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Preparation and Carbon-13 Nuclear Magnetic Resonance Structural Study of Protonated, Methylated, and Sb_5- or BF_3-Complexed Nitroalkanes and Nitroarenes[1]

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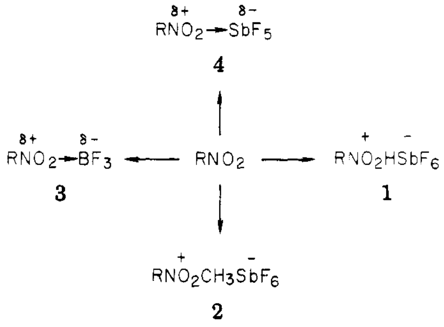
The nature of the ionic intermediates formed by the protonation, methylation, or Lewis acid fluoride complexation of aliphatic and aromatic nitro compounds was investigated by carbon-13 NMR spectroscopy at low temperatures (-40 to -100 °C). Protonation and methylation of the nitro compounds were carried out in FSO_3H-SbF_5 (1:1)/SO_2ClF and CH_3F-SbF_5/SO_2, respectively, whereas complexation was studied with BF_3 or SbF_5 in the same solvents. In all cases, the electrophiles interact with only one of the two oxygen atoms of the nitro group. In order to assess the carbon-13 NMR chemical shifts of the nitronium ions obtained, they were compared to the chemical shifts of the corresponding parent (neutral) nitro compounds. Whereas appreciable deshielding effects (downward shifts) were observed for the α-carbons in the case of aliphatic nitro compounds upon the formation of the nitronium salts, slight shielding effects were found for the carbons directly attached to the nitro group (ipso carbons) in aromatic nitro compounds. The probable origin of these effects is discussed with structural evaluation of the studied nitronium ions. The carbon-proton coupling constants of the nitronium salts were also determined.

Introduction

The chemistry and structure of nitro compounds have been the subject of extensive experimental and theoretical investigations.[2] In strongly acidic media, these compounds behave as weak bases and have been used in the spectroscopic determinations of the acidity of strong acids.[3] In basic media, aliphatic nitro compounds with α-hydrogens are readily ionized to the corresponding nitro carbanions.[2]

Structural aspects of nitro compounds in neutral, acidic, and basic solutions have been studied by various spectroscopic methods.[2] In NMR spectroscopy only limited investigations have been carried out on the nature of aliphatic or aromatic nitro species in the solutions mentioned above.[4] Proton, carbon-13, nitrogen-14, nitrogen-15, and oxygen-17 NMR spectra of nitro compounds have been reported[4-8] in neutral media. Recently, the NMR spectra of these nuclei have also been determined in basic media for some primary and secondary aliphatic nitro compounds.[7] However, in strongly acidic solutions only proton NMR spectroscopic studies have been carried out,[9-11] and this prompted us to initiate a carbon-13 NMR study of protonated nitro compounds. The results are reported in this paper. We also report on the hitherto unexplored structural features of the nitronium salts formed by the methylation of nitroalkanes and nitroarenes and complexation of these compounds with Lewis acid fluorides such as antimony pentafluoride and boron trifluoride.

Scheme I. Nitronium Salts Formed by Protonation (1), Methylation (2), and Boron Trifluoride (3) or Antimony Pentafluoride (4) Complexation of Nitroalkanes and Nitroarenes



R = alkyl or aryl group

Experimental Section

All the nitro compounds used in this study were commercially available, except for the 2- and 4-deuterionitrobenzenes which were synthesized by the reaction of the corresponding nitrodiazoniumbenzenes with deuterated hypophosphorous acid, as described by Murray and Williams.[12] Protonation was accomplished by the dissolution of the appropriate nitro compound in SO_2ClF at ca. -50 °C and the subsequent careful addition of this solution to a stirred solution of FSO_3H-SbF_5 (1:1) in SO_2ClF at -78 °C (dry ice-acetone bath) to obtain a ca. 10-15% solution. Addition of a nitro compound in SO_2 to a solution of SbF_5 in SO_2 at -40 °C resulted in the formation of the corresponding fluoroantimonate complex. The boron trifluoride complexes were formed by introducing boron trifluoride gas into solutions of nitro compounds in SO_2 at -40 °C.

