

Synthetic Applications of Nitronium Tetrafluoroborate

By R. E. Olsen, D. W. Fish and E. E. Hamel  
Aerojet-General Corporation  
Sacramento, California

Nitronium tetrafluoroborate has been shown to be a versatile nitrating agent for nitrogen compounds, giving the corresponding N-nitro derivative when reacted with secondary aliphatic amines, an acyl aliphatic amine, a carbamate ester, a diacyl amine and primary amides. Reaction of secondary aliphatic nitronate salts with nitronium tetrafluoroborate gave mixtures of the gem-dinitro alkane and psuedonitrole, while treatment of secondary aliphatic nitronate salts with nitrosonium tetrafluoroborate yielded only the corresponding psuedonitrole.

Interest in the chemistry of stable nitronium salts, such as  $\text{NO}_2\text{BF}_4$ ,  $\text{NO}_2\text{AsF}_6$ ,  $\text{NO}_2\text{PtF}_6$  and  $(\text{NO}_2)_2\text{SiF}_6$ , has been aroused by recent publications of Olah and co-workers concerning the preparation and use of such salts as nitrating agents for alcohols<sup>1</sup> and aromatics.<sup>2,3</sup> During an investigation into the mechanism of aromatic nitration, the perchlorate, sulfate and fluorosulfate nitronium salts were prepared and their ionic nature established spectrophotometrically;<sup>4</sup> however, these materials were not sufficiently stable to allow their use as nitrating agents. There appear to be no reported synthetic applications of nitronium salts to other types of organic compounds; this paper reports on the use of nitronium tetrafluoroborate to nitrate several amines, amine derivatives and alkyl nitronate salts.

The ease of preparation and stability of nitronium tetrafluoroborate has made it the nitronium salt of choice during our investigations. No difference in yields has been observed as due to an effect of different anions in nitronium salts;<sup>2</sup> hence, results similar to those reported here would be expected through employment of other stable nitronium salts. The only special requirements for the use of nitronium salts are the exclusion of moisture (which hydrolyzes the salt to nitric acid) and the selection of a solvent which does not react with nitronium ion.

1. G. A. Olah and S. J. Kuhn, Ber., **89**, 2374 (1956).

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

3. G. A. Olah, S. J. Kuhn, and A. Mlinko, J. Chem. Soc., **1956**, 4257.

4. C. K. Ingold and E. D. Hughes, et al., ibid., **1950**, 2400, and subsequent papers.

RESULTS AND DISCUSSION

Nitration reactions were carried out by adding nitronium tetrafluoroborate to a well-stirred acetonitrile or methylene chloride solution of substrate. The syntheses were carried out at low temperatures (-40 to 0°C) with short reaction times (10 minutes to one hour). The products were isolated by quenching of the reaction mixtures in ice water followed by purification using conventional techniques. In most of the reactions investigated, attempts were not made to find optimum conditions; hence, the reported yields may not represent maximum values.

Nitration of Amines and Amine Derivatives. - At present there are four good methods for the preparation of secondary nitramines. They are: (1) the oxidation of nitrosamines by peroxytrifluoroacetic acid,<sup>5</sup> (2) the chloride-ion catalyzed direct nitration of amines,<sup>6</sup> (3) the nitrolysis of dialkylamides with nitric acid,<sup>7</sup> and (4) the alkaline nitration of amines with acetone cyanohydrin nitrate.<sup>8</sup> All of the above methods have their limitations and are retarded by steric or electronic factors. The less basic aliphatic and alicyclic carbamates can be nitrated smoothly and in excellent yields with nitric acid and acetic anhydride,<sup>9</sup> while diacylamines are only nitrated with difficulty and in fair yields with a nitric acid - acetic anhydride mixture.<sup>10</sup>

Several secondary aliphatic amines of the type  $R_1R_2NH$  were converted to their N-nitro derivatives in yields ranging from 50 to 70 percent by the reaction of nitronium tetrafluoroborate with two equivalents of the amine in methylene chloride solvent. A quantitative yield of the ammonium fluoroborate salt was also recorded.

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5. W. D. Emmons, J. Am. Chem. Soc., **76**, 3468 (1954).
  6. W. J. Chute, K. G. Herring, L. E. Toombs and G. F. Wright, Can. J. Research., **26B**, 89 (1948).
  7. J. H. Robson and J. Reinhart, J. Am. Chem. Soc., **77**, 2453 (1955).
  8. W. D. Emmons and J. P. Freeman, ibid., **77**, 4387 (1955).
  9. H. M. Curry and J. P. Mason, ibid., **73**, 5043 (1951).
  10. H. F. Kauffman and A. Burger, J. Org. Chem., **19**, 1662 (1954).

