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## Aromatic Substitution. VII.<sup>1</sup> Friedel-Crafts Type Nitration of Aromatics<sup>2</sup>

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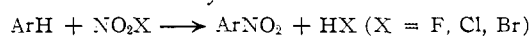
Friedel-Crafts type nitration of aromatics with nitryl halides, dinitrogen tetroxide, dinitrogen pentoxide and stable nitronium salts was investigated in homogeneous tetramethylene sulfone solutions. A simple new method of preparing nitronium tetrafluoroborate from nitric acid HF and BF<sub>3</sub> was found. The scope of preparative nitronium fluoroborate nitration was extended to a variety of substituted aromatics.

### Introduction

The general Friedel-Crafts acylation principle<sup>3</sup> can be applied easily to inorganic acid halides and anhydrides. Consequently, it is suggested that aromatic nitration involving nitryl halides, dinitrogen pentoxide and dinitrogen tetroxide (the halides and anhydrides of nitric acid) should be considered as a Friedel-Crafts type reaction, as obviously a very close analogy exists with the corresponding Friedel-Crafts ketone synthesis involving acyl halides and anhydrides. In a generalized sense, nitric acid nitrations catalyzed by protonating acids (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HF, etc.) or by Lewis acid type metal halides (BF<sub>3</sub>, AlCl<sub>3</sub>, etc.) could be also considered as reactions of Friedel-Crafts type, as an increasing number of Friedel-Crafts ketone syntheses is now known using aliphatic carboxylic acids (acetic, propionic, etc.) as acylating agents.

**Nitration with Nitryl Chloride.**—Friedel-Crafts type nitration using nitryl chloride has been previously reported by Price and Sears<sup>4</sup> who found AlCl<sub>3</sub> to be the most suitable catalyst. Deactivated aromatics, however, were nitrated only with difficulty and the method was, therefore, considered to be of limited value.

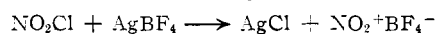
Our present investigations have shown that aromatic compounds, including deactivated ones such as halobenzenes and benzotrifluoride, can be nitrated with ease using nitryl halides and a suitable Friedel-Crafts catalyst.



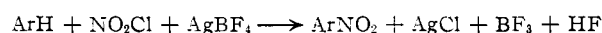
Using nitryl chloride as the nitrating agent, TiCl<sub>4</sub> was found to be the most suitable catalyst; FeCl<sub>3</sub>, ZrCl<sub>4</sub>, AlCl<sub>3</sub> and AlBr<sub>3</sub> are also effective but the reactions are more difficult to handle. With BCl<sub>3</sub> we obtained a smaller amount of nitrated product and considerable ring chlorination; SbCl<sub>5</sub> is also an active catalyst for the nitryl chloride nitration of aromatics; BF<sub>3</sub> was found to be inactive as a catalyst. The following yields were obtained upon nitration of the aromatics using TiCl<sub>4</sub> as catalyst: benzene 88%, toluene 81.5%, ethylbenzene 79%, fluorobenzene 91%, chlorobenzene 89%, bromobenzene 86.5%, *o*-dichlorobenzene 41.5%, benzo-trifluoride 32%. There is always a certain amount of ring chlorinated by-product formed in the nitrations. Reactions carried out either by using the excess of aromatic as solvent (TiCl<sub>4</sub> is miscible with many aromatics) or in carbon tetrachloride

solution always contain chlorinated by-products. The amount of chlorinated by-products can be decreased by using solvents of higher dielectric constants. Tetramethylene sulfone (sulfolane) was found to be a suitable solvent for the TiCl<sub>4</sub> and also for most of the other Lewis acid-catalyzed nitrations. It has excellent solvent properties for aromatics and the catalysts, as well as for nitryl halides. It is superior to other solvents that can be used such as nitromethane. As it is completely miscible with water, the work-up of the reaction mixtures after the reactions are completed is very easy.

Anhydrous silver tetrafluoroborate, suggested<sup>5</sup> as being a cation-forming agent in aromatic substitutions, was found a suitable reagent in forming nitronium tetrafluoroborate directly from nitryl chloride. In order to carry out the reactions, it



is not necessary to prepare the nitronium salt previously. Anhydrous silver tetrafluoroborate can be dissolved (or suspended) in the aromatic, or dissolved in a suitable solvent such as nitromethane or tetramethylene sulfone and added to the aromatic. Nitryl chloride then is introduced and the nitration takes place with the elimination of silver chloride



As aromatic compounds form rather stable complexes with anhydrous silver tetrafluoroborate, the reactions of nitryl chloride in reality take place with the aromatic-silver fluoroborate complexes. Silver halide is eliminated in a relatively slow reaction which takes place possibly simultaneously with the interaction of the NO<sub>2</sub> group with the aromatic. As a result, this type of nitration—as will be discussed in a later paper—gives a considerably higher selectivity in nitrations than the alternate process in which NO<sub>2</sub>Cl and AgBF<sub>4</sub> are first treated in nitromethane or tetramethylene sulfone solution to form, again with silver halide elimination, the nitronium salt followed by reaction of this solution with the aromatics.

As in the previously discussed Friedel-Crafts nitrations (with nitryl chloride in the presence of Lewis acid type catalysts), the nitryl chloride-silver tetrafluoroborate nitration method also gives chlorinated aromatics as by-products. This probably is due to the fact that even freshly prepared nitryl chloride may contain some free chlorine as contamination, which, in the presence of

(1) Part VI, *J. Am. Chem. Soc.*, **80**, 6541 (1958).  
 (2) Partly presented as a paper at the 137th Meeting of the American Chemical Society in Cleveland, Ohio, April 13, 1960.  
 (3) C. Friedel and J. M. Crafts, *Compt. rend.*, **84**, 1392 (1877).  
 (4) Ch. C. Price and C. A. Sears, *J. Am. Chem. Soc.*, **75**, 3276 (1953).