Preparation of an O-methylated nitro compound was effected in the following way: methyl fluoride (gas) was introduced into

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[1] Onium ions, Part 22; for Part 21, see G. A. Olah, G. K. S. Prakash, and M. Bruce, *J. Am. Chem. Soc.*, **101**, 6463 (1979).

[2] H. Feuer, Ed., "The Chemistry of the Nitro and Nitroso Group", Vol. I, John Wiley and Sons, Inc., New York, 1969.

[3] R. J. Gillespie and C. S. Solomons, *J. Chem. Soc.*, **1796** (1957); R. J. Gillespie, *ibid.*, 2592 (1950).

[4] P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, **70**, 841 (1958); H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); P. C. Lauterbur, *ibid.*, **38**, 1432 (1963).

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[6] M. Witanowski, T. Urbanski, and L. Stefaniak, *J. Am. Chem. Soc.*, **86**, 2569 (1964); M. Witanowski and L. Stefaniak, *J. Chem. Soc. B*, 1061 (1967); M. Witanowski and H. Januszewski, *ibid.*, 1062 (1967); M. Witanowski, L. Stefaniak, and G. A. Webb, *ibid.*, 1065 (1967); C. F. Povauski and W. B. Mouiz, *J. Phys. Chem.*, **71**, 1142 (1967); W. Bresmer, J. I. Kroschwitz, and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 6189 (1969).

[7] E. T. Llippmaa, M. J. Mägi, J. O. Past, S. A. Shevelev, V. I. Erashko, and A. A. Fainzil'berg, *Izv. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1006, 1012 (1971).

[8] S. S. Novikov, L. I. Khmelnitski, A. S. Prihodko, O. V. Lebedev, and L. V. Epishina, *Org. Mag. Reson.*, **4**, 153 (1972).

[9] G. A. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **90**, 6461 (1968).

[10] H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **87**, 1320 (1968).

[11] N. C. Deno, R. W. Gaugler, and T. Schulze, *J. Org. Chem.*, **31**, 1968 (1966).

[12] A. Murray and D. L. Williams, "Organic Synthesis with Isotopes", Interscience, New York, 1958, pp 1375 and 1592.

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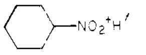
Table I. ^{13}C NMR Data[a,b] of Protonated,[c] Methylated,[d] and Complexed[e] Nitroalkanes

nitronium ion	C-1	C-2	C-3	C-4	C-5	added methyl
$CH_3NO_2^+H$	64.7, $\Delta = 2.7$, $J = 145.1$					
$CH_3CH_2NO_2^+H$	75.5, $\Delta = 5.5$, $J = 142.0$	8.9, $\Delta = -2.2$, $J = 130.2$				
$CH_3CH_2CH_2NO_2^+H$	80.4, $\Delta = 3.7$, $J = 143.4$	20.0, $\Delta = -0.6$, $J = 127.0$	9.0, $\Delta = -0.8$, $J = 127.0$			
$CH_3(CH_2)_3NO_2^+H$	80.6, $\Delta = 4.3$, $J = 150.0$	29.6, $\Delta = -0.6$, $J = 128.2$	19.8, $\Delta = -0.3$	13.5, $\Delta = 0.1$		
$CH_3(CH_2)_4NO_2^+H$	80.6, $\Delta = 4.5$, $J = 148.0$	28.1, $\Delta = -0.7$, $J = 127.5$	27.5, $\Delta = -0.2$	22.8, $\Delta = 0$	13.8, $\Delta = 0.1$	
$(CH_3)_2CHNO_2^+H$	87.8, $\Delta = 9.1$, $J = 153.0$	20.7, $\Delta = 0.8$, $J = 131.0$				
$^3CH_3{}^2CH_2{}^1CH(^4CH_3)NO_2^+H$	94.3, $\Delta = 9.3$, $J = 157.0$	30.9, $\Delta = 1.9$, $J = 131.5$	9.8, $\Delta = -0.4$, $J = 127.3$	17.8, $\Delta = -1.0$, $J = 134.7$		
 [f]	91.9, $\Delta = 7.2$, $J = 149.0$	31.3, $\Delta = 0.6$, $J = 134.0$	23.7, $\Delta = -0.2$	23.3, $\Delta = -0.8$		
$(CH_3)_3CNO_2^+H$[f]	88.7, $\Delta = 3.6$	26.6, $\Delta = -0.2$, $J = 127.0$				
$CH_3NO_2^+\text{-}CH_3$	65.0, $\Delta = 3.0$, $J = 154.3$					69.8, $J = 158.2$
$CH_3\overset{\delta+}{N}O_2\rightarrow\overset{\delta-}{B}F_3$	65.0, $\Delta = 3.0$, $J = 151.0$					
$CH_3\overset{\delta+}{N}O_2\rightarrow\overset{\delta-}{S}bF_3$	66.0, $\Delta = 4.0$, $J = 151.0$					
$CH_3CH_2\overset{\delta+}{N}O_2\text{-}CH_3$	76.2, $\Delta = 6.2$, $J = 149.0$	10.4, $\Delta = -0.7$				69.4, $J = 156.0$
$CH_3CH_2\overset{\delta+}{N}O_2\rightarrow\overset{\delta-}{B}F_3$	74.6, $\Delta = 4.6$, $J = 150.3$	10.8, $\Delta = -0.3$				
$CH_3CH_2\overset{\delta+}{N}O_2\rightarrow\overset{\delta-}{S}bF_5$	77.0, $\Delta = 7.0$, $J = 151.2$	10.8, $\Delta = -0.3$				
$(CH_3)_2CH\overset{\delta+}{N}O_2\text{-}CH_3$	89.0, $\Delta =$ 10.3, $J =$ 154.0	20.4, $\Delta = 0.5$, $J = 129.7$				69.5, $J = 154.0$
$(CH_3)_2CH\overset{\delta+}{N}O_2\rightarrow\overset{\delta-}{B}F_3$	85.0, $\Delta = 6.3$, $J = 153.3$	20.3, $\Delta = 0.4$				
$(CH_3)_2CH\overset{\delta+}{N}O_2\rightarrow\overset{\delta-}{S}bF_5$	89.0, $\Delta =$ 10.3, $J =$ 156.0	20.6, $\Delta = 0.7$, $J = 131.0$				

