution of 50 g of naphthalic anhydride in 200 ml of sulfuric acid was cooled to 0° and treated dropwise with a solution of 40 ml of nitric acid (d 1.5) in 50 ml of sulfuric acid. After addition was complete, the mixture was heated to 55° for 1 hour, cooled to 0°, stirred into 5 liters of ice-water, filtered, and the solid washed with water. The yellow-orange product was dissolved in toluene, decolorized with charcoal, filtered, and allowed to crystallize. The above product (20 g) was added to 40 ml of boiling

quinoline containing 5 g of copper powder during a 4 minute period. An additional 5 g of copper was added and heating was continued for 15 minutes. The mixture was cooled to room temperature, 200 ml of ether added, filtered, and the residue washed four times with ether. The ether washings were shaken twice with 15% hydrochloric acid, washed with 25 ml of cold saturated aqueous sodium carbonate followed by 100 ml of water. The ether was removed to provide a small amount of orange-yellow solid. This procedure was repeated on the remainder of the material to give a total of 2.8 g of 2,7-dinitronaphthalene (yield 5%). Recrystallization from ethanol gave yellow needles, mp 218-235° (lit. 234° (104)). The mass spectrum included peaks at m/e 218 (base), 172, and 126.

7-Nitro-2-naphthylamine

2,7-Dinitronaphthalene was reduced according to the procedure of Hodgson and Ward (104) to give 7-nitro-2-naphthylamine in 50% yield. Recrystallization from ethanol gave orange crystals, mp 185-187° (lit. 184.5° (104)). The mass spectrum included peaks at 188 (base), 142, and 115.

7-Nitro-2-fluoronaphthalene

7-Nitro-2-naphthylamine was diazotized and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 7-nitro-2-fluoronaphthalene in 25% yield.

Recrystallization from ethanol gave yellow needles, mp 88.5-89.5° (lit. 85-86.5 (86)). The infrared spectrum (KBr) had bands at 1538 and 1332 cm^{-1}. The mass spectrum included peaks at m/e 191 (base), 145, 133, and 125.

1,5-Difluoronaphthalene

1,5-Diaminonaphthalene was diazotized according to the procedure of Schiemann and coworkers (20), and the diazonium salt decomposed by the method used for 2-nitro-1-naphthylamine to give 1,5-difluoronaphthalene in 45% yield. Recrystallization from ethanol gave colorless needles, mp 64-66° (lit. 70.5° (20)). The mass spectrum included peaks at m/e 164 (base), 144, 143, 138, and 133.

4-Nitro-1,5-difluoronaphthalene

1,5-Difluoronaphthalene (0.7 g) was dissolved in 20 ml of acetic anhydride, and to the solution was added dropwise 2 ml of nitric acid (d 1.5) in 2 ml of acetic anhydride. The solution was heated to 70° for several minutes, cooled to 50°, and stirred at 50° for 3 hours. The solution was poured into 150 ml of ice-water, neutralized with potassium carbonate, and extracted with ether. The ether extracts were dried with magnesium sulfate, decolorized with charcoal, filtered, and the ether removed to give 0.5 g of orangish solid. The

orangish solid was chromatographed on alumina eluting with pentane-benzene mixtures to give 0.3 g (35% yield) of 4-nitro-1,5-difluoronaphthalene. Recrystallization from ether gave light yellow crystals, mp 110-111° (lit. 98° (105)). The infrared spectrum (KBr) had bands at 1537 and 1362 cm^{-1}. The mass spectrum included peaks at m/e 209 (base), 163, 162, 151, 150, and 143.

4-Nitro-1-cyanonaphthalene

4-Nitro-1-naphthylamine was diazotized by the method used for 2-nitro-1-naphthylamine. The diazonium fluoroborate (26 g) was added to 100 ml of cold water and sodium carbonate was added until the mixture was basic to litmus. A cuprous cyanide solution was prepared according to the procedure of Clarke and Read (106) by addition of a solution of 16 g of sodium cyanide in 25 ml of water to a suspension of 12 g of cuprous chloride in 50 ml of cold water. About 70 ml of toluene was added to the cuprous cyanide solution and the mixture was stirred vigorously at 0° as the diazonium salt suspension was added slowly in portions. The mixture was stirred at 0° for 30 minutes and then stirred at room temperature for 3 hours. The mixture was extracted with toluene, the extracts dried, decolorized with charcoal, filtered, and the toluene removed to give 5 g of reddish-orange solid. The

solid was dissolved in benzene and chromatographed on alumina eluting with benzene to give a yellow solid, mp 128-133.5°. Recrystallization from ethanol gave yellow needles of 4-nitro-1-cyanonaphthalene, mp 133-134° (lit. 133° (107)). The mass spectrum included peaks at m/e 198 (base), 152, 140, and 125.

4-Nitro-1-chloronaphthalene

4-Nitro-1-naphthylamine (15 g) was added to 60 ml of concentrated hydrochloric acid and 60 ml of water. After cooling to 0°, 7 g of sodium nitrite in 15 ml of water was added to the solution. The solution was stirred for 30 minutes at 0°, poured into a solution of 10 g of cuprous chloride in 50 ml of hydrochloric acid, heated to 60° for 5 minutes, cooled, and 100 ml of water added. The mixture was extracted with ether, the ether extracts dried, decolorized with charcoal, filtered, and the ether removed to give 6.5 g (40% yield) of 4-nitro-1-chloronaphthalene. Recrystallization from ethanol gave yellow needles, mp 85-87° (lit. 87-87.5° (108)). The infrared spectrum (KBr) had bands at 1516 and 1330 cm^{-1}. The mass spectrum included peaks at m/e 209, 207 (base), 172, 163, 161, and 126.

5-Nitro-1-chloronaphthalene

5-Nitro-1-naphthylamine was diazotized and treated with

cuprous chloride solution as described for 4-nitro-1-naphthylamine. Recrystallization of the product from ethanol gave 5-nitro-1-chloronaphthalene in 30% yield as yellow needles, mp 109-111° (lit. 111° (109)). The infrared spectrum (KBr) had bands at 1519 and 1333 cm^{-1}. The mass spectrum included peaks at m/e 209, 207, 172, 163, 161, and 126 (base).

2-Nitro-1-chloronaphthalene

2-Nitro-1-naphthylamine was diazotized and treated with cuprous chloride solution as described for 4-nitro-1-naphthylamine. The product was chromatographed on alumina, eluting with pentane and then pentane-benzene mixtures to give 2-nitro-1-chloronaphthalene in 25% yield. Recrystallization form ethanol gave yellow needles, mp 84-84.5° (lit. 80.5-81° (98)). The infrared spectrum (KBr) had bands at 1528 and 1348 cm^{-1}. The mass spectrum included peaks at m/e 209, 207 (base), 163, 161, and 126.

8-Nitro-1-chloronaphthalene

1-Naphthylamine was nitrated according to the procedure of Hodgson and Davey (101) to give 8-nitro-1-naphthylamine. Urea (14 g) and 28 g of 1-naphthylamine were dissolved in that order in 200 ml of concentrated sulfuric acid. The cooled solution was treated at 14° with 22 g of powdered

potassium nitrate, stirred for 90 minutes, and then poured on 400 g of ice. This was filtered, the filtrate diluted to 1 liter, filtered again, and the filtrate neutralized with cold ammonia. The precipitated solid was recrystallized from Skelly B to give 4.8 g (15% yield) of red-orange crystals of 8-nitro-1-naphthylamine, mp 90-97° (lit. 97° (101)). The 8-nitro-1-naphthylamine was diazotized as described for 2-nitro-1-naphthylamine, the diazonium salt was added to 40 ml of acetone, and treated with 1.5 g of cuprous chloride in 5 ml of hydrochloric acid at 35°. After 30 minutes, addition of water precipitated 8-nitro-1-chloronaphthalene in 40% yield. Recrystallization from ethanol gave yellow needles, mp 95-96.5° (lit. 94-95° (110)). The infrared spectrum had bands at 1530 and 1361 cm^{-1}. The mass spectrum included peaks at m/e 209, 207, 172 (base), 163, 161, and 126.