(5) G. Olah, A. Paviath and S. Kuhn, *Chemistry & Industry*, 50 (1957).

silver tetrafluoroborate, forms a very active cationic chlorination system



Benzene, toluene, ethylbenzene, xylenes, mesitylene, fluorobenzene, chlorobenzene and bromobenzene were nitrated with yields of 80–95%, 5–20% of the corresponding chloro aromatic being formed as by-product.

**Nitrations with Nitryl Fluoride.**—Nitryl fluoride is a more powerful nitrating agent than nitryl chloride, but is more difficult to handle. Hetherington and Robinson<sup>6</sup> reported nitration of aromatics with nitryl fluoride, in the absence of catalysts. They suggested, that in solution, nitryl fluoride dissociates into  $\text{NO}_2^+$  and  $\text{F}^-$  and the intermediate nitronium ion thus formed is the active reagent in the nitrations. Less reactive aromatics such as nitrobenzene were not nitrated and considerable tar formation occurred during the reactions. We found that by using a Lewis acid type fluoride catalyst such as  $\text{BF}_3$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$  and  $\text{SbF}_5$ , simple Friedel-Crafts type nitrations can be carried out with nitryl fluoride. Homolytic cleavage of nitryl fluoride, which causes most of the side reactions, is considerably suppressed under these conditions in favor of heterolysis, yielding the nitronium ion. The reactions are carried out preferably at low temperatures. Benzotrifluoride is nitrated to *m*-nitrobenzotrifluoride at  $-50^\circ$  with 90% yield using boron trifluoride as catalyst. Halobenzenes, including di- and polyhalobenzenes, are nitrated with ease and with yields of over 80%.

The nitrations are carried out either with an excess of the aromatic as diluent and introducing nitryl fluoride and the Lewis acid fluoride catalyst simultaneously at low temperatures into the well stirred reaction mixture or in a suitable solvent. Tetramethylene sulfone could be used as solvent advantageously if the catalyst fluoride does not interact with it ( $\text{SbF}_5$  being a strong fluorinating agent, it also attacks the solvent and cannot be used).

**Nitrations with Nitryl Bromide.**—Nitryl bromide has not been reported previously in the literature, with the exception of a paper by Zuskiné<sup>7</sup> who claimed to have prepared it at 200–250° when bromine vapor saturated with nitrogen peroxide was passed through a tube filled with bone-ash. We found it impossible to repeat this work and it is highly improbable that nitryl bromide exists at these temperatures. We have investigated the possibility of preparing nitryl bromide by the halogen exchange of nitryl chloride with KBr in liquid  $\text{SO}_2$ , by the reaction of  $\text{BBr}_3$  with anhydrous nitric acid or  $\text{N}_2\text{O}_5$ , as well as the reaction of bromosulfonic acid with nitric acid and the ozonolysis of nitrosyl bromide. In the halogen exchange reaction of nitryl chloride with KBr, we obtained a 45% exchange reaction based on analysis of potassium used. Attempts to isolate nitryl bromide from the  $\text{SO}_2$  solution were unsuccessful and resulted in decomposition to nitric oxide and bromine. In the reaction of  $\text{BBr}_3$  and nitric acid,

(6) O. Hetherington and F. L. Robinson, *J. Chem. Soc.*, 3512 (1954).

(7) N. Zuskiné, *Bull. soc. chim.*, [4] 37, 187 (1925).

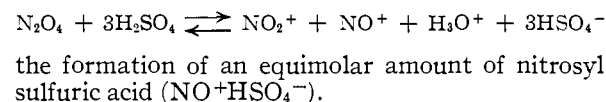
the isolated products were NOBr, nitric oxide and bromine. When the reactions were carried out in solution (e.g., liquid  $\text{SO}_2$ ), nitryl bromide was intermediately formed but, again, isolation in pure form was unsuccessful. The reaction of bromosulfonic acid with nitric acid and the ozonolysis of nitrosyl bromide gave also only highly contaminated products (containing free bromine, nitric oxide and dinitrogen pentoxide, respectively).

Nitration experiments with solutions obtained by the halogen exchange of nitryl chloride with KBr (not separated from unchanged nitryl chloride and decomposition product) were carried out in sulfur dioxide solutions at  $-20^\circ$  using  $\text{TiBr}_4$  as catalyst. Yields of nitrations are lower than those obtained with nitryl chloride due to the formation of more ring-brominated products. This could be attributed partly to free bromine being present from the decomposition of nitryl bromide and to the easier homolysis of nitryl bromide itself.

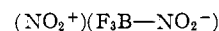
**Nitrations with Dinitrogen Tetroxide.**—It was Schaarschmidt<sup>8</sup> who first investigated the catalytic effect of  $\text{AlCl}_3$  and  $\text{FeCl}_3$  on nitration of aromatics with  $\text{N}_2\text{O}_4$ , the mixed anhydride of nitric and nitrous acids.

Pinck<sup>9</sup> used sulfuric acid to catalyze the nitration of aromatics with  $\text{N}_2\text{O}_4$ . He observed that only half of the dinitrogen tetroxide was used up in the nitrations, the remainder being present as nitrosyl sulfuric acid. Titov<sup>10</sup> dissolved  $\text{N}_2\text{O}_4$  in sulfuric acid and used this solution as nitrating agent.