[a] Chemical shifts (parts per million) were measured with reference to tetramethylsilane as external standard. [b] The following symbols are used: Δ = difference in chemical shifts between parent (neutral) nitro compound (RNO_2) and corresponding nitronium salt (RNO_2^+X). A negative Δ value indicates an upfield shift (shielding effect) for a specific carbon in the nitronium salt (RNO_2^+X) with respect to that carbon in the corresponding parent nitro compound. J is the ^{13}C–^1H coupling constant in hertz. [c] All chemical shifts of protonated species were measured in SO_2ClF at −60 °C, except where otherwise indicated. [d] All chemical shifts of methylated species were measured in SO_2 at −60 °C. [e] All chemical shifts of BF_3- and SbF_5-complexed species were measured in SO_2 at −40 °C. [f] At −100 °C.

a solution of SbF_5 in SO_2 at −78 °C to form the *o*-methylated SO_2 fluoroantimonate complex. To this solution was added a solution of the nitro compound in SO_2 to form the corresponding methylated nitro species.

The carbon-13 NMR spectra were obtained on a Varian Associates Model FT-80 NMR spectrometer equipped with a variable-temperature universal probe. Tetramethylsilane in acetone-d_6 was used as an external standard and the magnetic field was locked on the deuterium line of the solvent.

In general, the carbon-13 NMR shifts of the parent (neutral) nitro compounds and the corresponding protonated and methylated species were measured at −60 °C. The shifts of the BF_3- or SbF_5-complexed nitronium salts were determined at −40 °C.

Results and Discussion.

Carbon-13 NMR chemical shifts of the nitronium salts 1–4 (Scheme I), formed by the reaction of the nitro compounds with magic acid, methylsulfoxonium fluoroantimonate, boron trifluoride, and antimony pentafluoride, respectively, are listed in Tables I and II. In order to assess the effects of protonation, methylation, and complexation (BF_3 or SbF_5) on nitro compounds, the carbon-13 NMR spectra of the parent (neutral) nitroalkanes and nitroarenes were also determined (Table III). Differences in the chemical shifts (Δ) of carbon atoms in the nitro compounds and the corresponding nitronium salts are listed in Tables I and II. An upfield shift is denoted by a negative Δ value; positive Δ values correspond to downfield shifts. The ^{13}C–^1H coupling constants of the nitrosonium ions are also given in Tables I and II.

