(25) T. Shida and S. Iwata, *J. Phys. Chem.*, **75**, 2591 (1971).
(26) J. Smid, "Ions and Ion Pairs in Organic Reactions", Vol. 1, M. Szwarc, Ed., Wiley, New York, 1972.
(27) As an alternative continuation of the sequence in Scheme I, reaction 4 could be followed by

$$DNBB + B^- \rightleftarrows DNBB^- + BH$$

$$DNBB^- + PNT \rightleftarrows DNBB\cdot + PNT^-\cdot$$

$$DNBB\cdot + B^- \rightleftarrows DNS^-\cdot + BH$$

This reaction sequence would avoid the formation of the dianionic species $DNBB^{2-}$ in eq 5. We hope to be able to differentiate between these possibilities in future work.
(28) R. D. Guthrie, G. R. Welsman, and L. G. Burdon, *J. Am. Chem. Soc.*, **96**, 6955 (1974).
(29) R. D. Guthrie and G. R. Welsman, *J. Am. Chem. Soc.*, **96**, 6962 (1974).
(30) R. D. Guthrie, G. W. Pendygraft, and A. T. Young, *J. Am. Chem. Soc.*, **98**, 5877 (1976).
(31) R. D. Guthrie, "Comprehensive Carbanion Chemistry", Vol. 1, E. Buncel and T. Durst, Eds., Elsevier, Amsterdam, 1980.
(32) (a) The published pK_a values of PNT (20.5) and *t*-BuOH (19.0)[32b,33] refer respectively to Me_2SO and *t*-BuOH media. An uncertainty will arise in bringing these to a common standard or when a change in solvent is considered as in the present work. (b) F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, **42**, 1817 (1977).
(33) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, Chapter 1.
(34) A. J. Kresge, *Acc. Chem. Res.*, **8**, 354 (1975).
(35) J. R. Jones, "The Ionization of Carbon Acids", Academic Press, New York, 1973.
(36) E. Buncel, "Carbanions, Mechanistic and Isotopic Aspects", Elsevier, Amsterdam, 1975.
(37) E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, **14**, 133 (1977).
(38) C. K. Mann and K. K. Barnes, "Electrochemical Data in Nonaqueous Systems", Marcel Dekker, New York, 1970, Chapter 11.
(39) (a) The oxidation potential for Ph_3C^- is given for DME solvent,[39b] whereas the values for PNT and $PhNO_2$ refer to MeCN solvent. Other values for Ph_3C^- are as follows: −1.3 V vs. SCE in DME[40] and −1.46 V vs. ferrocene in Me_2SO.[41] (b) R. Breslow and S. Mazur, *J. Am. Chem. Soc.*, **95**, 584 (1973).
(40) H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).
(41) J. M. Kern and P. Federlin, *Tetrahedron Lett.*, 837 (1977).
(42) W. M. Latimer, "Oxidation Potentials", 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1952.
(43) F. G. Bordwell, *Pure Appl. Chem.*, **49**, 963 (1977).
(44) B. K. Janousek, A. H. Zimmerman, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 6142 (1978).
(45) From Latimer,[42] $E^\circ(HO^-) = -2.0$ V vs. normal hydrogen electrode, which is equivalent to −1.8 V vs. SCE.
(46) A. Streitwieser, Jr., E. Juaristi, and L. L. Nebenzahl, "Comprehensive Carbanion Chemistry", Vol. 1, E. Buncel and T. Durst, Eds., Elsevier, Amsterdam, 1980.
(47) H. A. Stanbury, Jr., and W. R. Proops, *J. Org. Chem.*, **26**, 4162 (1961).