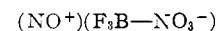
Raman spectroscopic<sup>11</sup> and cryoscopic<sup>12</sup> investigations of solutions of  $\text{N}_2\text{O}_4$  in sulfuric acid gave proof that the effective nitrating agent in the solutions is the nitronium ion ( $\text{NO}_2^+$ ) and also explained



Bachman<sup>13</sup> used the stable  $\text{N}_2\text{O}_4 \cdot \text{BF}_3$  complex prepared as a crystalline, insoluble salt from the components in aromatic nitrations. He suggested a nitronium salt structure for the complex



The crystalline complex, however, is only a moderate nitrating agent giving sufficient yields in nitrations of even such reactive aromatics as benzene and naphthalene but only after long reaction times (24 hours to one week). This obviously is not in agreement with the suggested nitronium ion structure. Also the  $\text{N}_2\text{O}_4 \cdot \text{BF}_3$  complex shows an ability to nitrosate and diazotate, thus acting also as a nitrosonium salt



(8) A. Schaarschmidt, *Ber.*, 57, 2065 (1924); *Angew. Chem.*, 39, 1457 (1926).

(9) L. A. Pinck, *J. Am. Chem. Soc.*, 49, 2536 (1927).

(10) A. I. Titov and A. N. Banyshnikova, *J. Gen. Chem. (U.S.S.R.)*, 6, 1800 (1936); A. I. Titov, *ibid.*, 7, 667 (1937).

(11) J. D. S. Goulden and D. J. Millen, *J. Chem. Soc.*, 2620 (1950); D. J. Millen, *ibid.*, 2600 (1950).

(12) R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold and E. R. A. Peeling, *ibid.*, 2504 (1950).

(13) G. B. Bachman, H. Feuer, B. R. Bluestein and C. M. Vogt, *J. Am. Chem. Soc.*, 77, 6188 (1955); G. B. Bachman and C. M. Vogt, *ibid.*, 80, 2987 (1958).

Raman spectroscopic investigations of the solid complex, carried out with Dr. J. C. Evans and to be published elsewhere, show only a relatively weak band at 1400  $\text{cm}^{-1}$ , but a strong one around 2340  $\text{cm}^{-1}$ . It must, therefore, be suggested that the addition compound  $\text{N}_2\text{O}_4 \cdot \text{BF}_3$ , which is not necessarily completely ionized in the solid state, is indeed an equilibrium mixture of the nitronium and nitrosonium forms in agreement with its observed reactivity and the fact that  $\text{N}_2\text{O}_4$  itself is the mixed anhydride of  $\text{HNO}_3$  and  $\text{HNO}_2$ .

The major difficulty in Friedel-Crafts type nitrations with  $\text{N}_2\text{O}_4$  was previously the fact that the  $\text{N}_2\text{O}_4$ -catalyst complexes were insoluble in the reaction media. This resulted not only in slow reactions and low yields, but also in many cases in undesirable side reactions.

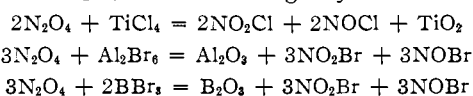
Schaarschmidt reported that when  $\text{AlBr}_3$  was tried instead of  $\text{AlCl}_3$  as a catalyst, in an unexpected way only ring bromination took place and no nitro product was formed. The use of a fluoride catalyst, such as  $\text{BF}_3$  in the work of Bachman, eliminated halogenation as side reaction but still dealt with a heterogeneous reaction medium.

In the course of the present investigation, we found that homogeneous Friedel-Crafts type nitrations with  $\text{N}_2\text{O}_4$  and Lewis acid catalyst such as  $\text{TiCl}_4$ ,  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{PF}_5$  and  $\text{AsF}_5$  can be carried out in tetramethylene sulfone solutions. It is not necessary to isolate the catalyst- $\text{N}_2\text{O}_4$  complex. Instead, a solution of  $\text{N}_2\text{O}_4$  and the catalyst is prepared and this solution is added to a tetramethylene sulfone solution of the aromatic to be nitrated.

Nitrobenzene was obtained from the nitration of benzene with yields of 32-67%, fluoronitrobenzene from fluorobenzene with 28-76% yields, the relative order of activity of the catalysts used being  $\text{AsF}_5 > \text{PF}_5 > \text{BF}_3 > \text{TiCl}_4 > \text{BCl}_3$ . With the chloride catalysts used, a considerable amount of chlorobenzene also was formed in the reaction, as was the case with  $\text{AlCl}_3$ .

Bromide Lewis acids such as  $\text{AlBr}_3$ ,  $\text{BBr}_3$  and  $\text{TiBr}_4$ , in agreement with previous observations of Schaarschmidt with  $\text{AlBr}_3$ , gave a high amount of ring bromination but simultaneously also about 10% of nitro aromatics was formed.

Subsequent investigations have proved that aluminum, titanium and boron halides tend to react with  $\text{N}_2\text{O}_4$  in the following way



$\text{NO}_2\text{Br}$ , being unstable, decomposes to  $\text{N}_2\text{O}_4 + \text{Br}_2$  and the bromine formed in the presence of the catalyst brominates the aromatic. In a similar manner, but to a lesser extent, chlorination takes place.

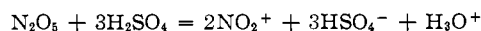
**Nitrations with Dinitrogen Pentoxide.**—Nitrations using nitrogen pentoxide, the anhydride of nitric acid, are well known.<sup>14</sup> Most of the work was carried out in solutions in the absence of catalyst. Solid nitrogen pentoxide at low temperatures is known to be nitronium nitrate,  $\text{NO}_2^+ \cdot \text{NO}_3^-$ .

(14) For an excellent summary, see P. B. D. De La Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Academic Press, Inc., New York, N. Y., 1959.

A study of the kinetics and mechanism of nitrogen pentoxide nitrations gave evidence, however, of the fact that other carriers of the nitronium ion may also play a role. Decomposition to  $\text{N}_2\text{O}_4$  and oxygen should also be considered if the  $\text{N}_2\text{O}_5$  used is not entirely pure.

Klemenz and Scholler<sup>15</sup> have shown that solutions of  $\text{N}_2\text{O}_5$  in sulfuric acid are very effective nitrating agents having nitrating properties closely similar to those of solutions of nitric acid in sulfuric acid.