Carbon-13 NMR spectra of the protonated nitro compounds 1 were determined in SO_2ClF solutions. Although both SO_2ClF and the more basic SO_2 are good solvents for oxonium salts,[13] generally, lower temperatures can be attained with SO_2ClF than with SO_2. Temperatures in the range of −60 to −100 °C were investigated in order to ensure the lack of intermolecular proton exchange between the protonated nitro species 1 and the solvent. The absence of such an exchange process was evident from the proton NMR absorption of the added proton in 1. Unfortunately these spectra give no information regarding the possible intramolecular proton exchange between the oxygen atoms of a nitro group. The protonation of nitro compounds occurs on oxygen, as indicated by the observed low-field absorption of the added (NO_2^+H) proton (^1H δ 16–17). Hogeveen[10] has concluded that protonation of a nitro group in superacidic media involves only one of the two oxygen atoms and has ruled out a nonclassical struc-

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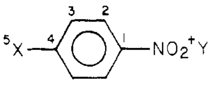
[13] G. A. Olah, *Aldrichimica Acta*, 6, 7 (1973).

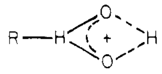
Table II. ^{13}C NMR Chemical Shifts of Protonated, Methylated, and Complexed Nitrobenzenes[a,b]



nitronium ion	C-1	C-2	C-3	C-4	C-5	added methyl
X = H, Y = H	141.9, $\Delta = -6.2$	129.3, $\Delta = 5.7$, $J = 172.6$	132.5, $\Delta = 2.7$, $J = 172.1$	147.3, $\Delta = 12.0$, $J = 166.3$		
X = H, Y = CH_3	142.9, $\Delta = -5.2$	128.8, $\Delta = 5.2$, $J = 171.7$	132.8, $\Delta = 3.0$, $J = 172.0$	146.2, $\Delta = 10.9$, $J = 167.7$		67.5, $J = 157.0$
X = H, Y = BF_3		126.5, $\Delta = 2.9$, $J = 170.0$	131.6, $\Delta = 1.8$, $J = 176.0$	141.5, $\Delta = 6.2$, $J = 166.6$		
X = H, Y = SbF_5		128.9, $\Delta = 5.3$, $J = 172.0$	132.9, $\Delta = 3.1$, $J = 172.0$	144.5, $\Delta = 9.2$, $J = 168.0$		
X = F, Y = H	137.9, $\Delta = -6.4$	134.4, $\Delta = 8.1$, $J_{C\text{-}F} = 14.0$, $J = 175.0$	121.0, $\Delta = 4.6$, $J_{C\text{-}F} = 24.4$, $J = 175.0$	175.0, $\Delta = 8.5$, $J_{C\text{-}F} = 282.5$, $J = 175.0$		
X = F, Y = CH_3	138.9, $\Delta = -5.4$	133.3, $\Delta = 7.0$, $J_{C\text{-}F} = 13.8$, $J = 174.5$	120.9, $\Delta = 4.5$, $J_{C\text{-}F} = 25.0$, $J = 175.0$	174.5, $\Delta = 8.0$, $J_{C\text{-}F} = 282.0$, $J = 174.0$		67.3, $J = 158.0$
X = F, Y = BF_3		130.1, $\Delta = 3.8$, $J_{C\text{-}F} = 11.8$, $J = 170.0$	119.0, $\Delta = 2.6$, $J_{C\text{-}F} = 24.5$, $J = 170.0$	170.2, $\Delta = 3.7$, $J_{C\text{-}F} = 266.0$		
X = F, Y = SbF_5		132.4, $\Delta = 6.1$, $J_{C\text{-}F} = 12.7$, $J = 168.0$	120.3, $\Delta = 2.6$, $J_{C\text{-}F} = 24.6$, $J = 171.0$	172.3, $\Delta = 5.8$, $J_{C\text{-}F} = 272.4$, $J = 170.0$		
X = CH_3, Y = H[c]	138.8	133.6, $\Delta = 10.3$, $J = 175.0$	130.0, $\Delta = 0$, $J = 175.0$	165.2, $\Delta = 18.8$	23.3, $\Delta = 2.8$, $J = 125.0$	
X = CH_3, Y = CH_3	134.6	133.6, $\Delta = 10.3$, $J = 174.5$	130.0, $\Delta = 0$, $J = 175.2$	163.0, $\Delta = 16.6$	23.6, $\Delta = 3.1$	66.6, $J = 158.0$
X = CH_3, Y = SbF_5		133.1, $\Delta = 9.8$, $J = 175.0$	129.0, $\Delta = 1.0$, $J = 174.5$	160.1, $\Delta = 13.7$	23.2, $\Delta = 2.7$	
X = CH_3, Y = BF_3		132.0, $\Delta = 8.7$, $J = 176.0$	126.5, $\Delta = 3.5$, $J = 175.0$	154.6, $\Delta = 8.2$	22.5, $\Delta = 2.0$	
X = Br, Y = H[c]		137.3, $J = 175.0$	131.0, $J = 175.0$	148.8		
X = Cl, Y = H[c]		134.2, $J = 175.0$	131.6, $J = 175.0$	158.1		