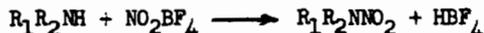
The exact role of solvent is not clear, as the same reaction run in acetonitrile gave a quantitative yield of the ammonium fluoroborate, and little, if any, of the desired secondary aliphatic nitramine. Nitration of an acyl aliphatic amine, a urethane and a diacyl amine was accomplished in good yield by treatment of the amine derivative with one equivalent of nitronium tetrafluoroborate. Table I presents the amines and amine derivatives which were nitrated with nitronium tetrafluoroborate.

Reaction of a primary aliphatic amine, n-butylamine, with nitronium tetrafluoroborate in methylene chloride or acetonitrile did not give the desired primary nitramine, but rather gave n-butyl nitrate in 20 percent yield. However, treatment of an electronegatively substituted primary aromatic amine, picramide, with nitronium tetrafluoroborate did give the primary nitramine, N,2,4,6-tetranitroaniline, in 85 percent yield. Previously, Olah<sup>11</sup> had reported that aniline was vigorously oxidized by nitronium tetrafluoroborate.

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11. G. A. Olah and S. J. Kuhn, Chem. & Ind., 1956, 98.

TABLE I

NITRATION OF AMINES AND AMINE DERIVATIVES WITH NITRONIUM TETRAFLUOROBORATE

<u>Amine or Derivative</u>	<u>Yield of N-nitro derivative, %</u>	<u>b.p. (m.p.), °C</u>	<u>Ref.</u>
Di- <u>n</u> -butylamine	54 <sup>a</sup>	127-129 at 10 mm	12
Morpholine	72 <sup>a</sup>	(51.0-52.0)	12
$\beta, \beta'$ - <u>Bis</u> (cyanoethyl)amine	62 <sup>a</sup>	(55.5-57.0)	13
Ethyl <u>n</u> -butylcarbamate	91	75-77 at 0.8 mm	7
<u>n</u> -Butylacetamide	40	45-47 at 0.5 mm	14
Succinimide	43	(92.0-93.0)	8
Picramide	85	(78.0 <sup>b</sup> (def.))	15

<sup>a</sup>Methylene chloride solvent; all others used acetonitrile.

<sup>b</sup>Caution should be exercised during recrystallization, as N,2,4,6-tetranitroaniline has been found to deflagrate at temperatures near 50°C while in an impure state. An analytical sample was obtained by recrystallization from chloroform.

12. G. S. Myers and G. F. Wright, Can. J. Research, **26B**, 257 (1948).
13. W. J. Chute, G. E. Dunn, J. C. MacKenzie, G. S. Meyers, G. N. R. Smart, J. W. Suggitt and G. F. Wright, ibid., **26B**, 114 (1948).
14. E. H. White, J. Am. Chem. Soc., **77**, 6008 (1955).
15. A. H. Blatt, "Data on Organic Explosives", OSRD-2014, February 28, 1944.

Nitration of Primary Amides. - Kauffman and Burger<sup>8</sup> have reported the preparation of materials tentatively identified as methyl N-nitrosuccinamate and ethyl N-nitrophthalamidate by the alcoholysis of N-nitrosuccinimide and N-nitrophthalimide. The only other primary nitramide reported is N-nitroacetamide, which was described as "quite unstable in the free state".<sup>14</sup> In a review article on the chemistry of nitramines, Lamberton<sup>15</sup> has briefly commented on the rarity of primary nitramides and has speculated that this may be due to their decomposition under normal nitration conditions.

Utilizing nitronium tetrafluoroborate with acetonitrile or methylene chloride solvent in the presence of one equivalent of potassium acetate (to react with the hydrofluorobasic acid formed during the reaction), aliphatic and aromatic primary amides were converted to their N-nitro derivatives in fair yields. With the exception of N-nitroacetamide, the primary nitramides prepared thus far have proved to be relatively stable solids which decompose above their melting points. N-Nitroacetamide could be obtained only in low yields and decomposed during attempted purification. As expected, the primary nitramides were acidic in nature and could be converted to their alkali metal salts by stirring the nitramide with an acetate salt in a nonaqueous solvent. Infrared spectra were consistent with the proposed structure as the following characteristic<sup>16</sup> absorption bands were observed; a sharp single NH band at  $3374-3390\text{ cm}^{-1}$ , two strong N-nitro bands at  $1620-1610\text{ cm}^{-1}$  and  $1507-1502\text{ cm}^{-1}$ , and a carbonyl band shifted down to  $1751-1739\text{ cm}^{-1}$ . Table II shows the primary nitramides which were prepared, along with their yields and melting points.