Millen<sup>16</sup> found the ionization of  $\text{N}_2\text{O}_5$  in sulfuric acid to be



Bachman<sup>17</sup> reported on the use of the stable insoluble  $\text{N}_2\text{O}_5 \cdot \text{BF}_3$  complex in aromatic nitrations, the active nitrating agent being  $\text{NO}_2^+ \cdot \text{BF}_3 \cdot \text{ONO}_2^-$ . We have found in present investigations that  $\text{N}_2\text{O}_5$  can be used as a very effective nitrating agent in Friedel-Crafts type nitrations in the presence of Lewis acid catalysts such as  $\text{BF}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  and  $\text{PF}_5$  in tetramethylene sulfone solution. It is not necessary to isolate the intermediate  $\text{N}_2\text{O}_5$ -Lewis acid complexes as the solutions of  $\text{N}_2\text{O}_5$  and the catalyst can be used directly. The nitrations are quite vigorous, but can be well controlled in homogeneous solutions. In general, the solution of  $\text{N}_2\text{O}_5$  and the Lewis acid catalyst (in equimolar quantities) is run into the stirred and cooled solution of the aromatic in tetramethylene sulfone. After the addition is completed, the mixture is allowed to come to room temperature and is then stirred for another 15 minutes. Alkylbenzenes (benzene, toluene, xylene, ethylbenzene, propylbenzene, butylbenzene, mesitylene) were nitrated with yields of 87-95%. As the reactions are carried out in homogeneous media, the amount of dinitro products is negligible if an excess of alkylbenzene is used. Halobenzenes (fluoro-, chloro-, bromo-, dihalobenzenes, benzotrifluoride) were nitrated with yields of 79-89%.

When the  $\text{N}_2\text{O}_5$  nitration is carried out in liquid anhydrous HF as solvent (which does not appear to react with  $\text{N}_2\text{O}_5$  at a temperature below 0°) using a catalyst such as  $\text{BF}_3$ ,  $\text{SbF}_5$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{SiF}_4$ ,  $\text{NbF}_5$ ,  $\text{TaF}_5$ ,  $\text{WF}_6$ , etc., a quantitative formation of the corresponding nitronium salts takes place. As HF also acts as a good ionizing solvent, an extremely active nitration medium is obtained. Nitrobenzene and benzotrifluoride are nitrated with yields of over 90% at temperatures between -20 and 0°.

One of the difficulties of using anhydrous HF as solvent (aside from some inconveniences arising from its being handled in laboratories not equipped for fluorine work) is the fact that it is a rather poor solvent for aromatics (solubilities are generally less than 2%) and, therefore, the reactions must be carried out by vigorous stirring of the heterogeneous reaction mixtures.

**Nitrations with Stable Nitronium Salts.**—As previously reported,<sup>18</sup> it is possible to isolate

(15) A. Klemenz and K. Scholler, *Z. anorg. Chem.*, **141**, 231 (1924).

(16) D. J. Millen, *J. Chem. Soc.*, 2600 (1950).

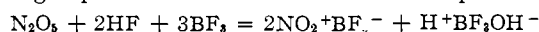
(17) G. B. Bachman and J. L. Dever, *J. Am. Chem. Soc.*, **80**, 5871 (1958).

(18) G. Olah, S. Kuhn and A. Mlinko, *J. Chem. Soc.*, 4257 (1956).

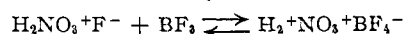
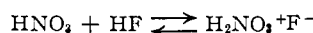
stable nitronium salts, *e.g.*,  $\text{NO}_2^+\text{BF}_4^-$ ,  $\text{NO}_2^+\text{AsF}_6^-$ ,  $\text{NO}_2^+\text{PF}_6^-$ ,  $(\text{NO}_2^+)_2\text{SiF}_6^{2-}$ , etc., from nitromethane solutions of the dinitrogen pentoxide + catalyst + anhydrous HF systems



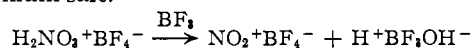
This method has now been considerably improved. We have observed that in the presence of increasing amounts of HF and  $\text{BF}_3$  relative to the  $\text{N}_2\text{O}_5$  used, the yields of  $\text{NO}_2^+\text{BF}_4^-$  are increased to a point where almost complete conversion of the nitrogen present into nitronium salt takes place



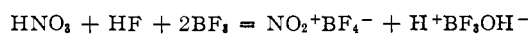
An investigation of the unexpectedly high yields revealed that nitric acid itself is transformed by  $\text{HF} + \text{BF}_3$  into nitronium tetrafluoroborate. The reaction is practically quantitative in the presence of excess  $\text{BF}_3$ . Nitric acid is first protonated to the nitric acidium ion.



Excess boron trifluoride then acts as a dehydrating agent for the nitric acidium ion to form the nitronium salt.

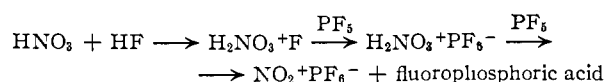


The over-all reaction thus is



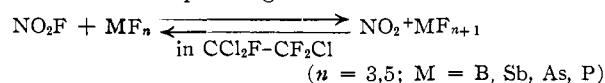
As the excess Lewis acid acts as the dehydrating agent, it is advantageous that  $\text{BF}_3 \cdot \text{H}_2\text{O}$  (or  $\text{H}^+\text{BF}_3\text{OH}^-$  as it is now known) is stable and can be removed easily by simply filtering the separated, solid nitronium salt from the nitromethane mother liquor containing the hydroxyfluoroboric acid.

Other Lewis acid fluorides such as  $\text{PF}_5$  and  $\text{AsF}_5$  also can be used in the reaction



$\text{SiF}_4$  and  $\text{SbF}_5$  also react to give nitronium salts, but these are contaminated with the hydrolysis products of the Lewis acid fluorides.