2-Fluoro-1-naphthoic acid

2-Fluoro-1-naphthoic acid was obtained from the lithiation of 2-fluoronaphthalene as previously described in the preparation of 2-fluoro-3-naphthoic acid. Recrystallization of 2-fluoro-1-naphthoic acid from ethanol gave colorless needles, mp 151-153°. The ^{19}F-nmr (DMF) showed four peaks at 6375 Hz from $CFCl_3$. The proton nmr in dimethylacetamide showed a multiplet at 440-468 Hz (integrated for 3 hydrogen),

a multiplet at 478-500 Hz (integrated for 3 hydrogen), and a broad singlet at approximately 750 Hz (integrated for 1 hydrogen). The infrared spectrum (KBr) had bands at 3400, 1690, and 1285 cm^{-1}. The mass spectrum included peaks at m/e 190 (base), 173, 145, and 125.

Anal. Calculated for $C_{11}H_7FO_2$: C, 69.47; H, 3.71.
Found: C, 69.50; H, 3.59.

Methyl 2-fluoro-1-naphthoate

Treatment of an ether solution of 2-fluoro-1-naphthoic acid with an excess of an ether solution of diazomethane yielded methyl 2-fluoro-1-naphthoate, bp 157-159° at 11 mm of Hg. The ^{19}F-nmr (DMF) showed 4 peaks at 6352 Hz from $CFCl_3$. The proton nmr ($CDCl_3$) showed a singlet at 238 Hz (integrated for 3 hydrogen), and a complex multiplet at 410-490 Hz (integrated for 6 hydrogen). The mass spectrum included peaks at m/e 204, 173 (base), 145, and 125.

Anal. Calculated for $C_{12}H_9FO_2$: C, 70.58; H, 4.44.
Found: C, 70.43; H, 4.48.

2-Fluoro-1-naphthamide

2-Fluoro-1-naphthoic acid (1 g) was heated with 3 ml of thionyl chloride on a steam bath for 10 minutes. The solution was cooled and to the solution was added gradually 10

ml of ammonium hydoxide to give 0.8 g (80% yield) of 2-fluoro-1-naphthamide as a white solid. Recrystallization from ethanol gave colorless needles, mp 172-173°. The ^{19}F-nmr (DMF) showed 4 peaks at 6552 Hz from $CFCl_3$. The infrared spectrum (KBr) had bands at 3380, 3180, and 1640 cm^{-1}. The mass spectrum included peaks at m/e 189 (base), 173, 145, and 125.

Anal. Calculated for $C_{11}H_8FNO$: C, 69.83; H, 4.27; N, 7.40. Found: C, 70.11; H, 4.22; N, 7.30.

2-Fluoro-3-naphthamide

To 1 g of 2-fluoro-3-naphthoic acid was added 10 ml of thionyl chloride. The mixture was heated on the steam bath for 30 minutes. Most of the excess thionyl chloride was removed under reduced pressure. Then 100 ml of benzene was added, and ammonia was bubbled through the solution. Ammonium chloride, was removed by filtration and benzene evaporated to give a 50% yield of 2-fluoro-3-naphthamide. Recrystallization from ethanol gave colorless needles, mp 150-151°. The ^{19}F-nmr (DMF) showed a multiplet at 6634 Hz from $CFCl_3$. The infrared spectrum (KBr) included bands at 3440, 3200, and 1660 cm^{-1}. The mass spectrum included peaks at m/e 189, 173 (base), 145, and 125.

Anal. Calculated for $C_{11}F_8FNO$: C, 69.83; H, 4.27; N, 7.40. Found: C, 69.89; H, 4.33; N, 7.24.

Nitrations

All nitrations were carried out under nitrogen in a three-necked flask equipped with a mechanical stirrer. The reaction flask was held in a constant temperature bath maintained at the desired temperature $\pm$ 0.1 C^{o}.

Nitration in acetic anhydride

In 25 ml of acetic anhydride was dissolved 0.01 mole of the substrate, and to this was added dropwise over 10 minutes, with stirring, 0.4 ml of nitric acid (d 1.5) dissolved in 1.5 ml of acetic anhydride. Stirring was continued for a time which depended upon the temperature and the solution was poured into 200 ml of ice-water. The mixture was neutralized with potassium carbonate and extracted with ether. The ether extracts were re-extracted with water, and the water extracts re-extracted with ether. The decolorized ether extracts were combined, dried with magnesium sulfate, filtered, and concentrated. These samples were then ready for injection into the gas chromatograph for analysis.

Nitration in nitromethane

In 25 ml of nitromethane was dissolved 0.01 mole of the substrate, and to this was added, dropwise over 10 minutes with stirring, 0.4 ml of nitric acid (d 1.5) dissolved in 1.0 ml of nitromethane. The remainder of the procedure is similar to that for the nitration in acetic anhydride.

Nitration with mixed acid in acetic acid

In 25 ml of acetic acid was dissolved 0.01 mole of the substrate, and to this was added dropwise over 10 minutes 1.2 ml of an equimolar mixture of nitric acid (d 1.5) and sulfuric acid (d 1.9) in acetic acid prepared by mixing 1.7 ml of nitric acid, 2.0 ml of sulfuric acid, and 1.2 ml of acetic acid. The remainder of the procedure is the same as that for the nitration in acetic anhydride.

Nitration with nitronium fluoroborate in sulpholane

In 15 ml of sulpholane was dissolved 0.01 moles of the substrate, and to this was added dropwise over 30 minutes 0.50 g of nitronium fluoroborate in 15 ml of sulpholane. Upon completion of the addition, the solution was poured into 500 ml of ice-water. The remainder of the procedure is the same as that for the nitration in acetic anhydride.

Nitration in acetic acid

In 10 ml of acetic acid was dissolved 5 g of the substrate, and to this was added 10 g of fuming nitric acid according to the procedure of Schiemann and coworkers (20). The mixture was stirred at 60° for 5 hours and allowed to cool. The remainder of the procedure is the same as that for the nitration in acetic anhydride.

Check for dinitration

Several sample nitrations were carried out in which the product and the basic extracts were analyzed for dinitration. Mass spectral analysis indicated only trace amounts of dinitration under the above nitration conditions.

The amount of time the nitration mixtures were stirred before quenching varied with temperature, and may be found in Table 29.

Nitration Product Analysis

The product mixtures dissolved in ether were analyzed by gas chromatography on a F and M Model 500 gas chromatograph. Analyses were made using a LAC-446 column, 6 foot length, with the column temperature at 183°, injection port at 200°, and detector at 210°. The retention times of the

Table 29. Nitration times (minutes)

Temperature °C	Substrate	Ac_2O	CH_3NO_2	Mixed	NO_2BF_4
25	1-Fluoronaphthalene	180	180	180	30
25	2-Fluoronaphthalene	240	240	240	30
35	1-Fluoronaphthalene	90	90		
35	2-Fluoronaphthalene	90	90		
45	1-Fluoronaphthalene	45	45		
45	2-Fluoronaphthalene	45	45		

nitronaphthalenes and nitrofluoronaphthalenes under these conditions are given in Table 30.

The traces from the gas chromatographic analysis of the product mixtures showed a number of peaks which were numbered I though V in the order of increasing retention time. The retention times of these peaks are given in Table 31.