Aromatic Substitution. 45.[1] Transfer Nitration of Aromatics with *N*-Nitropyridinium and Quinolinium Ions

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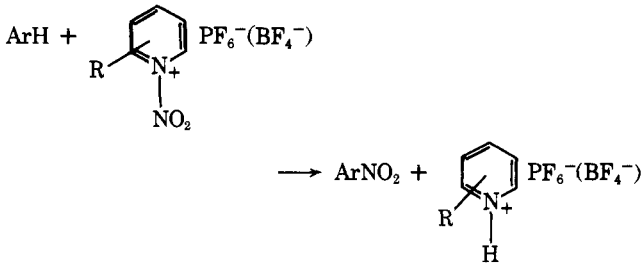
Abstract: The transfer nitration of aromatics with various *N*-nitropyridinium and quinolinium salts (PF_6^- or BF_4^-) was studied. The nitrations were found to take place via a nucleophilic displacement pathway, involving the *N*-nitropyridium ions themselves and not free nitronium ion. Steric factors were, however, shown to play an insignificant role in determining the positional selectivity of nitration. Positional and substrate selectivities were found to be independent of one another and are suggested to be determined in two separate steps.

Introduction

Electrophilic aromatic nitration is usually carried out with nitric acid, generally in the presence of sulfuric acid.[2] Nitration can also be effected with alkyl or metal nitrates, catalyzed by Lewis or Brønsted acids.[2-5] Acyl and aroyl nitrates are capable of nitrating aromatics in the absence of catalysts.[5] These nitrating agents can be considered to be precursors of the nitronium ion and nitrate aromatics in displacement-type reactions.

We report now on the transfer nitration of aromatics with *N*-nitropyridinium and *N*-nitroquinolinium salts.



* University of Southern California.

Nitrations with these salts can be carried out under essentially neutral conditions, because the only acid present, due to proton elimination from the nitration of aromatics, will bind with the liberated heterocyclic base. At the same time, the reactivity of the nitrating agent can be varied by altering the electron demand as well as the steric crowding of the heterocyclic ring with suitable substituents.

In 1968, Olah and Olah[7] first reported on transfer nitration with *N*-nitropyridinium tetrafluoroborate, primarily of n-donor substrates. Cupas and Pearson[8] subsequently, in a preliminary communication, extended the work to substituted *N*-nitropyridinium salts, which were found capable of nitrating aromatics. In continuation of our joint interest, we herein report in full extended studies on the transfer nitration of aromatics with *N*-nitropyridinium and *N*-nitroquinolinium salts.

Results and Discussion

N-Nitropyridinium and *N*-nitroquinolinium salts were prepared by the method of Olah and Olah.[7] Dropwise addition of the corresponding pyridine derivative to an equivalent amount of the nitronium salt in acetonitrile, nitromethane, or sulfolane solution gives the corresponding *N*-nitropyridinium ions in practically quantitative yield. The salts were studied

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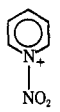
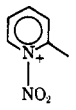
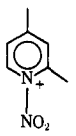
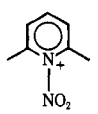
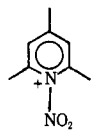
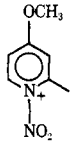
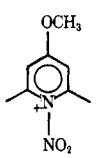
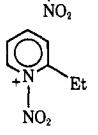
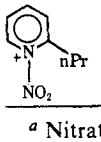
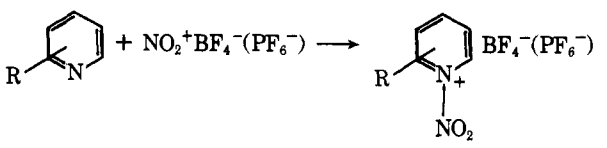
Table I. Competitive Nitration of Benzene and Toluene with *N*-Nitropyridinium Salts at 25 °C