Nitronium salts were obtained in highest purity by treating fluorocarbon solutions of nitril fluoride with the corresponding Lewis acid fluorides<sup>19</sup>



Infrared spectroscopic investigation of the isolated nitronium salts<sup>19</sup> was in agreement with the linear  $\text{O}=\text{N}=\text{O}$  ion structure. Electric conductivity measurements in nitromethane<sup>18</sup> and tetramethylene sulfone solutions are also in accordance with the ionic salt structure of the complexes.

Conductivity measurements of  $\text{NO}_2^+\text{BF}_4^-$  in purified tetramethylene sulfone (heated to  $100^\circ$  for 24 hours with anhydrous sodium hydroxide and twice vacuum distilled) were carried out under exclusion of moisture. The tetramethylene sulfone used had a specific conductance of  $1.35 \times 10^{-7}$  mho/cm. and  $\text{NO}_2^+\text{BF}_4^-$  was purified in the manner

(19) D. Cook, S. J. Kuhn and G. A. Olah, *J. Chem. Phys.*, **33**, 1669 (1960).

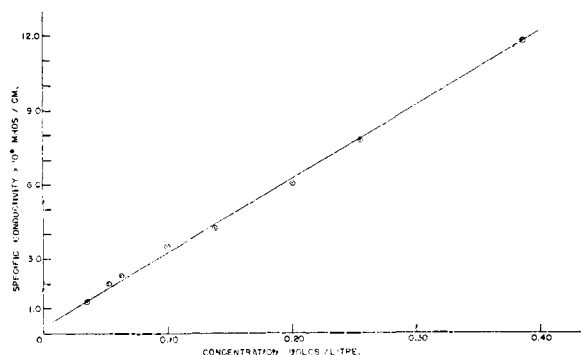


Fig. 1.—Specific conductivity of  $\text{NO}_2\text{BF}_4$  in tetramethylene sulfone solution.

described previously, by heating the crystalline salt obtained from Freon solutions of  $\text{NO}_2\text{F} + \text{BF}_3$  to  $100^\circ$  in vacuum for 24 hours. All materials were handled under vacuum conditions, the solutions having been made up by dilution technique. The specific conductance of the solutions was found to vary linearly with the concentration of  $\text{NO}_2\text{BF}_4$  in tetramethylene sulfone as shown in Fig. 1.

The complex nitronium salts are colorless, crystalline, very stable compounds;  $\text{NO}_2^+\text{BF}_4^-$  decomposes at atmospheric pressure only above  $+170^\circ$ , without subliming, into its components:  $\text{NO}_2\text{F} + \text{BF}_3$ . The hexafluorophosphate, hexafluoroarsenate and hexafluoroantimonate salts are even more stable. The higher thermal stability may be partially also a consequence of the higher boiling points of the corresponding Lewis acid fluorides over that of boron trifluoride.

Stable nitronium salts, first of all nitronium tetrafluoroborate, have been used by us now for more than six years in quantities up to a few kilos at a time and no accident has ever occurred from spontaneous decomposition, a danger faced when working with nitronium perchlorate.<sup>20</sup> Nitronium tetrafluoroborate samples can be stored at room temperature indefinitely without decomposition. Refrigeration is unnecessary and no other special precautions are required. All nitronium salts are, however, very hygroscopic and must be stored and handled with precautions to avoid moisture.

As reported first in 1956,<sup>18,21</sup> nitronium tetrafluoroborate and related nitronium salts are extremely active nitrating agents for aromatics



The nitrations are carried out under anhydrous conditions. This is of special advantage in dealing with compounds which under usual strong acidic nitration conditions may undergo hydrolysis or oxidation. Aryl nitriles, for example, are easily hydrolyzed under nitration conditions and no direct dinitration, requiring forceful conditions, previously was possible. The nitronium fluoroborate method enabled us to carry out mono- and dinitrations of aryl nitriles with high yields without any hydrolysis of the  $-\text{CN}$  group.

Results of preparative nitrations of arenes, haloarenes, nitroarenes, arylcarboxylic acid esters

(20) Personal communication by Sir Christopher Ingold.

(21) G. Olah and S. Kuhn, *Chemistry & Industry*, 98 (1956).

TABLE I  
NITRATION OF ARENES WITH  $\text{NO}_2^+\text{BF}_4^-$ <sup>a</sup>

Substrate	Product	Reaction time, min.	Yield of isolated mononitro product, %
(1) Benzene	Nitrobenzene	10	93
(2) Toluene	Nitrotoluenes	10	95
(3) <i>o</i> -Xylene	Nitroxylenes	10	91
(4) <i>m</i> -Xylene	Nitroxylenes	10	90
(5) <i>p</i> -Xylene	Nitro- <i>p</i> -xylene	10	93
(6) Mesitylene	Nitromesitylene	10	89
(7) Ethylbenzene	Nitroethylbenzenes	10	93
(8) <i>n</i> -Propylbenzene	Nitro- <i>n</i> -propylbenzenes	10	91
(9) <i>i</i> -Propylbenzene	Nitro- <i>i</i> -propylbenzenes	10	93
(10) <i>n</i> -Butylbenzene	Nitro- <i>n</i> -butylbenzenes	10	90
(11) <i>sec</i> -Butylbenzene	Nitro- <i>sec</i> -butylbenzenes	10	92
(12) <i>t</i> -Butylbenzene	Nitro- <i>t</i> -butylbenzenes	10	88
(13) Naphthalene	Nitronaphthalenes	25	79
(14) Anthracene	9-Nitroanthracene	25	85

<sup>a</sup> All nitrations were carried out in tetramethylene sulfone solutions at temperatures between 0 and +5°.

and halides and aryl nitriles are summarized in Tables I-V.