The product peaks were identified by correlation of the retention times of the authentic samples of the nitronaphthalenes and nitrofluoronaphthalenes with the retention times of the product peaks. The assignments were also checked by peak enhancement methods using authentic compounds. The results of this correlation are given in Table 32.

Table 30. Retention times of nitronaphthalenes (minutes)

Position of nitro	1-Fluoro-naphthalene	2-Fluoro-naphthalene	Naphthalene
1	---	21.5	29.5
2	34.2	---	36.8
3	22.9	41.8	
4	20.4	17.5	
5	20.7	24.8	
6	26.1	37.2	
7	28.7	36.3	
8	49.4	28.3	

Table 31. Retention times of product mixtures (minutes)

Peak	1-Fluoro-naphthalene	2-Fluoro-naphthalene	Naphthalene
I	20.9	17.8	29.8
II	28.4	21.4	37.0
III	33.5	24.5	
IV	46.9	28.5	
V		36.6	

Table 32. Correlation of nitronaphthalenes to product mixtures

Product peak	1-Fluoro-naphthalene	2-Fluoro-naphthalene	Naphthalene
I	4- and 5-NO_2-	4-NO_2-	1-NO_2-
II	7-NO_2-	1-NO_2-	2-NO_2-
III	2-NO_2-	5-NO_2-	
IV	8-NO_2-	8-NO_2-	
V		6-NO_2-	

It was observed that both 6- and 7-nitro-2-fluoronaphthalene come under peak V in the product mixture of the nitration of 2-fluoronaphthalene. However when a column of Bentone 34 was used three peaks were observed, and 6-nitro-2-fluoronaphthalene come under peak II and 7-nitro-2-fluoronaphthalene came under peak III. Comparison of the results between the two columns, as shown in Table 33 indicated that 6-nitro-2-fluoronaphthalene is present in the nitration product, while 7-nitro-2-fluoronaphthalene is either not present or is present in only trace amounts. The values shown in Table 33 are direct from VPC areas of one nitration. The nitrations with nitronium fluoroborate are not given, since residual

Table 33. Comparison of results between LAC-446 and Bentone 34

Conditions	Bentone 34		LAC-446	
	Peak	Yield	Peak	Yield
Ac_2O	I	1.5%	I	1.5%
	II	49.5	III+ V	50.3
	III	49.0	II+IV	48.3
CH_3NO_2	I	2.2	I	2.4
	II	26.8	III+ V	26.4
	III	70.9	II+IV	71.1
Mixed	I	2.7	I	2.9
	II	28.3	III+ V	26.7
	III	69.0	II+IV	70.4

sulpholane in the mixture obscured the products when using the Bentone 34 column.

Conductivity checks were carried out on the gas chromatograph to determine the relationship between the observed peak areas and the actual relative amount of material injected. All the nitronaphthalenes were compared to 1-chloronaphthalene as a common standard. The conductivity

Table 34. Conductivity factors

Compound	T. C.
1-Nitronaphthalene	1.07
2-Nitro-1-fluoronaphthalene	1.23
4-Nitro-1-fluoronaphthalene	1.02
5-Nitro-1-fluoronaphthalene	1.02
7-Nitro-1-fluoronaphthalene	1.04
8-Nitro-1-fluoronaphthalene	1.21
2-Nitronaphthalene	1.15
1-Nitro-2-fluoronaphthalene	1.05
4-Nitro-2-fluoronaphthalene	1.10
5-Nitro-2-fluoronaphthalene	1.11
6-Nitro-2-fluoronaphthalene	1.19
8-Nitro-2-fluoronaphthalene	1.13

factors were obtained from the following expression:

$$\text{T. C.} = \frac{\frac{\%\ \text{Standard VPC}}{\%\ \text{Compound VPC}}}{\frac{\%\ \text{Standard Weighed}}{\%\ \text{Compound Weighed}}}$$

The conductivity factors determined are listed in Table 34. The areas of the gas chromatographic peaks of the observed products were multiplied by the corresponding T. C. to give

Table 35. ^{19}F-nmr of product of nitration of 1-fluoronaphthalene

Component	Hz from 1-fluoronaphthalene	
	Mixture	Individual isomer
2-Nitro-1-fluoronaphthalene	+ 64	+ 76
5- and 7-Nitro-1-fluoronaphthalene	-192	-196, -188
8-Nitro-1-fluoronaphthalene	-468	-446
4-Nitro-1-fluoronaphthalene	-720	-720

the "corrected areas" which were then used to obtain the percentages of the products.

^{19}F-nmr (DMF) were obtained on product mixtures from the nitration of each fluoronaphthalene with nitric acid in acetic anhydride. The chemical shift values of the components in the mixtures were compared to those of the individual isomers as shown in Tables 35 and 36.

Relative Rates

The relative rates of the nitration of the fluoronaphthalenes to naphthalene were determined by comparing the amounts of products formed. If the competing substrates react by the same mechanism, are present in excess over the reagent, and the reactions are first order in substrate, then

Table 36. ^{19}F-nmr of product of nitration of 2-fluoronaphthalene

Component	Hz from 2-fluoronaphthalene Mixture	Hz from 2-fluoronaphthalene Individual isomer
1-Nitro-2-fluoronaphthalene	+428	+436
4-Nitro-2-fluoronaphthalene	- 32	- 43
5-Nitro-2-fluoronaphthalene	-152	-132
6- and 8-Nitro-2-fluoronaphthalene	-402	-364, -380

$$\frac{k_F}{k_{NAPH}} = \frac{\log C_F - \log (C_F - N_F)}{\log C_{NAPH} - \log (C_{NAPH} - N_{NAPH})}$$

where C_F and C_{NAPH} are the initial concentrations of the substrates, and N_F and N_{NAPH} are the concentrations of the nitro products. Expansion gives the following expression (16).

$$\frac{k_F}{k_{NAPH}} = \frac{N_F}{N_{NAPH}}\left(1 + \frac{N_F - N_{NAPH}}{2C} + \frac{N_F N_{NAPH}}{4C^2}\right)$$

Checks indicated that the extent of nitration was generally less than 20%, except in the nitrations in nitromethane in which the reaction ranged up to approximately 30% completion. Thus the approximation is quite good, and in the extreme case, nitration in nitromethane, in which $k_F/k_{NAPH} = 0.05$,

$$\frac{N_F}{N_{NAPH}} < \frac{k_F}{k_{NAPH}} < .85\,\frac{N_F}{N_{NAPH}}$$

Nitrations of mixtures of 1-fluoronaphthalene with 1-chloronaphthalene or 1-bromonaphthalene were carried out as in the competitive nitrations of the fluoronaphthalenes with naphthalene. Analytical samples of the halonaphthalenes were prepared, and the areas determined by gas chromatography. The nitration products were diluted to 10.00 ml and the area of the remaining starting materials were determined by gas chromatography. From this the amount of halonaphthalene used was determined, and the relative rate determined.

$$\frac{k_{F\text{-NAPH}}}{k_{X\text{-NAPH}}} = \frac{[\text{F-NAPH used}]}{[\text{X-NAPH used}]}$$

Lithiations

Lithiation of 2-fluoronaphthalene with n-butyllithium

All lithiations were carried out under an atmosphere of argon or nitrogen. To a three-necked round bottom flask containing 22.1 g of 2-fluoronaphthalene in 150 ml of THF was added at -60° 96 ml of a solution of n-butyllithium in hexane (1.6 M). The mixture was stirred at approximately -60° for 6 hours, poured into a slurry of Dry Ice in ether, and allowed to stand overnight. The mixture was extracted with

aqueous potassium hydroxide and the basic extracts acidified with hydrochloric acid to yield a mixture of fluoronaphthoic acids in approximately 70% yield.