14. V. Hinsberg, Ber., 25, 1092 (1892).

15. A. H. Lamberton, Quart. Revs., 5, 75 (1951).

16. K. Nakanishi, "Infrared Absorption Spectroscopy, Practical", Holden-Day, Inc., San Francisco, 1962.

TABLE II

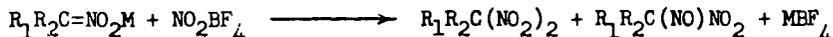
## NITRATION OF PRIMARY AMIDES WITH NITRONIUM TETRAFLUOROBORATE



Primary Amide	Yield of N-nitro derivative, %	m.p., °C	Analysis					
			Calcd:			Found:		
			C	H	N	C	H	N
Acetamide	12.5 <sup>a</sup>	65-72 <sup>a</sup>						
2-Chloroacetamide	54.5	80-82	17.4	1.4	20.2	17.4	2.2	20.1
2,2,2-Trichloroacetamide	61.7	72-73	11.6	0.5	13.5	11.9	1.0	13.1
Benzamide	52.5	91-93	50.6	3.7	16.9	50.6	3.7	16.9
p-Chlorobenzamide	50.0	152-154	41.8	2.5	14.0	41.6	2.7	14.0
p-Nitrobenzamide	52.5	178-180	38.0	2.3	19.0	40.8	2.9	18.3

<sup>a</sup>Data obtained from crude reaction product which was identified as N-nitroacetamide by infrared analysis. Product decomposed during attempted purification.

Nitration of Alkyl Nitronates. - The oxidative nitration reaction of Kaplan and Shechter<sup>17</sup> appears to be the only general method for the preparation of secondary gem-dinitro compounds. We have found that secondary alkyl nitronates (i.e., the potassium, sodium and lithium salts of 2-nitropropane and nitrocyclohexane), when treated with nitronium tetrafluoroborate in acetonitrile give secondary gem-dinitro alkanes, although the yields were lower than those obtainable by the oxidative nitration technique and the reactions were characterized by the formation of considerable amounts of psuedonitrole byproduct. The cation appears to have a considerable influence on the reaction, as the potassium salts of 2-nitropropane and nitrocyclohexane, when treated with nitronium tetrafluoroborate, gave no gem-dinitro materials and only a 5 percent yield of the corresponding psuedonitrole. Under the same conditions, the sodium salt of 2-nitropropane gave a 50 percent yield of a one-to-one mixture of 2,2-dinitropropane and the psuedonitrole, 2-nitroso-nitropropane. With lithium isopropyl nitronate, a 35 percent yield of 2,2-dinitropropane and a 25 percent yield of the psuedonitrole were obtained. The sodium and lithium salts of nitrocyclohexane gave similar yields of gem-dinitro and psuedonitrole derivatives when reacted with nitronium tetrafluoroborate. The reactions of alkyl nitronate salts with nitronium tetrafluoroborate are summarized in Table III.



M = K, Na, and Li

Dinitro products were separated from psuedonitroles by extraction of the reaction mixture with hexane followed by evaporation of the hexane to yield relatively pure 2,2-dinitropropane or 1,1-dinitrocyclohexane. The hexane-insoluble psuedonitroles were identified by elemental and infrared analysis and by their characteristic blue solutions in benzene.<sup>18</sup>

17. R. B. Kaplan and H. Shechter, J. Am. Chem. Soc., **83**, 3535 (1961).

18. H. Shechter and R. B. Kaplan, ibid., **75**, 3980 (1955).

Treatment of a primary alkyl nitronate (i.e., the potassium, sodium or lithium salt of 1-nitropropane) with nitronium tetrafluoroborate gave a low yield of the corresponding unstable nitrolic acid derivative which was identified by infrared analysis and neutralization with caustic to give a brilliant red solution.<sup>19</sup>



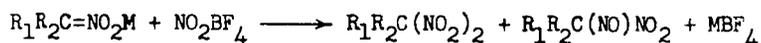
M = K, Na, and Li

The formation of psuedonitroles and nitrolic acid derivatives during the reactions of nitronium tetrafluoroborate led us to investigate similar reactions with nitrosonium tetrafluoroborate ( $\text{NOBF}_4$ ). Again, the reaction of salts of secondary alkyl nitronates with nitrosonium tetrafluoroborate appeared to be influenced by the cation, as the potassium, sodium and lithium salts of 2-nitropropane when treated with nitrosonium tetrafluoroborate gave 60, 80 and 95 percent yields, respectively, of the psuedonitrole. Similar yields of psuedonitrole were obtained when salts of nitrocyclohexane were reacted with nitrosonium tetrafluoroborate. Table IV presents the experimental data obtained from the reaction of alkyl nitronate salts with nitrosonium tetrafluoroborate.