All nitro compounds in the tables, if not stated otherwise, were known from the literature. Yields relate to isolated nitro compound in preparative scale nitrations and *not* to infrared or gas chromatographic analyses. No attempt was made to obtain optimum yields. In the case of mononitrations, which are generally very fast, with the exception of highly deactivated substrates the nitrations are almost quantitative. Di- and trinitrations could also give considerably higher yields than presently reported, with longer reaction times, higher temperatures or by simply finding more suitable reaction conditions.

Identification of nitro products was carried out by comparison of physical constants with those known from literature, comparison of infrared spectra, gas-liquid chromatography and elementary analyses when required. No effort was made in the present work to determine isomer ratios of the nitro compounds formed, as this will be treated in subsequent papers on the investigation of the nitronium salt nitration of alkyl and halobenzenes.

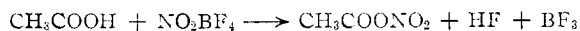
If not stated otherwise, nitrations were carried out in tetramethylene sulfone solutions. The use of homogeneous, acid free (with the exception of  $\text{HBF}_4$  which is formed as by-product in equimolar quantities and is quite stable as the conjugate acid in tetramethylene sulfone solution) reaction media makes it possible to carry out mononitrations, using an excess of the aromatic substrate, with almost complete exclusion of any higher nitrated products. This is one of the advantages over mixed-acid nitrations where, due to the higher solubility of the mononitro products in the acid layer, dinitrations must always be considered.

Nitronium salts have generally very low solubilities in organic solvents which themselves do not react with  $\text{NO}_2^+$ . Nitromethane, previously found by us to be suitable in electric conductivity measurements,<sup>18</sup> dissolves less than 0.3%  $\text{NO}_2^+\text{BF}_4^-$ .  $\text{NO}_2^+\text{SbF}_6^-$ ,  $\text{NO}_2^+\text{PF}_6^-$  and  $\text{NO}_2^+\text{AsF}_6^-$  are, however, quite soluble in nitromethane (up to 50% solutions can be prepared at 25°) and, therefore, suited for preparative nitrations. Tetramethylene sulfone is a good solvent for nitronium

salts and aromatic substrates alike. The saturated tetramethylene sulfone solution of  $\text{NO}_2\text{BF}_4$  is about 7% (0.5 molar). Its high dielectric constant ( $\epsilon = 44$ )<sup>22</sup> is particularly advantageous and as it is completely miscible with water the separation of products from the nitration mixtures is very easy. The only disadvantage is its relatively high freezing point (+28.9°) which is, however, somewhat compensated by its high molar depression (66.2°) which allowed us to carry out nitrations at reasonably low temperatures when required.

A number of other solvents was found to be applicable to a certain degree in nitronium salt nitrations. One of these is acetonitrile. The saturated solution of  $\text{NO}_2^+\text{BF}_4^-$  in acetonitrile at room temperature is about 10% (weight). As acetonitrile is also an excellent solvent for most aromatics and is also miscible with water, it has the same advantages as tetramethylene sulfone. It reacts, however, at higher temperatures and even slowly on standing at room temperatures with nitronium salts. Therefore, only fresh solutions can be used and nitrations must be carried out at lower temperatures.

Further possible solvents for nitronium salt nitrations are trifluoroacetic acid (the solubility of  $\text{NO}_2^+\text{BF}_4^-$  is, however, very low), nitroethane and nitropropanes (the solubility of the nitronium tetrafluoroborate is again very small but other salts as the fluorophosphate, arsenate and antimonate are quite soluble). Dimethylacetamide, although otherwise an excellent solvent, does react with nitronium salts, therefore cannot be generally applied. Anhydrous acetic acid was suggested together with methanesulfonic acid as solvents for nitronium tetrafluoroborate nitrations by Giaccio and Marcus.<sup>23</sup> Acetic acid, although a good solvent for both nitronium salts and aromatics, does react with nitronium tetrafluoroborate even on standing at room temperature, with the formation of acetyl nitrate. The nitrating power of



acetyl nitrate is quite different from nitronium tetrafluoroborate, as is its stability. This inhibits its use as a suitable solvent in preparative nitrations as well as in kinetic and reaction mechanism investigations. Aromatic hydrocarbons are almost completely insoluble in methanesulfonic acid, thus making homogeneous nitrations possible only in very high dilutions; 100% sulfuric acid could be used successfully in heterogeneous nitrations with  $\text{NO}_2^+\text{HS}_2\text{O}_7^-$  when forceful reaction conditions were required for highly deactivated compounds.

Nitronium salt nitrations previously<sup>18,21</sup> could be carried out only under heterogeneous and rather difficult to control conditions by adding the solid nitronium salt or its suspension to the stirred aromatic substrate solution. Finding suitable solvents, first of all tetramethylene sulfone, has enabled us to extend considerably the scope and application of preparative scale nitronium salt nitrations.

(22) R. L. Burwell and C. H. Langford, *J. Am. Chem. Soc.*, **81**, 3799 (1959); **82**, 1503 (1960).

(23) L. L. Giaccio and R. A. Marcus, Abstr. 133rd Meeting, Am. Chem. Soc., 1958, San Francisco, Calif., p. 24-Q.