Lithiation of 2-fluoronaphthalene with t-butyllithium

Lithiation using t-butyllithium in pentane (1.25 M) was carried out using the same procedure as with n-butyllithium.

Lithiation of naphthalene with n-butyllithium

Lithiation of naphthalene in THF was carried out according to the same procedure used for lithiation of 2-fluoronaphthalene, except that the reaction was carried out at room temperature and maintained for 15 hours before quenching in Dry Ice. The acids were obtained in 20% yield with the remainder of the naphthalene recovered.

Lithiation Product Analysis

The mixture of products were analyzed by proton nmr of the mixture in dimethylacetamide. The nmr of 2-fluoro-3-naphthoic acid showed a doublet at 520 Hz from TMS which was separate from the remainder of the spectrum of the mixed acids. Simple integration of the spectrum of the mixture was used to determine the amount of this acid present.

Esterification of the acid mixture with an excess of diazomethane in ether gave a mixture of esters which were injected into the gas chromatograph and the quantitative results obtained were in agreement with those from the above nmr measurements on the free acids. Integration of the nmr spectrum of the esters also gave the same results.

The mixture of naphthoic acids from the lithiation of naphthalene was also analyzed by nmr in dimethylacetamide. The spectrum of 1-naphthoic acid contained a one proton doublet of doublets at 550 Hz which was separate from the rest of the absorption, and the spectrum of 2-naphthoic acid contained a one proton singlet at 526 Hz which was also separate from the rest of the absorption. In the mixture of the acids, these protons were separate from each other and the rest of the spectrum, and integration and comparison of the areas of these two protons yielded the relative amounts of the products.

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APPENDIX

Table 37. 2-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	2.5	12.5	125	8.2	41.4
191	19.7	100.0	121	.7	3.3
190	.7	3.3	120	.5	2.6
176	.5	2.6	119	.4	2.1
175	.3	1.3	118	.5	2.4
173	1.1	impurity	115	1.3	impurity
164	.4	2.2	108	.8	4.2
163	4.2	21.4	107	.7	3.3
161	1.0	5.0	105	.4	1.8
158	.2	1.2	100	.3	1.4
148	.7	3.6	99	1.9	9.8
147	1.8	8.9	98	.7	3.4
146	1.4	7.0	95	.6	3.1
145	11.4	57.9	94	.9	4.7
144	5.3	26.7	93	.7	3.3
143	.2	1.2	92	.4	1.8
136	0.4	1.8	87	.5	2.6
135	1.3	6.5	86	.4	2.1
134	1.8	8.9	83	.6	2.8
133	14.7	74.5	81	.5	2.7
132	.7	3.3	77	.2	1.2
131	.4	1.9	76	.4	2.1
127	1.4	7.1	75	3.3	16.5
126	1.5	7.5	74	1.5	7.7

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	163	139	139.1
161	135	113	113.2
191	145	110	110.1
161	133	110	109.9
145	125	107.8	107.8
135	108	86.3	86.5
125	99	78.5	78.4

Table 38. 3-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	2.3	10.8	125	8.6	40.5
191	21.4	100.0	120	.4	1.7
190	1.3	6.2	108	1.0	4.9
164	.3	1.6	107	.7	3.3
163	3.5	16.2	105	.3	1.6
161	1.3	6.3	99	2.3	10.6
148	.9	4.3	98	.8	3.6
147	1.3	6.2	95	.8	3.6
146	1.9	8.8	94	1.1	5.3
145	15.1	70.9	93	.7	3.3
144	3.8	17.6	87	.6	2.7
136	.6	2.7	86	.5	2.3
135	1.3	6.2	83	.6	2.8
134	1.6	7.5	81	.6	2.7
133	14.4	67.5	76	.4	2.0
132	.6	2.7	75	3.1	14.6
126	1.3	6.2	74	1.7	7.8
			72	.6	2.6

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	163	139	139.1
161	135	113	113.2
191	145	110	110.1
161	133	110	109.9
145	125	108	107.8

Table 39. 4-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
193	.2	.8	121	.3	1.2
192	2.9	11.3	119	.4	1.7
191	25.3	100.0	118	.4	1.7
190	2.1	8.4	117	.2	.8
189	.6	2.3	113	.2	.7
175	.3	1.4	108	.9	3.8
164	.3	1.0	107	.7	2.8
163	2.3	9.3	106	.3	1.1
162	.3	1.4	105	.3	1.4
161	1.4	5.5	100	.3	1.1
149	.2	.9	99	2.0	7.9
148	.3	1.4	98	.6	2.5
147	.6	2.3	95	.6	2.5
146	1.7	6.8	94	.9	3.6
145	14.6	57.7	93	.5	2.1
144	3.7	14.7	92	.3	1.1
136	1.1	4.5	87	.5	2.1
135	2.3	9.1	86	.4	1.7
134	1.5	6.1	83	.5	1.8
133	10.8	42.4	81	.5	2.1
132	.5	2.1	76	.3	1.4
131	.2	.8	75	2.8	11.1
126	1.2	4.8	74	1.5	5.9
125	8.1	32.2	72.5	.3	1.2
123	0.3	1.1	72	.6	2.3
122	.2	.9			

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	163	139	139.1
161	135	113	113.2
191	145	110	110.1
161	133	110	109.9
145	125	108	107.7
135	108	86.4	86.5
125	99	78.5	78.4
125	75	45.0	45.0

Table 40. 5-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	2.1	11.6	126	1.2	6.8
191	17.8	100.0	125	8.5	47.9
171	.7	4.1	117	.9	4.8
163	3.3	18.4	115	.7	4.1
161	1.5	8.5	108	.9	5.2
147	1.0	5.8	107	.6	3.6
146	1.7	9.8	99	2.2	12.2
145	14.9	83.6	98	.7	3.9
144	3.5	19.8	94	1.0	5.8
143	.9	4.8	93	.6	3.6
135	1.4	7.8	75	3.4	19.3
134	1.8	10.3	74	1.8	9.9
133	16.3	91.5	72	.6	3.6

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	163	139	139.1
161	135	113	113.2
191	145	110	110.1
161	133	110	109.9
145	125	107.8	107.8
135	108	86.4	86.5
125	99	78.5	78.4
125	75	45.0	45.0

Table 41. 6-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	2.2	10.8	118	.7	3.2
191	18.7	90.7	108	.7	3.4
175	.3	1.3	107	.7	3.3
163	1.0	4.7	106	.5	2.4
162	.4	1.7	105	.5	2.4
161	.8	3.7	100	.4	2.1
147	.9	4.3	99	2.7	13.1
146	.8	3.8	98	.9	4.4
145	20.6	100.0	95	.9	4.5
144	4.3	20.8	94	1.3	6.2
143	.4	2.0	93	.7	3.3
135	1.1	5.4	92	.5	2.2
134	2.0	9.5	87	.7	3.3
133	16.4	79.3	86	.7	3.3
132	.7	3.3	83	.5	2.3
131	.5	2.5	81	.7	3.3
126	1.6	7.6	76	.5	2.2
125	9.4	45.6	75	3.2	15.7
123	.4	2.0	74	2.1	10.2
119	.7	3.4	72	.6	2.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	163	139.0	139.1
163	133	108.5	108.5
145	125	107.8	107.8
		95	
133	107	86.0	86.1
125	99	78.5	78.4
95	75	59.2	59.2
125	75	45.0	45.0