N-nitropyridinium salt	solvent	isomer distribution, % ortho	meta	para	*o/p* ratio	*k*(toluene)/*k*(benzene)
 PF_6^-	CH_3NO_2	57	5	38	1.50	26.6[a]
 BF_4^-	CH_3CN	64	3	33	1.94	36.5
 BF_4^-	CH_3CN	63	3	34	1.85	40.5
 BF_4^-	CH_3CN	64	3	33	1.94	39.0
 BF_4^-	sulfolane	66	2	32	2.06	43.5
	CH_3CN	63	3	34	1.85	41.4
	CH_3NO_2	62	3	35	1.77	41.5
 BF_4^-	CH_3CN	63	3	34	1.85	46.4
 BF_4^-	CH_3CN	64	3	33	1.94	44.5
 BF_4^-	CH_3CN	64	3	33	1.94	37.3
 BF_4^-	CH_3CN	64	3	33	1.94	36.4

[a] Nitration was carried out at 50 °C.

by NMR, IR, and UV spectroscopy, as reported elsewhere.[7,9]



The *N*-nitropyridinium salts can be isolated as stable (although hygroscopic), crystalline salts or can be used in situ, in solution, as was the case in the present study. Except for *N*-nitropyridinium hexafluorophosphate, other substituted salts are readily soluble in acetonitrile, nitromethane, or sulfolane, whereas the former is soluble only in nitromethane. Nitrations were studied in nitromethane, acetonitrile, and sulfolane solution.

All the nitrations studied were carried out under homogeneous conditions at room temperature. Competitive nitrations of toluene and benzene (and other substituted benzenes) were also carried out, with the aromatic substrates present in large excess to ensure a constant ratio of the aromatics. The substrate and positional selectivities of nitration of benzene and toluene with various *N*-nitropyridinium salts are summarized in Table I.

One interesting feature of the transfer nitrations is the increased range of substrate selectivity compared to that obtained with acetyl nitrate, nitric acid, or nitronium salt nitrations. *N*-Nitropyridinium hexafluorophosphate does not nitrate benzene and toluene at room temperature, whereas *N*-nitro-2-picolinium tetrafluoroborate nitrates aromatics (k_t/k_b = 36.5) with relative ease at 25 °C. This ease of nitration can be ascribed to steric hindrance to resonance with concomitant weakening of the N-N bond. It might be argued that the presence of an additional α-methyl group, as in the *N*-nitro-2,6-lutidinium ion, would further decrease the resonance interaction with a corresponding lowering of *k*(toluene)/*k*(benzene) (k_t/k_b) ratio. However, with this latter ion, the k_t/k_b ratio increased slightly from 36.5 to 39.0. The most reasonable explanation for this result is that, in the 2-picolinium salt, the nonbonded interaction of an α-methyl with the nitro group is sufficient to completely impede the resonance interaction. Thus, the steric effect of an additional α-methyl group is negligible. However, the basicity of the pyridine nitrogen is increased owing to the inductive effect of the addi-

Table II. Competitive Nitration of Benzene and Toluene with *N*-Nitroquinolinium Tetrafluoroborates at 25 °C

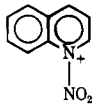
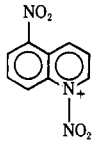
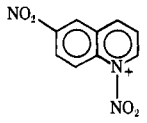
N-nitro salt	solvent	isomer distribution, %			*o/p* ratio	*k*(toluene)/*k*(benzene)
		ortho	meta	para		
	CH_3CN	63	4	33	1.91	32.6
	CH_3NO_2	62	2	36	1.72	13.2
	CH_3NO_2	62	2	36	1.72	14.5

Table III. Nitration of Substituted Benzenes with *N*-Nitro-2,4,6-collidinium Tetrafluoroborate at 25 °C

substrate	solvent	isomer distribution, %		isomer ratio	*k*(Ar)/*k*(benzene)
	CH_3NO_2	2-nitro	9	0.11	29.5
		3-nitro	10		
		4-nitro	81		
	CH_3CN	2-nitro	17	0.20	439.0
		4-nitro	83		
	CH_3CN	2-nitro	75	3.0	1200.0
		3-nitro			
		4-nitro	25		
	CH_3NO_2	2-nitro	22	0.30	0.04
		3-nitro	4		
		4-nitro	74		

tional methyl group, thereby strengthening the N–N bond, resulting in higher substrate selectivity.