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19. C. R. Noller, "Textbook of Organic Chemistry", W. B. Saunders and Co., London, 1958, p. 200.

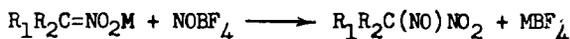
TABLE III

NITRATION OF ALKYL NITRONATE SALTS WITH NITRONIUM TETRAFLUOROBORATE

Cation	Alkyl Nitronate	% Yield		Alkyl Nitronate	% Yield	
		Dinitro	Psuedonitrole		Dinitro	Psuedonitrole
Li	isopropyl	35	25	cyclohexyl	35	25
Na	isopropyl	25	25	cyclohexyl	25	25
K	isopropyl	0	5	cyclohexyl	0	5
Na	propyl	0	5 <sup>a</sup>			

<sup>a</sup>Yield data estimated from weight of crude reaction product which was shown to be propylnitrolic acid by infrared analysis and neutralization to give a red solution. Product decomposed before further characterization could be accomplished.

TABLE IV

NITROSATION OF ALKYL NITRONATE SALTS WITH NITROSONIUM TETRAFLUOROBORATE

Cation	Alkyl Nitronate	% Yield,		Alkyl Nitronate	% Yield,	
		Psuedonitrole			Psuedonitrole	
Li	isopropyl	95		cyclohexyl	95	
Na	isopropyl	80		cyclohexyl	80	
K	isopropyl	60		cyclohexyl	60	
Na	propyl	85 <sup>a</sup>				

<sup>a</sup>Yield data estimated from weight of crude reaction product, which decomposed before complete characterization could be accomplished. Product tentatively identified as propylnitrolic acid by infrared and neutralization to give a red solution.

EXPERIMENTAL.

Melting and boiling points are uncorrected. Reactions involving nitronium tetrafluoroborate were carried out in a dry box under a nitrogen atmosphere. Elemental analyses were conducted at the Analytical Laboratories of Aerojet-General Corporation, Sacramento, California.

Nitronium Tetrafluoroborate. - The procedure of Olah and Kuhn<sup>2</sup> was followed, in which nitric acid, hydrogen fluoride and boron trifluoride were allowed to react in a suitable solvent. The previously reported solvent was nitromethane; however, in view of the reported mineral acid sensitization of nitromethane toward detonation, it was decided to employ 2-nitropropane as solvent. In this modified procedure it was necessary to wash the nitronium tetrafluoroborate with Freon 113 and dry the nitronium salt for four hours at 60°C under reduced pressure (1 mm) to ensure complete removal of solvent.

At this point, it should be mentioned that occasional batches of nitronium tetrafluoroborate have exhibited poor nitrating ability. The poor reactivity has usually been associated with the sample of nitronium tetrafluoroborate adsorbing moisture, even under dry box conditions.

Preparation of Secondary Aliphatic Nitramines. - The following procedure is typical of that used during the reaction of secondary aliphatic amines with nitronium tetrafluoroborate. A solution of  $\beta,\beta'$ -bis(cyanoethyl)amine (10.0 g, 0.08 mole) in 60 ml of methylene chloride was cooled to -30°C and 5.3 g (0.04 mole) of nitronium

tetrafluoroborate was added over a ten-minute period. The mixture was stirred for one hour at 0°C, then four hours at room temperature. The hydrofluoroboric acid salt of  $\beta,\beta'$ -bis(cyanoethyl)amine, (8.3 g, 99% yield, m.p. 159-160°C) was removed by filtration.

Anal.: Calcd. for  $C_6H_{10}N_3BF_4$ : C, 34.2; H, 4.8; N, 19.9. Found: C, 34.8; H, 4.9; N, 21.2.

The filtrate was concentrated under reduced pressure to leave crude  $\beta,\beta'$ -bis(cyanoethyl)-nitramine, which after one recrystallization from methanol gave a product (3.3 g, 62% yield) which melted at 55.5-57.0°C (lit. value<sup>13</sup> 55.5-56.8°C). The other secondary aliphatic nitramines prepared, along with their yields and melting or boiling points are presented in Table I.