Table 42. 7-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	2.6	12.2	121	1.0	4.6
191	21.4	100.0	120	.4	1.8
190	.6	2.9	119	0.6	2.7
175	.3	1.4	118	0.5	2.4
171	.2	1.1	115	0.5	2.5
163	1.5	7.0	108	1.2	5.5
162	.3	1.6	107	.6	2.9
161	1.3	6.1	106	.3	1.5
149	.5	2.3	105	.4	1.8
147	.5	2.5	100	.3	1.5
146	.8	3.8	99	2.4	11.1
145	18.3	85.5	98	.8	3.6
144	4.3	19.9	95	.9	4.2
143	.5	2.2	94	1.2	5.5
136	.8	3.7	93	.7	3.5
135	2.5	11.5	92	.3	1.6
134	1.4	6.4	86	.5	2.2
133	9.9	46.2	83	.4	2.1
132	.6	2.6	81	.6	2.9
131	.4	1.8	76	.4	1.8
126	1.2	5.8	75	3.0	13.9
125	8.9	41.8	74	1.6	7.7
123	.9	4.2	72.5	.4	2.1
122	.5	2.4	72	.6	2.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	171	153.0	153.1
191	163	139.0	139.1
145	125	107.8	107.8
163	125	96.0	95.9
133	107	86.3 82.5	86.1
125	99	78.5	78.4
95	75	59.3	59.2
163	94	54.0	54.2
125	75	45.0	45.0

Table 43. 8-Fluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	2.3	12.1	118	.6	3.0
191	18.8	100.0	117	.4	2.3
190	.3	1.8	116	1.7	9.2
175	.3	1.7	115	1.0	5.4
163	.6	3.1	108	1.1	5.6
162	.9	4.6	107	.8	4.4
161	.9	4.9	106	1.3	7.1
146	2.0	10.7	105	.4	2.2
145	16.3	86.2	99	2.4	12.8
144	6.8	36.0	98	.7	3.8
143	.6	3.4	95	.6	3.3
136	.5	2.6	94	1.1	5.7
135	2.0	10.5	93	.7	3.9
134	3.7	19.6	92	.5	2.5
133	9.1	48.2	87	.5	2.8
132	.6	3.3	86	.5	2.4
131	.3	1.8	83	.5	2.4
126	1.1	6.0	81	.6	3.1
125	8.4	44.4	80	.4	2.0
123	.5	2.4	78	.7	3.7
122	.3	1.8	76	.5	2.4
121	.7	3.5	75	3.2	16.9
119	.5	2.5	74	1.5	8.7
			72	.4	2.1

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
175	145	120.5	120.1
163	133	108.5	108.5
145	125	107.8	107.8
144	116	93.5	93.4
133	107	86.2	86.1
125	99	78.3	78.4
125	75	45.0	45.0

Table 44. 1-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	3.9	12.7	108	.5	1.7
191	30.4	100.0	107	.5	1.7
161	2.8	9.1	99	2.8	9.1
146	1.7	5.5	98	.7	2.3
145	23.7	78.4	95	.5	1.6
144	4.7	15.4	94	1.0	3.4
134	1.1	3.6	87	.7	2.3
133	11.6	38.2	81	.8	2.6
126	1.4	4.7	77	1.3	4.4
125	8.2	27.0	75	4.3	14.0
			74	1.5	4.9

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	161	136	135.7
191	145	110	110.1
161	133	110	109.9
145	125	107.8	107.8

Table 45. 3-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
193	.3	1.1	108	.4	1.4
192	3.5	12.7	107	.4	1.4
191	27.7	100.0	106	.2	.7
175	.4	1.4	105	.4	1.4
161	1.1	4.0	100	.2	.7
158	.2	.7	99	1.9	6.9
146	2.5	9.0	98	.6	2.2
145	20.8	75.2	95	.7	2.5
144	4.4	15.9	94	1.0	3.6
143	.3	1.1	93	.6	2.2
134	.9	3.2	92	.5	1.8
133	8.2	29.6	91	.2	.7
132	.3	1.1	87	.4	1.4
131	.2	.7	86	.4	1.4
127	.2	.7	85	.3	1.1
126	1.2	4.3	83	.4	1.4
125	8.0	28.9	81	.5	1.8
123	.3	1.1	79	.2	.7
122	.2	.7	78	2.8	10.1
119	.5	1.8	77	.5	1.8
118	.5	1.8	76	.5	1.8
117	.2	.7	75	2.3	8.3
112	.2	.7	74	1.3	4.7
111	.2	.7	73	.2	.7
109	.2	.7	71	.2	.7

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	161	136	135.7
191	145	110	110.1
161	133	110	109.9
145	125	107.7	107.8
		99.0	
191	133	93.0	92.6
119	99	82.5	82.3
125	99	78.2	78.4
125	75	45.0	45.0

Table 46. 4-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	3.6	11.8	105	.3	.8
191	30.6	100.0	99	2.0	6.5
161	.3	.8	98	.7	2.3
146	2.7	9.0	95	.6	1.9
145	24.6	80.6	94	1.0	3.4
144	4.0	13.1	93	.5	1.8
134	.8	2.8	92	.3	.8
133	8.5	27.8	87	.5	1.7
132	.4	1.3	86	.4	1.3
126	1.3	4.1	81	.5	1.6
125	9.4	30.8	76	.4	1.4
119	.4	1.2	75	3.1	10.1
118	.4	1.4	74	1.6	5.4
108	.4	1.3	72	.4	1.2
107	.3	.8			

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	161	136	135.7
191	145	110	110.1
161	133	110	109.9
145	125	107.7	107.8
191	133	93.0	92.6
125	99	78.5	78.4
125	75	45.0	45.0

Table 47. 5-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
193	.3	1.0	108	.4	1.6
192	3.1	11.5	107	.5	1.7
191	26.8	100.0	106	.3	1.0
175	.3	1.0	105	.4	1.5
161	.1	.4	100	.3	1.1
158	.2	.8	99	2.3	8.8
146	2.8	10.4	98	.8	2.9
145	25.9	97.6	95	.7	2.5
144	4.0	15.1	94	1.1	4.2
143	.3	1.2	93	.6	2.4
134	.7	2.8	92	.4	1.4
133	7.2	27.1	87	.5	2.0
132	.4	1.6	86	.4	1.6
131	.3	1.1	85	.2	.9
126	1.3	4.8	83	.3	1.1
125	8.8	33.2	81	.5	2.0
124	.2	.8	76	.4	1.5
123	.4	1.4	75	3.1	11.6
122	.3	1.0	74	1.6	6.1
119	.5	1.9	72.5	.3	1.0
118	.5	2.0	72	.4	1.5
117	.3	1.0	70	.3	1.1

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	145	110	110.1
161	133	110	109.9
145	125	107.7	107.8
125	75	45.0	45.0

Table 48. 6-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
192	3.5	11.7	107	.4	1.3
191	29.7	100.0	99	2.0	6.9
161	1.0	3.2	98	.7	2.3
146	2.6	8.8	95	.8	2.6
145	25.5	85.7	94	1.1	3.5
144	3.9	13.0	93	.6	1.9
134	.8	2.6	87	.5	1.6
133	7.6	25.4	86	.4	1.3
132	.4	1.3	81	.5	1.7
126	1.1	3.5	75	2.5	8.5
125	7.5	25.2	74	1.4	4.7
119	.4	1.4	72	.4	1.3
118	.4	1.3			

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	161	136	135.7
191	145	110	110.1
161	133	110	109.9
145	125	108	107.8
191	133	93.0	92.6
119	99	82.5	82.3
125	99	78.5	78.4
125	75	45.0	45.0