[a] See footnotes in Table I for meaning of symbols and experimental conditions. [b] $J = {}^{13}C{-}{}^1H$ coupling constant (Hz); $J_{C\text{-}F} = {}^{13}C{-}{}^{1}F$ coupling constant (Hz). [c] At −100 °C C-2 of the following protonated compounds gave rise to two absorptions (1:1): X = CH_3, Y = H (134.6 and 133.9 ppm); X = Br, Y = H (137.4 and 136.7 ppm); X = Cl, Y = H (134.2 and 133.5 ppm). All the remaining carbons in these compounds exhibited more or less the same chemical shift at both −100 and −60 °C.

ture (below) on the basis of IR data obtained on a crystalline protonated nitronium salt.



Methylation of the nitro compounds was carried out in SO_2 solutions. Although the solvent can itself be readily methylated by $CH_3F{-}SbF_5$, this process has been shown to be reversible,[13,14] and the methyl group is transferred to a more nucleophilic donor, such as a nitro group. As in the protonation discussed above, methylation of nitro compounds involves only one of the two oxygen atoms of a nitro group. This is indicated by the proton and carbon-13 NMR chemical shifts of the added methyl group, which occur generally at ca. ^1H δ 5.0 and ^{13}C δ 67, respectively.

The complexes formed by the reaction of the nitro compounds with boron trifluoride and antimony pentafluoride in SO_2 solutions were found to be generally less soluble than the corresponding protonated and methylated nitronium salts. At temperatures below ca. −50 °C, most of the complexes **3** and **4** precipitated out of solution as white powders. Furthermore, these complexes were generally found to be rather unstable and sensitive to moisture. All attempts to isolate and completely purify **3** and **4** were unsuccessful. Although no elemental analyses of satisfactory accuracy were obtained for the reasons mentioned, it is very likely that 1:1 complexes are formed in the reactions of nitro compounds with boron trifluoride. This Lewis acid has been shown to form 1:1 molecular adducts with aromatic aldehydes, and these complexes have recently been reported to involve σ–σ rather than charge-transfer bonding between the carbonyl groups and boron trifluoride.[15] The complexes formed by the reaction of nitro compounds with antimony pentafluoride (**4**) are most probably 1:1 adducts, too. In general, all the fluoroantimonate complexes (**4**) exhibited carbon-13 NMR chemical shifts which are very similar to the shifts observed for the corresponding protonated (**1**) and methylated (**2**) nitronium salts (Tables I and II).

Carbon-13 NMR spectra of the parent (neutral) nitro compounds (RNO_2) were determined in SO_2ClF solution at −60 °C (Table III). In general, no changes in the chemical shifts of these compounds were observed when the spectra were determined in SO_2 as a solvent. Furthermore, the chemical shifts of the carbons in the parent (neutral) nitro compounds did not exhibit any significant temperature dependence over the range of −40 to −80 °C. The absorption for the carbon directly attached to the nitro group (henceforth referred to as α-carbon and ipso carbon in aliphatic and aromatic compounds, respectively)

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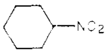
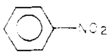
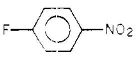
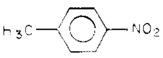
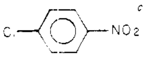
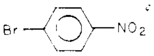
(14) G. A. Olah and D. J. Donavan, *J. Am. Chem. Soc.*, **100**, 5163 (1978).

(15) A. Greenvald and M. Rabinovitz, *Chem. Commun.*, 642 (1962); R. Lombard and J. P. Stephan, *C. R. Hebd. Seances Acad. Sci.*, **239**, 887 (1954); P. C. Myhre, C. D. Fisher, A. T. Nielsen, and W. M. Schubert, *J. Am. Chem. Soc.*, **87**, 29 (1965); M. Rabinovitz and A. Grinvald, *Tetrahedron Lett.*, 641 (1971).