Ingold[10] postulated that the reactivity of a nitrating agent of the NO_2–X type would depend upon the nature of X. With increasing electronegativity of X, the reactivity of the nitrating agent should increase. The predicted reactivity order

$$NO_2^+ > NO_2\text{–}OH_2^+ > NO_2\text{–}NO_3 > NO_2\text{–}OH$$

is, indeed, followed in practice. If we apply Ingold's postulate to the reactivity of substituted *N*-nitropyridinium salts, it would be anticipated that the substrate selectivity would increase as the basicity of the pyridine base increases. The k_t/k_b values were found to increase with increasing pK_a.[11] Consequently, after the resonance interaction between the nitro group and the pyridine nucleus has been impeded by an α-alkyl group, the magnitude of substrate selectivity is mainly dependent upon the basicity of the pyridine nitrogen.

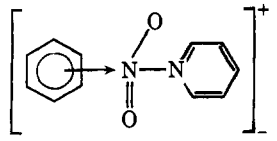
As anticipated from the results of the nitrations with the series of substituted *N*-nitropyridinium ion salts, the peri interaction in *N*-nitroquinolinium salts sufficiently weakens the N–N bond and, therefore, allows transfer nitration to occur even more readily. The results are summarized in Table II. The lower substrate selectivities obtained with the *N*-nitroquinolinium salts are probably due to the decreased basicities of these heterocyclic compounds, with the 5- and 6-nitroquinolinium salts showing the lowest substrate selectivity.

One could have also expected a considerable steric effect, in the studied transfer nitrations, for concomitant with an increase in substrate selectivity is the implied greater association between the nitro group and the heterocyclic base in the transition state. However, the substitution patterns in the nitration of toluene indicate that the steric effect must be negligible. The *N*-nitropyridinium salt is probably involved as such only in the initial interaction with the aromatic (probably of π-complex nature), which subsequently collapses to the various individual σ complexes determining regioselectivity. To further confirm these conclusions, *m*-xylene was nitrated with *N*-nitro-2,4,6-collidinium tetrafluoroborate. If there were a larger steric interaction in the transition state, the amount of 4-nitro-*m*-xylene should increase at the expense of 2-nitro-*m*-xylene, owing to the obviously higher steric requirements of the 2 position. Nevertheless, comparison of the results of nitrations with *N*-nitro-2,4,6-collidinium tetrafluoroborate (Table III) and conventional nitrating agents shows no increased steric interaction.

Nitration of anisole gave an ortho–para ratio of 3.0, which is similar to that obtained with nitronium salts. Nitration of *tert*-butylbenzene and chlorobenzene also gave ortho–para ratios of nitro products (Table III) similar to those obtained with conventional nitrating agents.

The competitive nitration data for toluene and benzene (Table I) show that *N*-nitropyridinium salts are more substrate-selective nitrating reagents than conventional nitrating agents,[12,13] and, therefore, demand more assistance from the π-aromatic systems in the initial transition state of the reactions, which, thus, lie later on the reaction coordinate than is the case in other nitrations. The variation of the substrate selectivity data further indicates that the *N*-nitropyridinium ions themselves participate in the rate-determining transition state, because, if "free" nitronium ion were itself involved, substrate selectivities would be expected to stay constant.

The studied reactions are, therefore, considered as transfer nitrations from *N*-nitropyridinium ion to aromatics, not involving in situ formation of the NO_2^+ ion. Not only the elec-



trophilicity of the nitrating reagent (which, in this case, depends upon the basicity of the substituted pyridine base), but also the nucleophilicity of the aromatic substrate can affect the relative position of the transition state involved.