Table 49. 7-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
193	.2	.7	108	.5	1.7
192	2.3	8.0	107	.5	1.7
191	18.6	65.0	106	.3	.9
175	.3	1.1	105	.4	1.4
161	.2	.6	100	.3	1.0
159	.1	.4	99	2.5	8.7
158	.4	1.2	98	.9	3.2
147	.2	.6	95	1.0	3.3
146	3.0	10.5	94	1.3	4.4
145	35.0	100.0	93	.8	2.6
144	5.1	17.7	92	.4	1.3
143	.5	1.6	87	.6	2.0
134	1.0	3.4	86	.5	1.7
133	9.5	33.2	85	.2	.8
132	.6	1.9	83	.3	1.0
131	.3	1.1	81	.6	2.0
126	1.3	4.4	76	.3	1.0
125	9.0	31.3	75	3.0	10.5
124	.2	.5	74	1.8	6.1
123	.4	1.3	73	.1	.4
122	.3	1.0	72.5	.1	.4
119	.6	2.1	72	.3	.9
118	.6	1.9	71	.1	.4
117	.3	1.0	70	.3	.9

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	145	110	110.1
161	133	110	109.9
145	125	108	107.8
191	133	93	92.6
125	99	79	78.4

Table 50. 8-Fluoro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
193	.2	.8	113	.1	.4
192	3.6	13.0	111	.1	.4
191	27.7	100.0	110	.1	.5
175	.3	1.0	109	.1	.4
161	.2	.9	108	.4	1.4
159	.1	.4	107	.4	1.4
158	.2	.8	106	.2	.7
157	.1	.4	105	.3	1.2
147	.1	.5	100	.2	.8
146	3.2	11.4	99	2.1	7.4
145	24.8	89.4	98	.6	2.3
144	4.2	15.2	95.5	.1	.4
143	.3	1.1	95	.6	2.2
134	.9	3.3	94	1.1	4.0
133	7.3	26.3	93	.6	2.3
132	.5	1.7	92	.3	1.1
131	.3	1.3	87	.4	1.5
129	.1	.4	86	.3	1.2
127	.2	.6	85	.2	.7
126	1.2	4.2	83	.3	.9
125	7.6	27.5	81	.4	1.6
124	.2	.6	80	.1	.4
123	.3	1.1	76	.3	1.1
122	.2	.8	75	2.7	9.7
120	.1	.4	74	1.4	4.9
119	.4	1.6	73	.5	1.7
118	.5	1.9	72.5	.2	.8
117	.3	1.1	72	.3	.9

Metastable transition

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
191	145	110	110.1
161	133	110	109.9
145	125	107.8	107.8
191	133	92.5	92.6
125	99	79.0	78.4
125	75	45.0	45.0

Table 51. 1-Chloro-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
210	.7	3.7	126	14.9	77.0
209	6.4	32.9	125	3.5	18.0
208	2.2	11.4	123	.3	1.6
207	19.3	100.0	114	1.0	5.4
191	.3	1.3	113	.7	3.5
179	.3	1.5	111	.3	1.5
177	.8	4.3	100	.7	3.7
172	.4	1.9	99	2.2	11.2
164	.4	2.2	98	1.1	5.9
163	3.8	19.9	97	.4	2.1
162	1.7	8.9	89	.6	2.9
161	12.0	62.2	88	.4	1.9
160	.7	3.7	87	.9	4.8
152	.3	1.7	86	.7	3.5
151	2.9	15.1	85	.4	2.3
150	.9	4.9	77	.4	2.2
149	9.2	47.7	76	1.5	7.8
128	.3	1.8	75	3.0	15.6
127	1.6	8.5	74	2.2	11.3
			73	.3	1.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
207	172	143	142.9
207	161	126	125.2
209	151	108	109.1
207	149	108	107.3
161	126	98.8	98.6
149	114	87	87.2
125	99	78.8	78.4
114	88	68	67.9
126	76	45.9	45.8
125	75	45.0	45.0

Table 52. 4-Chloro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
210	.9	4.2	151	3.5	16.0
209	7.3	33.6	150	.9	4.0
208	3.3	15.2	149	7.3	33.3
207	21.8	100.0	144	1.1	4.9
206	2.0	9.4	142	.5	2.2
205	.3	1.5	128	.9	4.3
191	.3	1.3	127	1.3	6.0
181	.8	3.8	126	10.1	49.9
180	.3	1.5	125	2.7	12.4
179	2.6	12.0	124	.3	1.3
177	.9	4.1	123	.3	1.3
173	.4	1.9	122	.3	1.3
172	3.5	15.9	116	1.0	4.3
164	.6	2.8	115	1.1	5.2
163	2.4	11.2	113	.6	2.9
162	1.1	4.9	100	.6	2.7
161	7.1	32.4	99	1.6	7.3
160	.7	3.1	98	.8	3.8
156	.4	2.0	87	.6	2.8
154	.3	1.4	86	.5	2.2
153	.5	2.2	76	1.0	4.7
152	1.0	4.5	75	2.0	9.4

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
207	172	143	142.9
161	126	98.8	98.6

Table 53. 5-Chloro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
210	.4	3.4	129	.3	2.5
209	3.6	28.0	128	2.6	19.9
208	1.4	10.5	127	1.6	12.6
207	10.3	80.1	126	12.9	100.0
181	1.5	11.5	125	3.7	28.6
180	.6	4.4	124	.4	3.4
179	4.6	35.9	123	.4	3.4
178	.3	2.1	122	.4	3.4
177	1.5	11.8	117	.8	6.3
172	1.4	10.7	116	1.2	9.5
164	.3	2.5	115	.8	6.3
163	2.4	18.5	114	2.0	15.8
162	1.0	8.0	113	1.0	7.6
161	6.2	48.2	101	.3	2.1
160	.6	5.0	100	.8	6.5
156	.7	5.7	99	3.0	23.3
153	.3	2.3	98	1.3	9.9
152	.9	6.9	97	.4	2.9
151	4.2	32.1	89	.3	2.5
150	1.3	10.1	88	.4	3.2
149	11.3	87.9	87	1.1	8.4
145	.4	3.4	86	.8	6.3
144	.7	5.7	85	.5	3.6
143	.3	2.3	77	.3	2.1
142	.4	3.2	76	1.5	11.3
135	.4	3.2	75	4.0	30.6
133	.3	2.1	74	2.8	21.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
209	151	108	109.1
207	149	108	107.3
161	126	98.5	98.6
149	114	87.3	87.2
125	99	78.5	78.4

Table 54. 8-Chloro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
210	.5	2.1	142	2.7	11.9
209	4.2	18.6	134	.8	3.7
208	1.5	6.8	133	.7	2.9
207	11.1	49.4	128	1.3	5.8
181	.4	1.6	127	1.8	8.2
179	1.3	5.8	126	12.9	57.0
177	.9	4.0	125	4.8	21.1
173	3.4	15.0	117	.4	1.6
172	22.5	100.0	116	2.1	9.3
171	.6	2.7	115	.7	3.2
164	.4	1.7	114	3.6	15.8
163	3.4	15.0	113	.9	4.2
162	1.5	6.5	100	.8	3.4
161	8.3	36.6	99	2.9	13.0
160	.9	3.8	98	1.1	5.1
156	.8	3.7	89	.4	1.7
152	.9	4.0	88	.6	2.5
151	2.3	10.4	87	1.0	4.4
150	.8	3.7	86	.7	3.2
149	7.0	30.9	85	.4	1.7
145	1.2	5.5	78	.4	1.8
144	1.6	7.3	75	4.6	20.2
143	.7	2.9	74	2.5	11.3
			73	.4	1.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
207	172	143	142.9
172	144	120.5	120.6
209	151	108	109.1
207	149	108	107.3
161	126	98.8	98.6
163	126	97.8	97.4
144	116	93.5	93.4
142	114	91.5	91.5
149	114	87.2	87.2
125	99	78.2	78.4
114	75	49.4	49.3
125	75	45.0	45.0