Table III. ^{13}C NMR Chemical Shifts of Nitro Compounds[a,b]

nitronium ions	C-1	C-2	C-3	C-4	C-5
CH_3NO_2	62.0				
$CH_3CH_2NO_2$	70.0	11.1			
$CH_3CH_2CH_2NO_2$	76.7	20.6	9.8		
$CH_3(CH_2)_3NO_2$	76.3	30.2	20.1	13.4	
$CH_3(CH_2)_4NO_2$	76.1	28.8	27.7	22.8	13.7
$(CH_3)_2CH$-NO_2	78.7	19.9			
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H$-$(^4CH_3)NO_2$	85.0	29.0	10.2	18.8	
	84.7	30.7	23.9	24.1	
	148.1	123.6	129.8	135.3	
	144.3	126.3	116.4	166.5	
		123.3	130.0	146.4	20.5
 [c]	146.4	124.8	129.4	141.2	
 [c]	147.6	124.7	132.5	129.7	

[a] All chemical shifts of nitro compounds were measured in SO_2ClF at −60 °C with respect to tetramethylsilane as an external standard. [b] The numbering of the carbons in the aromatic system is the same as in Table II. [c] Owing to the low solubility of this compound in SO_2 and SO_2ClF, its ^{13}C NMR spectrum was determined in $CDCl_3$ at room temperature.

in the parent (neutral) nitro compounds were broadened. This is mainly caused by the spin–spin coupling of the carbon-13 nucleus with the nitrogen-14 nucleus (of the nitro group) which undergoes fast quadrupole relaxation.[5,16] For the aromatic nitro compounds, the ipso carbons are further broadened by the absence of directly attached hydrogens, in contrast to the α-carbons of the primary and secondary aliphatic nitro species. Indeed, in some of the aromatic nitro compounds, the resonances of the ipso carbons are so broad and weak that it is not possible to locate these resonances accurately.

By comparison with the shifts of the parent nitroalkanes, it is apparent that protonation causes a deshielding (downfield shift) of 2–9 ppm for the α-carbons (Table I). The β-carbons, on the other hand, are more or less unaffected or, in the case of primary nitro compounds, exhibit a slight shielding effect (upfield shift) upon protonation. It is possible that this shielding effect is due to the interaction of the β-hydrogens with an oxygen atom of the nitro group. Such an interaction has previously been suggested in order to explain the variations observed for the chemical shifts of the α- and β-carbons in nitroalkanes as compared to the corresponding (hydrocarbons) alkanes.[5] The introduction of a nitro group in a given alkane results in a relatively large ($\Delta \simeq 60$ ppm) deshielding effect for the α-carbons and an unexpectedly small ($\Delta \simeq 3$–5 ppm) deshielding effect for the β-carbons.[5]

For some nitro compounds temperatures lower than −60 °C were required in order to observe the protonated species. For example, protonated 2-methyl-2-nitropropane was studied at −100 °C. Protonated nitrocyclohexane was also formed at −100 °C and was observed to undergo cleavage rearrangement to the 1-methylcyclopentyl cation at elevated temperatures (ca. −80 °C). On the other hand, all attempts to generate the protonated α-nitrotoluene were unsuccessful, even at −120 °C, because of the instantaneous cleavage of this ion to the benzyl cation, which subsequently polymerizes. The chemical shifts of the γ-carbons remain more or less unaffected upon protonation of the nitroalkane, and this is also the case for the carbons, which are separated from the nitro group by three or more carbon atoms.

Methylation and complexation with BF_3 or SbF_5 of the primary nitroalkanes (nitromethane, -ethane, and -propane) result in nitronium ions whose chemical shifts and coupling constants closely resemble those of the corresponding protonated species (Table I). This is also true for the secondary isopropylnitronium ion. The chemical shift of the added methyl in **2** is at ca. 70 ppm and its ^{13}C–^1H coupling constant is of the order of 156 Hz. It was not possible to obtain the chemical shifts of the *tert*-butylnitronium salts **3** and **4** because of the ready cleavage of these ions into the *tert*-butyl cation at the studied temperatures.