Despite a variation in substrate selectivity (k_t/k_b) of 13.2–46.4, the ortho–para isomer ratio in the nitration of toluene does not show a corresponding change, and varies only from 1.94 to 1.72. Even in that small range, there is no direct relationship between substrate and positional selectivity. When nitrating more reactive substrates, such as *m*-xylene and anisole, the substrate selectivity in the studied transfer nitration increases substantially (k_t/k_b = 439 and 1200, respectively) with regioselectivity similar to those observed previously in nitrations with nitronium salts and other electrophilic nitrations. Thus, on the basis of these observations, we restate our previous view[12,13] that substrate and positional selectivities in nitrations of reactive aromatics can be independent of each other, involving separate steps, even when the reactions reach diffusion or encounter controlled limit, and regioselectivity remains high in all nitrations.

Experimental Section

All solvents, as well as pyridines, quinolines, toluene, benzene, *tert*-butylbenzene, *m*-xylene, anisole, chlorobenzene, and methyl nitrate, were commercially available highest purity materials, purified by the usual methods before use. 4-Methoxy-2-picoline and 4-methoxy-2,6-lutidine were prepared according to the method of Ochiai.[14] Nitronium salts were prepared by the method of Olah and Kuhn[15] and were thoroughly purified from nitrosonium ion impurities by repeated precipitation from nitromethane solution with methylene chloride.

Nuclear Magnetic Resonance Spectra. The ^1H nuclear magnetic resonance spectra of *N*-nitroalkylpyridinium salts were recorded on a Varian Associates high-resolution spectrometer, Model HA-100.

Infrared Spectra, Elemental Analysis, and Melting Points. The infrared spectra were recorded on a Beckman infrared spectrophotometer, Model IR-8. The spectra of the *N*-nitrotetrafluoroborate salts were obtained as a Fluorolube mull from 4000 to 1360 cm^{-1} and as a Nujol mull from 1360 to 400 cm^{-1}.

The elemental analysis for this investigation was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected.

***N*-Nitropyridinium Tetrafluoroborate.** The procedure of Olah, Olah, and Overchuk[7] was used to prepare this crystalline salt, mp 164–165 °C dec (lit. mp 164–165 °C)[7] (91% yield). λ_{max}: 273 nm (ϵ 3200). IR: ν cm^{-1} 3140, 1810, 1700, 1605, 1460, 1300, 1200–960, 805, 785, 720, 650. ^1H NMR (CD_3CN): δ (external Me_4Si) 8.49 (m, 2 H), 9.11 (m, 1 H), 9.83 (m, 2 H).

***N*-Nitro-2-picolinium Tetrafluoroborate.** To a well-stirred suspension of nitronium tetrafluoroborate (5.34 g, 0.04 mol) in acetonitrile (5 mL) under a dry nitrogen atmosphere at 0 to −10 °C was added slowly 2-picoline (3.72 g, 0.04 mol) in acetonitrile (3 mL). The reaction mixture was allowed to stir for 0.5 h at 0 to −30 °C. Carbon tetrachloride (10 mL) was added to cause complete precipitation of the salt and the mixture was cooled to −30 °C and transferred to a drybox. The light yellow salt was filtered through a sintered-glass filter and washed with carbon tetrachloride (3 × 20 mL). Trace amounts of solvent were removed under vacuum to give 4.7 g (52% yield) of *N*-nitro-2-picolinium tetrafluoroborate, mp 94–98 °C dec, λ_{max} 263 nm (ϵ 6600). IR: ν cm^{-1} 3200, 1820, 1705, 1610, 1495, 1465, 1285, 1220, 1180–980, 800, 780, 725, 670. ^1H NMR (CD_3CN): δ (external Me_4Si) 3.26 (s, 3 H), 8.29 (m, 1 H), 8.34 (m, 1 H), 8.88 (m, 1 H), 9.64 (m, 1 H).