Table 55. 4,8-Difluoro-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
210	2.4	10.7	139	.5	2.2
209	22.1	100.0	134	1.9	8.6
193	.5	2.2	133	1.0	4.4
191	.5	2.2	131	.5	2.4
181	.5	2.2	126	.8	3.6
180	1.6	7.2	125	.6	2.5
179	1.2	5.4	123	1.6	7.4
164	1.8	8.4	117	.6	2.9
163	18.6	84.5	111	.5	2.3
162	8.2	37.3	105	.5	2.4
161	1.7	7.5	99	.5	2.2
153	.8	3.6	94	.5	2.2
152	1.3	5.9	93	.7	3.1
151	7.0	31.9	37	.7	3.0
150	.6	26.5	81	.9	4.3
144	1.6	7.2	75	.6	2.9
143	9.4	42.7	74	1.1	4.9

Metastable transitions

Parent ion	Daughter ion	Metasable	
		Observed	Calculated
209	181	156	156.7
181	151	126	126.0
153	133	115.5 111.5	115.6
143	123	106	105.6

Table 56. 2-Amino-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	2.6	12.3	116	3.3	15.8
188	21.2	100.0	115	14.9	70.6
187	.4	1.7	114	3.1	14.7
171	.4	1.9	113	1.8	8.4
160	1.0	4.7	105	.3	1.5
159	1.1	5.4	104	.7	3.2
158	2.9	13.5	103	2.2	14.3
153	.3	1.5	102	1.2	5.5
144	.5	2.6	101	.6	3.0
143	1.4	6.6	90	.5	2.6
142	3.7	17.3	89	1.9	9.2
141	1.5	7.3	88	1.5	7.0
140	3.0	14.0	37	.7	3.5
132	1.4	6.4	86	.4	2.0
131	5.0	23.8	78	.4	1.7
130	5.0	23.7	77	1.8	8.5
129	.5	2.2	76	1.0	4.9
128	.7	3.1	75	1.1	5.0
127	.8	4.0	74	.7	3.3
118	.3	1.8	71	.9	4.4
117	1.0	4.6	70.5	2.4	11.4

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	160	137	136.2
158	131	109	108.6
142	115	93	93.1
130	103	82	81.6

Table 57. 3-Amino-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
190	.2	.9	115	22.3	82.8
189	3.2	12.0	114	2.3	8.6
188	26.8	100.0	113	1.4	5.2
187	.2	.9	104	.3	1.2
160	.2	.6	103	1.2	4.3
159	.2	.7	102	.7	2.5
158	.8	3.1	101	.3	1.0
143	1.5	5.4	94	.6	2.2
142	10.9	40.8	90	.3	1.2
141	1.4	5.4	89	2.1	7.7
140	2.7	9.9	88	1.0	3.8
131	.9	3.2	87	.7	2.5
130	5.6	20.7	86	.4	1.5
129	.3	1.2	78	.2	.9
128	.3	1.1	77	1.0	3.8
126	.2	.9	76	.6	2.2
117	.3	1.1	75	.8	3.1
116	3.5	12.9	74	.6	2.4
			71	.9	3.4
			70.5	2.7	10.2

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	172	158	157.4
188	161	139	137.9
188	142	107.5	107.3
142	115	93.1	93.1

Table 58. 4-Amino-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	3.7	13.8	114	2.0	7.6
188	27.0	100.0	113	1.4	5.2
172	.6	2.1	104	.6	2.3
159	1.2	4.4	103	1.7	6.4
158	7.0	25.9	102	.9	3.4
143	1.4	5.0	90	.5	16.7
142	9.3	34.3	89	1.9	6.9
141	1.6	5.8	88	1.1	3.9
140	2.6	9.7	87	.8	2.8
131	.9	3.5	86	.5	1.7
130	3.0	11.3	80	.9	3.4
129	.7	2.5	77	1.6	5.8
128	.7	2.7	76	.9	3.1
127	.4	1.6	75	1.0	3.8
117	.5	2.0	74	.7	2.6
116	4.3	15.8	71	.9	3.2
115	12.4	45.8	70.5	1.9	6.9

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	161	138.5	137.9
188	158	134.5 131.5	133.3
188	142	107.5	107.3
142	115	93	93.1
130	103	81.6	81.6
115	89	68.5	68.9

Table 59. 5-Amino-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	1.7	12.4	115	13.3	95.1
188	14.0	100.0	114	1.6	11.6
187	1.0	7.2	113	.8	5.5
160	.6	4.5	105	1.4	10.1
159	1.0	7.4	104	.8	5.9
158	.8	5.5	103	2.3	16.6
143	1.2	8.3	102	1.3	9.2
142	1.9	13.8	94	1.8	12.6
141	1.0	7.4	93	2.9	20.7
140	.7	5.2	92	.6	4.6
133	.6	4.0	91	2.4	17.3
132	.6	4.1	90	4.8	34.1
131	.7	5.0	89	1.8	12.6
130	2.6	18.3	88	.7	5.1
129	.6	4.1	79	.7	4.9
123	2.3	16.2	78	3.9	28.1
122	8.3	59.6	77	7.1	50.8
121	5.3	38.1	76	1.5	10.7
120	1.0	7.2	75	1.0	7.3
119	.7	4.9	74	.9	6.2
116	1.5	10.8	71	.6	4.1
			70.5	1.1	7.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	160	136	136.2
158	131	109	108.6
142	115	93.1	93.1
142	113	90	89.9
130	103	81.6	81.6
122	94	72.5	72.4

Table 60. 6-Amino-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	3.4	12.1	113	1.2	4.2
188	28.3	100.0	103	.7	2.6
158	.5	1.7	102	.8	2.8
143	2.6	9.1	89	1.4	5.0
142	19.6	69.2	88	.9	3.0
141	2.8	9.9	87	.5	1.8
140	1.5	5.5	78	2.2	7.6
131	.6	2.1	77	1.1	4.0
130	4.8	16.8	76	.6	2.2
116	1.8	6.5	75	.7	2.6
115	11.2	39.6	74	.7	2.3
114	2.4	8.5	71	1.2	4.2
			70.5	3.0	10.4

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	142	107.5	107.3
142	115	93	93.1
142	113	90	89.9
130	103	81.5 77	81.6
115	89	68.5	68.9

Table 61. 7-Amino-1-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	2.3	11.9	114	2.1	10.8
188	19.5	100.0	113	1.2	6.3
187	1.0	5.0	105	.5	2.6
171	1.8	9.3	104	.9	4.4
162	.4	2.3	103	1.6	8.2
159	.6	3.0	102	1.0	5.2
158	3.0	15.3	94	.7	3.8
144	.9	4.6	90	.4	2.3
143	3.4	17.3	89	1.6	8.4
142	8.8	45.1	88	1.4	7.3
141	2.6	13.5	87	.7	3.4
140	1.6	8.2	83	.4	2.3
133	.4	2.3	77	1.2	6.0
131	1.1	5.6	76	.6	3.1
130	3.9	20.2	75	.7	3.4
129	.7	3.8	74	.4	2.3
128	.5	2.6	73	.4	2.3
117	1.0	4.9	71	1.5	7.5
116	2.6	13.4	70.5	3.7	19.2
115	12.6	64.8	70	.7	3.4

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	171	155.5	155.5
188	158	133	133.3
158	131	108.7	108.6
142	115	93	93.1
130	103	81.7	81.6
115	89	68.5	68.9