TABLE II  
NITRATION OF HALOARENES AND HALOARALKANES WITH  $\text{NO}_2^+\text{BF}_4^-$

Substrate	Product	Reaction temp., °C.	Reaction time, min.	Yield of mononitro prod., %
(1) Fluorobenzene	<i>o,p</i> -Fluoronitrobenzenes	5	10	90
(2) Chlorobenzene	<i>o,p</i> -Chloronitrobenzenes	10	10	92
(3) Bromobenzene	<i>o,p</i> -Bromonitrobenzenes	10	10	87
(4) Iodobenzene	<i>o,p</i> -Iodonitrobenzenes	10	10	90
(5) Benzotrifluoride	<i>m</i> -Nitrobenzotrifluoride	30	20	20
(6) <i>p</i> -Fluorobenzotrifluoride	3-Nitro-4-fluoro-benzotrifluoride <sup>a</sup>	50	20	85
(7) <i>o</i> -Dichlorobenzene	Nitro- <i>o</i> -dichlorobenzenes	50	20	70
(8) <i>m</i> -Dichlorobenzene	Nitro- <i>m</i> -dichlorobenzenes	50	20	74
(9) <i>p</i> -Dichlorobenzene	Nitro- <i>p</i> -dichlorobenzene	50	20	80
(10) <i>o</i> -Difluorobenzene	Nitro- <i>o</i> -difluorobenzenes	50	20	82
(11) <i>m</i> -Difluorobenzene	Nitro- <i>m</i> -difluorobenzenes	50	20	79
(12) <i>p</i> -Difluorobenzene	Nitro- <i>p</i> -difluorobenzene	50	20	85
(13) $\alpha$ -Fluoronaphthalene	Nitro- $\alpha$ -fluoronaphthalenes	30	20	75
(14) $\beta$ -Fluoronaphthalene	Nitro- $\beta$ -fluoronaphthalenes	30	20	79
(15) Benzyl chloride	Nitrobenzyl chlorides	0	10	52
(16) $\beta$ -Fluoroethylbenzene	Nitro- $\beta$ -fluoroethylbenzenes	0	10	69
(17) $\beta$ -Chloroethylbenzene	Nitro- $\beta$ -chloroethylbenzenes	10	15	82
(18) $\beta$ -Bromoethylbenzene	Nitro- $\beta$ -bromoethylbenzenes	10	15	78

<sup>a</sup> New compound: b.p. 65-66° (5 mm.),  $n_D^{25}$  1.4604. Anal. Calcd.: N, 6.70; F, 36.40. Found: N, 6.63; F, 35.96.

TABLE III  
NITRATION OF NITROARENES AND NITROHALOARENES WITH  $\text{NO}_2^+\text{BF}_4^-$ <sup>a</sup>

Substrate	Product	Reaction		Yield of nitro prod., %
		Temp., °C.	Time	
(1) Nitrobenzene	<i>m</i> -Dinitrobenzene	25	20 min.	81
(2) $\alpha$ -Nitronaphthalene	Dinitronaphthalenes	25	20 min.	85
(3) <i>p</i> -Fluoronitrobenzene	2,4-Dinitrofluorobenzene	30	30 min.	78
(4) <i>o</i> -Fluoronitrobenzene	2,4-Dinitrofluorobenzene	30	30 min.	84
(5) 2,4-Dinitrofluorobenzene	Picryl fluoride	120	12 hr.	40
(6) <i>p</i> -Nitrochlorobenzene	2,4-Dinitrochlorobenzene	30	30 hr.	75
(7) <i>o</i> -Nitrochlorobenzene	2,4-Dinitrochlorobenzene	30	20 hr.	77
(8) 2,4-Dinitrochlorobenzene	Picryl chloride	100	10 hr.	80

<sup>a</sup> Tetramethylene sulfone was used as the solvent in all cases except for 2,4-dinitrofluoro- and 2,4-dinitrochlorobenzene when 100%  $\text{H}_2\text{SO}_4$  was used.

TABLE IV  
NITRATION OF ARYL CARBOXYLIC ACID ESTERS AND HALIDES WITH  $\text{NO}_2^+\text{BF}_4^-$ <sup>a</sup>

Substrate	Product	Reaction		Yield of mononitro prod., %
		Temp., °C.	Time, min.	
(1) Methyl benzoate	<i>m</i> -Nitromethyl benzoate	30	20	88
(2) Ethyl benzoate	<i>m</i> -Nitromethyl benzoate	30	20	79
(3) Propyl benzoate	<i>m</i> -Nitropropyl benzoate	30	20	82
(4) <i>m</i> -Nitroethyl benzoate	3,5-Dinitroethyl benzoate	85-90	120	60
(5) Benzoyl fluoride	<i>m</i> -Nitrobenzoyl fluoride	50	30	69
(6) Benzoyl chloride	<i>m</i> -Nitrobenzoyl chloride <sup>b</sup>	50	30	70

<sup>a</sup> All nitrations were carried out in tetramethylene sulfone solutions. <sup>b</sup> Halogen exchange to acid fluoride takes place with by-product HF.

TABLE V  
NITRATION OF ARYL AND ARALKYL NITRILES WITH  $\text{NO}_2^+\text{BF}_4^-$ <sup>a</sup>

Substrate	Product	Reaction		Yield of nitro prod., %
		Temp., °C.	Time, min.	
(1) Benzointrile	3-Nitrobenzointrile	20-35	30	85
(2) <i>o</i> -Toluenitrile	2-Methyl-5-nitrobenzointrile	20-35	30	90
(3) <i>m</i> -Toluenitrile	Nitrotoluenitriles	20-35	30	85
(4) <i>p</i> -Toluenitrile	4-Methyl-3-nitrotoluenitrile	20-35	30	92
(5) Nitro- <i>o</i> -toluenitrile	3,5-Dinitro- <i>o</i> -toluenitrile	100	60	93
(6) Nitro- <i>m</i> -toluenitrile	Dinitro- <i>m</i> -toluenitriles	100	60	84
(7) Nitro- <i>p</i> -toluenitrile	3,5-Dinitro- <i>o</i> -toluenitrile	100	60	89
(8) <i>p</i> -Fluorobenzointrile	4-Fluoro-3-nitrobenzointrile	40-50	30	90
(9) <i>p</i> -Chlorobenzointrile	4-Chloro-3-nitrobenzointrile	50-55	40	92
(10) 1-Naphthonitrile	Nitronaphthonitrile	20-35	30	91
(11) Benzyl cyanide	Nitrobenzyl cyanides	0-15	15	84

<sup>a</sup> All nitrations were carried out in tetramethylene sulfone solutions using a ratio of  $\text{ArCN}:\text{NO}_2\text{BF}_4$  of 1:1.25 in mononitrations and a ratio of  $\text{ArNO}_2\text{CN}:\text{NO}_2\text{BF}_4$  of 1:2 in dinitrations.