Usual Procedure of Nitration of Aromatics with in Situ Prepared *N*-Nitropyridinium Salts. To a well-stirred suspension of nitronium tetrafluoroborate (2.66 g, 0.02 mol) in acetonitrile, nitromethane, or sulfolane (15 mL) under a dry nitrogen atmosphere at 0 to −10 °C was slowly added 0.02 mol of the corresponding pyridine, lutidine, collidine, or quinoline in the corresponding solvent (5 mL). The resulting homogeneous solution was allowed to stir for 0.5 h at 0 to −30 °C and then allowed to warm up to 25 °C. The above solution (10 mL) (approximately 0.01 mol of the nitrating agent) was taken by syringe and added slowly to a well-stirred solution of 0.05 mol of benzene and 0.05 mol of toluene or other alkylbenzene dissolved in the corresponding solvent (10 mL) under a dry nitrogen atmosphere at 25 °C. Aliquots were removed after stirring for 1 h and quenched with hydrochloric acid–ice water. The organic layer was separated, washed, and dried in the usual manner and analyzed by GLC. The results, listed in Tables I–III, were all obtained in a similar manner. The *N*-nitro-2,4,6-collidinium tetrafluoroborate prepared by this procedure was also reacted with mesitylene under preparative conditions to give nitromesitylene in 93% isolated yield. Other pyridinium salts gave similar yields.

Analytical Procedure. Analyses of nitroaromatic products were carried out using Perkin-Elmer Model 226 and Varian Model 3700 gas chromatographs equiped with hydrogen flame ionization detectors and either open tubular or packed columns. Peak areas were determined with an Infotronics Model CRS-100 electronic printing integrator. Details of the procedures were reported in our previous work.

The results listed in Tables I–III are the average of three independent runs each of which was analyzed three times. The average deviation of the substrate selectivities was less than ±1.0 and that of the isomer distributions was ±1%.

Acknowledgment. Support of our work by the U.S. Army Office of Research is gratefully acknowledged.

References and Notes

(1) For part 44, see: Olah, G. A.; Narang, S. C.; Olah, J. A. *J. Am. Chem. Soc.*, **1979**, *101*, 1805–1807.
(2) For a comprehensive review, see: Olah, G. A.; Kuhn, S. J. "Friedel-Crafts and Related Reactions," Vol. 3, Part 2; Interscience; New York, 1964; pp 1393–1491.
(3) Topchiev, A. V. "Nitration of Hydrocarbons and Other Organic Compounds"; Pergamon Press: Oxford, 1959; pp 283–314.
(4) Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 2892–2898.
(5) Narang, S. C.; Thompson, M. J. *Aust. J. Chem.* **1978**, *31*, 1839–1840.
(6) Hoggett, J. G.; Moodie, R. B.; Penton, J. R.; Schoefield, K., "Nitration and Aromatic Reactivity"; Cambridge University Press: New York, 1971; pp 76–106.
(7) Olah, G. A.; Olah, J. A.; Overchuk, N. A. *J. Org. Chem.* **1965**, *30*, 3373–3376.
(8) Cupas, C. A.; Pearson, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 4742–4743.
(9) Pearson, R. L. Ph.D. Thesis, Case Western Reserve University, 1971.
(10) Benford, G. A.; Ingold, C. K. *J. Chem. Soc.* **1938**, 929–955.
(11) Albert, A. "Physical Methods in Heterocyclic Chemistry", Vol. 1; Academic Press: New York, 1963; pp 1–108.
(12) Olah, G. A.; Lin, H. C.; Olah, J. A.; Narang, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 545–548.
(13) Olah, G. A.; Lin, H. C.; Olah, J. A.; Narang, S. C. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 1045–1049.
(14) Ochiai, E.; Katoh, T. J. *Pharm. Soc. Jpn.* **1951**, *71*, 156–160.
(15) Olah, G. A.; Kuhn, S. J. *Org. Synth.* **1967**, *47*, 56–61.