No attempts were made to study the nature of the alkylnitronium ions **1**–**4** at elevated temperatures. Undoubtedly, these ions undergo cleavage to carbenium ions at these temperatures.[9] However, our experience, as well as the experience of other workers in the field[10] is that explosions might occur with strongly acidic solutions of nitroalkanes (i.e., alkylnitronium ions) at or above room temperatures.

For nitroarenes, only para-substituted nitrobenzenes were investigated (Table II) because they exhibit rather simple carbon-13 NMR spectra and in order to avoid any complications due to steric interactions which can prevail, especially in the case of ortho-substituted systems, where the copolarity of the nitro group and the phenyl ring is reduced.[4] Assignments of the various carbons in the parent (neutral) nitrobenzenes (Table III) are consistent with those reported in the literature for the same compounds in other solvents.[4,5,19,20] For the nitronium salts (**1**–**4**) of the para-substituted nitrobenzenes (Table II), assignment were based on relative peak intensities, off-resonance decoupling experiments, and the dynamic NMR effect observed for the carbons ortho (C-2) to the nitronium group.[9] Such an effect is attributed to the hindered rotation of the protonated nitro group about the N–C (ipso) bond at temperatures lower than ca. −60 °C. The chemical shifts of the para-substituted nitronium salts were determined at temperatures where the rotation of the protonated nitro group is fast on the NMR time scale. However, for these compounds the chemical shifts of the carbons ortho to the nitronium group (C-2) are also reported at −100 °C, where these carbons exhibit two absorptions of equal intensities due to the hindered rotation of the NO_2H^+ group. For the nitronium salts **1**–**4** of nitrobenzene itself, the assignments were made by determining the spectra of the 2- and 4-monodeuterated nitrobenzenium salts **1**–**4**. The carbon–

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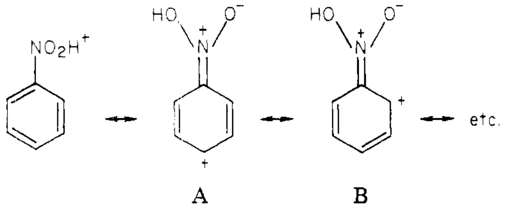
fluorine couplings (J_{C-F}), on the other hand, allowed unambiguous assignments to be made for the carbons of the nitronium ions 1–4 of *p*-fluoronitrobenzene.

For all the studied nitroarenes, protonation, methylation, and BF_3 or SbF_5 complexation occurred at the nitro groups, and no competing reactions at the phenyl rings were observed. This is, however, not surprising in view of the well-documented deactivation of a phenyl ring toward electrophiles upon the introduction of a nitro group.

In the aromatic nitro compounds studied, significant deshielding (downfield shifts) effects were observed for the carbons ortho and para to the nitro group upon protonation, methylation, and complexation with BF_3 or SbF_5 (Table II). As expected, the smallest changes occurred at the positions meta (to the nitro group), although in some cases paramagnetic shifts as large as 5 ppm were found for these carbons. The observed variations in the chemical shifts of the ortho, meta, and para carbons of the aromatic nitronium salts (1–4), in comparison to the corresponding carbons in the parent (neutral) nitro compounds, can be rationalized in terms of the inductive and conjugative (below) effects of the highly electronegative nitronium (NO_2X^+) groups.



The inductive effects are expected to be most profound at the ipso (C-1) and ortho positions. The change in the π-electron density in the para position reflects the degree of conjugation of the nitronium group with the ring (resonance structure A). As shown above, this effect is also present for the ortho compounds (resonance structure B), but it is expected to be modified by the inductive effect of the nearby protonated nitro group, as well as by possible 1,4-interaction with one of the two oxygens of the nitro group. Such an interaction has been discussed above, and it has been previously invoked in order to rationalize the chemical shifts of the ortho carbons in nitrobenzene which are more shielded (4.8 ppm) than the carbons in benzene itself.[21] On the basis of the inductive and conjugative effects of the nitro group, however, the chemical shifts of the ortho carbons in nitrobenzene are expected to exhibit at least a 10-ppm paramagnetic shift relative to the chemical shift observed in benzene.[8]