Table 62. 1-Amino-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	3.7	10.4	127	1.5	4.2
188	35.4	100.0	116	3.6	10.2
173	.7	1.9	115	13.8	38.8
158	1.5	4.2	114	2.4	6.7
153	1.0	2.7	113	1.4	3.9
149	1.1	3.2	103	.7	1.9
143	1.1	3.2	94	.7	2.1
142	8.5	24.1	89	1.0	2.7
141	1.4	3.9	88	.9	2.5
140	2.9	8.3	77	1.0	2.7
130	1.8	5.2	75	.6	1.8
129	.6	1.8	71	1.5	4.3
128	.6	1.8	70.5	2.2	6.1

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	158	133	133.3
188	142	107.5	107.3
142	115	93.2	93.1

Table 63. 4-Amino-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	2.9	11.9	102	.6	2.5
188	24.0	100.0	97	.6	2.7
158	1.4	5.9	95	.6	2.5
149	.9	3.7	94	.9	3.8
143	2.1	8.8	93	.6	2.3
142	17.0	70.6	89	1.7	7.2
141	2.4	8.6	88	.9	3.8
140	4.1	16.9	87	.8	3.3
130	2.8	11.7	85	.7	2.9
129	8.2	3.4	83	.9	3.7
116	4.7	19.4	81	.7	2.8
115	12.8	53.3	77	.8	3.4
114	2.2	9.2	76	.6	2.3
113	1.6	6.6	75	.7	2.9
112	.6	2.7	74	.6	2.4
111	.5	2.1	73	1.0	4.1
109	.5	2.2	71	2.3	9.4
103	.6	2.4	70.5	2.6	10.8
			70	.9	3.8

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	172	158	157.4
188	161	138.5	137.9
188	158	133	133.3
188	142	107.5	107.3
142	115	93.2	93.1
142	113	90	89.9
115	89	68.5	68.9

Table 64. 5-Amino-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	2.2	13.2	110	1.2	6.9
188	16.9	100.0	109	1.9	11.5
167	.7	4.1	107	.8	4.9
151	.8	4.6	99	.9	5.3
149	2.2	13.2	98	.9	5.3
143	1.0	5.8	97	3.1	18.1
132	6.8	40.3	96	1.4	8.2
141	1.7	9.9	95	2.9	17.4
140	1.4	8.2	94	1.0	6.1
139	.7	4.2	93	1.1	6.4
137	.9	5.6	89	1.2	6.9
135	.7	4.1	88	.8	4.8
130	1.6	9.5	87	.8	4.6
126	.8	4.8	85	2.1	12.3
125	1.3	7.4	84	1.2	6.9
124	.8	4.6	83	3.6	21.0
123	1.4	8.2	82	1.4	8.4
121	.7	3.9	81	3.0	18.0
116	1.7	9.9	79	.7	4.3
115	12.8	75.8	77	.7	4.3
114	2.1	12.3	73	.9	5.4
113	1.7	9.9	71	3.6	21.4
112	1.0	5.8	70.5	1.0	5.8
111	2.0	11.7	70	1.7	10.0

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	142	107.5	107.3
142	115	93.1	93.1

Table 65. 6-Amino-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	3.2	12.0	99	.6	2.3
188	26.4	100.0	97	1.0	3.8
158	3.5	13.1	95	.9	3.4
149	3.4	13.0	91	.6	2.3
143	2.0	7.5	89	1.4	5.3
142	16.0	60.8	88	1.1	4.3
141	2.8	10.6	87	.7	2.8
140	1.7	6.3	85	1.1	4.1
130	3.5	13.3	84	.7	2.5
116	1.8	7.0	83	1.4	5.2
115	9.7	36.9	82	.7	2.5
114	2.7	10.4	81	.9	3.6
113	1.7	6.5	77	1.1	4.2
112	.7	2.5	76	.7	2.7
111	.8	3.1	75	.8	2.9
109	.6	2.3	74	.7	2.6
105	.6	2.1	73	.7	2.8
103	.7	2.7	71	2.1	8.1
102	1.0	3.9	70.5	1.4	5.4
			70	1.1	4.3

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	172	157	157.4
188	158	134	133.3
188	142	107.6	107.3
142	115	93.1	93.1
115	89	69	68.9

Table 66. 7-Amino-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	4.0	12.9	105	.6	2.1
188	30.8	100.0	102	.7	2.4
149	2.6	8.4	99	.8	2.6
143	2.2	7.1	98	.8	2.5
142	15.9	51.6	97	1.9	6.2
141	2.4	7.7	96	.9	3.0
140	1.5	5.0	95	1.5	5.0
137	.6	2.1	94	1.0	3.2
130	1.6	5.2	93	.7	2.3
125	.9	2.8	89	.9	2.9
123	.8	2.7	88	.7	2.4
116	1.3	4.1	85	1.6	5.2
115	6.7	21.8	84	.8	2.6
114	1.6	5.2	83	2.0	6.6
113	1.3	4.2	82	1.0	3.4
112	.7	2.3	81	1.5	5.0
110	.6	1.9	71	2.6	8.4
109	1.1	3.5	70.5	1.2	3.9
107	.8	2.5	70	1.3	4.2

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
188	142	107.3	107.3
142	115	93.1	93.1

Table 67. 8-Amino-2-nitronaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
189	3.4	12.2	97	.7	2.6
188	28.0	100.0	96	.5	1.8
158	.6	2.0	95	1.0	3.6
149	1.3	4.6	94	.6	2.0
143	.6	2.3	93	.6	2.1
142	4.8	17.0	89	1.5	5.3
141	1.8	6.3	88	1.1	3.8
140	1.2	4.4	87	.7	2.4
130	1.9	6.7	85	.7	2.5
123	.5	1.9	83	1.1	4.0
116	3.4	12.0	82	.6	2.0
115	27.3	97.3	81	1.1	4.0
114	3.5	12.4	77	.8	2.8
113	1.7	6.1	76	.5	1.7
111	.8	2.7	75	.6	2.2
109	.8	2.7	74	.6	2.0
107	.5	1.8	71	1.6	5.6
103	.7	2.4	70.5	1.7	5.9
102	.8	2.7	70	.6	2.2

Metastable transitions

Parent ion	Daughter ion	Metastable Observed	Metastable Calculated
188	158	133	133.3
188	142	107.4	107.3
142	115	93.1	93.1

Table 68. 4-Nitro-1-cyanonaphthalene

m/e	% Σ^{M}_{70}	% base	m/e	% Σ^{M}_{70}	% base
199	2.4	13.2	127	.7	4.0
198	18.5	100.0	126	1.5	8.4
197	2.8	15.1	125	5.4	29.3
196	.4	2.3	124	.8	4.4
171	.5	2.9	123	.4	1.9
170	3.2	17.1	115	1.1	6.1
169	.5	2.5	114	.7	3.6
168	.8	4.5	113	1.4	7.8
156	.5	2.7	112	.4	2.0
155	1.6	8.5	102	.6	3.5
154	.8	4.5	101	1.5	8.4
153	1.7	9.4	100	1.0	5.5
152	12.9	70.0	99	1.9	10.2
151	2.8	15.3	98	.7	3.8
143	1.5	7.9	88	.6	3.0
142	3.0	16.0	87	.8	4.1
141	1.8	9.7	86	.5	2.8
140	14.4	78.2	77	2.0	11.1
139	.5	2.6	76	1.4	7.8
128	.4	2.1	75	3.5	18.9
			74	2.0	10.7

Metastable transitions

Parent ion	Daughter ion	Metastable	
		Observed	Calculated
198	170	146.5	146.4
171	143	120	119.9
152	125	103	102.9
142	115	93.2	93.0
140	113	91.4	91.4
125	99	78.5	78.4
101	75	55.5	55.7
125	75	45.0	45.0