Preparation of Acyl N-Nitroamine Compounds. - The following procedure is typical of that employed for the preparation of acyl N-nitro derivatives. Ethyl n-butylcarbamate (4.0 g, 0.03 mole) was dissolved in 50 ml of acetonitrile, cooled to -30°, and treated with 4.0 g (0.03 mole) of nitronium tetrafluoroborate. The solution was allowed to warm, with stirring, to 0°C and quenched into 200 ml of ice water. A yellow oil separated which was dissolved in methylene chloride and dried over anhydrous magnesium sulfate. After removal of solvent, 5.0 g (91% yield) of ethyl N-nitro-n-butylcarbamate (b.p. 75-77 at 0.8 mm, n<sub>D</sub><sup>24</sup> 1.4476, lit. value<sup>7</sup> n<sub>D</sub><sup>21</sup> 1.4488) was obtained by fractional distillation under reduced pressure. Other acyl N-nitroamine derivatives, with their yields and melting or boiling points are shown in Table I.

Preparation of Primary Nitramides. - The following is typical of the procedure used for the preparation of primary nitramides. To a stirred suspension of 9.0 g (0.10 mole) of 2-chloroacetamide and 10.5 g (0.11 mole) of potassium acetate in 50 ml of acetonitrile at -35° was slowly added 15.0 g (0.11 mole) nitronium tetrafluoroborate.

The temperature was maintained at  $-35$  to  $-30^{\circ}$  for 30 minutes. Methylene chloride (25 ml) was added and the mixture allowed to warm to  $10^{\circ}$  and this temperature maintained for 30 minutes. The suspended solids were removed by filtration and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in methylene chloride and passed through a silica gel column to yield 12.5 g of a light yellow solid, m.p.  $76-77^{\circ}$ . Recrystallization from butyl chloride gave 7.4 g (54.5% yield) of a white solid, m.p.  $80-82^{\circ}$ , identified as N-nitro-2-chloroacetamide by infrared and elemental analyses. The yields of primary nitramides, their melting points and analytical data are presented in Table II.

Preparation of gem-Dinitroalkanes. - A methanolic solution of alkali metal hydroxide (Li, Na, or K) was treated with 10% excess nitroalkane and allowed to stir for 30 minutes. The solution was then evaporated to dryness in vacuo and the alkali metal alkyl nitronate dried over phosphorous pentoxide under reduced pressure (0.1 mm) for 24 hours.

(Caution: Nitronate salts may be shock sensitive and have been known to explode after prolonged storage).

Shown below is a procedure typical of that used for the preparation of gem-dinitroalkanes. A slurry of 3.3 g (0.02 mole) of lithium cyclohexylnitronate in 50 ml of acetonitrile was cooled to  $-35^{\circ}\text{C}$  and 2.7 g (0.02 mole) of nitronium tetrafluoroborate was slowly added. The reaction was not exothermic and the reaction mixture turned a brilliant blue color upon the first addition of nitronium tetrafluoroborate. The reaction mixture was stirred for two hours at  $-30$  to  $-40^{\circ}\text{C}$ , then filtered to give a quantitative yield of potassium tetrafluoroborate. The filtrate was quenched into 100 ml of ice water to yield an insoluble oil, which was dissolved in methylene

chloride and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure left a semisolid which was extracted with hexane. The hexane-insoluble residue (0.8 g, 25% yield) was a white powder identified as 1-nitroso-1-nitrocyclohexane, m.p. 78.0-79.0 (blue melt).

Anal.: Calcd. for  $C_6H_{10}N_2O_3$ : C, 46.6; H, 6.4; N, 17.7. Found: C, 46.4; H, 6.4; N, 18.0.

Evaporation of the hexane extract under reduced pressure followed by fractional distillation gave 1.2 g (35% yield) of 1,1-dinitrocyclohexane (b.p. 62-63° at 0.5 mm, lit. value<sup>17</sup> b.p. 67° at 0.7 mm). The yields of gem-dinitro and psuedonitrole derivatives obtained from the reaction of other salts of alkyl nitronates are shown in the Table III.

Preparation of Psuedonitroles. - The procedure used during the preparation of psuedonitroles was identical to that described above for the preparation of gem-dinitro alkanes, except that nitrosonium tetrafluoroborate was used in place of nitronium tetrafluoroborate. The yields of psuedonitrole obtained from the various nitronate salts are presented in Table IV.

#### ACKNOWLEDGEMENT

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