The degree of conjugative interaction between the nitronium group and the phenyl ring in the ions 1–4 is further evident in the carbon–fluorine coupling constants (J_{C-F}) of these ions in *p*-fluoronitrobenzene. This coupling is large and varies from 282 Hz in 1 and 2 to 272 and 266 Hz in 4 and 3, respectively; in the parent (neutral) *p*-fluoronitrobenzene molecule the para J_{C-F} is 256.5 Hz. It has been shown that in a series of para-substituted fluorobenzenes, the J_{C-F} increases in magnitude with the increasing ability of substituents to withdraw electrons from the ring.[18]

The carbon carrying the nitro group (i.e., the ipso carbon) in nitrobenzene and *p*-fluoronitrobenzene undergoes shielding (upfield shifts) of 2–6 ppm upon the formation of ions 1–4 (Table II). Unfortunately, the ipso carbon absorptions in the other aromatic nitro compounds studied were so broad that no definite assignment for these resonances could be made. The reason for the observed diamagnetic shift of the ipso carbons in the nitronium salts as compared to the ipso carbons in the corresponding parent nitrobenzenes is not clear at the present time. However, we have also observed a shielding effect upon the protonation of a wide variety of other monosubstituted aromatic compounds, each being substituted by a highly electronegative group. The diamagnetic shift observed in the carbon-13 NMR spectra for the ipso carbon in the following monosubstituted benzenes upon protonation in SbF_5–FSO_3H (1:1)/SO_2 solution at −78 °C is (Δ, ppm) the following: benzaldehyde (−8.3), benzophenone (−7.0 and 5.0), benzoic acid (−10.2), benzonitrile (−12.7), diphenylsulfone (−12.5), and diphenyl sulfoxide (−13.1). For theoretical calculations the ipso positions are known to be particularly sensitive to the choice of geometry,[17] and this represents a problem for any estimation of the chemical shifts of the ipso carbons. It is difficult to assess the accuracy of calculations of charge distribution at these positions, especially since diverse substituents are involved. However, preliminary CNDO/2 calculations of the charge distribution at ipso carbons in some of the protonated monosubstituted benzenes listed above show a trend of polarization toward the ipso carbons.

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Registry No. 1 (R = Me), 74610-17-6; 1 (R = Et), 74610-18-7; 1 (R = Pr), 74610-19-8; 1 (R = Bu), 74610-20-1; 1 (R = pentyl), 74610-21-2; 1 (R = *i*-Pr), 19441-66-8; 1 (R = *sec*-Bu), 74610-22-3; 1 (R = cyclohexyl), 74610-23-4; 1 (R = *t*-Bu), 74610-24-5; 1 (R = Ph), 74610-25-6; 1 (R = *p*-FC_6H_4), 74610-26-7; 1 (R = *p*-$CH_3C_6H_4$), 74610-27-8; 1 (R = *p*-BrC_6H_4), 74610-28-9; 1 (R = *p*-ClC_6H_4), 74610-29-0; 2 (R = Me), 29827-03-0; 2 (R = Et), 74610-31-4; 2 (R = *i*-Pr), 74610-33-6; 2 (R = Ph), 29827-05-2; 2 (R = *p*-FC_6H_4), 74610-35-8; 2 (R = *p*-$CH_3C_6H_4$), 74610-37-0; 3 (R = Me), 74610-38-1; 3 (R = Et), 74610-39-2; 3 (R = *i*-Pr), 74610-40-5; 3 (R = Ph), 368-96-7; 3 (R = *p*-FC_6H_4), 74610-41-6; 3 (R = *p*-$CH_3C_6H_4$), 74610-42-7; 4 (R = Me), 74610-43-8; 4 (R = Et), 74610-44-9; 4 (R = *i*-Pr), 74610-45-0; 4 (R = Ph), 74610-46-1; 4 (R = *p*-FC_6H_4), 74610-47-2; 4 (R = *p*-$CH_3C_6H_4$), 74610-48-3; nitromethane, 75-52-5; nitroethane, 79-24-3; 1-nitropropane, 108-03-2; 1-nitrobutane, 627-05-4; 1-nitropentane, 628-05-7; 2-nitropropane, 79-46-9; 2-nitrobutane, 600-24-8; nitrocyclohexane, 1122-60-7; nitrobenzene, 98-95-3; 1-fluoro-4-nitrobenzene, 350-46-9; 1-methyl-4-nitrobenzene, 99-99-0; 1-chloro-4-nitrobenzene, 100-00-5; 1-bromo-4-nitrobenzene, 586-78-7; 2-methyl-2-nitropropane, 594-70-7.

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