Besides nitronium tetrafluoroborate, used predominantly as nitrating agent, a series of comparative nitrations was also carried out with nitronium hexafluorophosphate, hexafluoroantimonate, hexachloroantimonate, hexafluoroarsenate, hexafluorosilicate, hydrogen bisulfate and perchlorate. No specific differences in yields could be observed as due to an effect of the different anions in nitronium salts. The ease of preparation and increased stability over certain other salts (first of all of the perchlorate) makes nitronium tetrafluoroborate the most advantageous nitronium salt in the nitrations investigated.

### Experimental

Nitryl chloride was prepared according to Seel and Nogrady,<sup>24</sup> and Kaplan and Schechter.<sup>25</sup> Nitryl fluoride was prepared according to Faloon and Kinna.<sup>26</sup> Anhydrous silver tetrafluoroborate was prepared according to Olah and Quinn.<sup>27</sup> PF<sub>5</sub> and AsF<sub>5</sub> were obtained from the Ozark-Mahoning Corp., Tulsa, Okla. N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub> were purchased from the Matheson Co., East Rutherford, N. J. N<sub>2</sub>O<sub>5</sub> was prepared according to Gruchut, Goldfrank, Cushing and Caesar.<sup>28</sup> Tetramethylene sulfone (sulfolane) was a commercial product (Shell Development Co., Emeryville, Calif.). It was purified by vacuum fractionation.

All known nitro products were identified by their physical constants and when needed by their infrared spectra, gas-liquid chromatography or elementary analysis.

**Preparation of Nitronium Salts.** (a) From Nitryl Fluoride.—Into 100 g. of 1,1,2-trifluoroethane (Freon 113) 32.5 g. (0.5 mole) of NO<sub>2</sub>F and an equimolar amount of boron trifluoride was introduced simultaneously at 0°. The white precipitate which formed was filtered and dried in vacuum at 50°, pumping off all volatile materials. The NO<sub>2</sub>BF<sub>4</sub> obtained is very pure<sup>10</sup> and the yield is 126 g. (95%).

NO<sub>2</sub>PF<sub>6</sub>, NO<sub>2</sub>AsF<sub>6</sub> and (NO<sub>2</sub>)<sub>2</sub>SiF<sub>6</sub> were prepared in an identical manner. Yields of 90 to 94% were obtained. NO<sub>2</sub>SbF<sub>6</sub> was prepared by passing into an ice-cold solution of SbF<sub>5</sub> in Freon 113, the equimolar quantity of NO<sub>2</sub>F. The yield obtained was 97%.

(b) From Dinitrogen Pentoxide.—N<sub>2</sub>O<sub>5</sub> (54 g., 0.5 mole) and 20 g. (1.0 mole) of anhydrous HF were dissolved in 200 g. of nitromethane at -5°. The solution then was saturated with boron trifluoride, the temperature being kept below 0°. The white precipitate was filtered, washed twice with small amounts of nitromethane and then with Freon 113. The still wet material was then transferred into a round bottom flask and dried in vacuum at 100° by pumping off all volatile materials. A yield of 89% of the theoretical based on N<sub>2</sub>O<sub>5</sub> was obtained. The nitronium salt obtained, although suitable for preparative nitration, contains about 4-5% (by Raman spectroscopy) NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> as impurity. This is due to the N<sub>2</sub>O<sub>4</sub> which is present as an impurity in the N<sub>2</sub>O<sub>5</sub> which is used as starting material.

NO<sub>2</sub>PF<sub>6</sub> and NO<sub>2</sub>SbF<sub>6</sub> were obtained with yields of 87 and 92%, respectively, in an identical manner.

(a) From Nitric Acid.—Fuming nitric acid (90%, sp. gr. 1.49, 70 g.) and 20 g. of anhydrous HF were dissolved in 100 g. of nitromethane. The solution was saturated at -5° with boron trifluoride. The white crystalline precipitate obtained was filtered, washed and dried according to product obtained in previous preparations. The yield obtained (based on HNO<sub>3</sub> used) was 90% of the theoretical. NO<sub>2</sub>PF<sub>6</sub> was obtained in 86% NO<sub>2</sub>AsF<sub>6</sub> in 82% yield under identical conditions.

**Nitration of Aromatics with NO<sub>2</sub>Cl + TiCl<sub>4</sub>.** (a) In Excess Aromatic as Solvent.—TiCl<sub>4</sub> (0.1 mole, 19 g.) was

dissolved in 0.4 mole of the aromatic, and into this solution 0.2 mole (16.3 g.) of NO<sub>2</sub>Cl was introduced at temperatures below 0°. The mixture was stirred, after the introduction of NO<sub>2</sub>Cl was completed, for 15 minutes. Then it was allowed to come to room temperature and kept for another hour. The reaction mixture now was poured on crushed ice, the organic layer separated, washed with water, dried with calcium chloride and after distilling off the excess aromatic solvent, the nitro product was either fractionated or crystallized.

(b) In Carbon Tetrachloride Solution.—NO<sub>2</sub>Cl (0.2 mole) and 0.1 mole of TiCl<sub>4</sub> were dissolved in 35 ml. of carbon tetrachloride and this solution was added dropwise to a stirred solution of 0.4 mole of aromatic substrate in 35 ml. of carbon tetrachloride. The temperature was kept around -15° during the addition and after that the mixture was allowed to come to room temperature. It was stirred for an additional hour, poured on crushed ice and treated as under (a).

(c) In Tetramethylene Sulfone Solution.—NO<sub>2</sub>Cl (0.2 mole) and 0.1 mole of TiCl<sub>4</sub> were dissolved in 100 ml. of tetramethylene sulfone and this solution was added dropwise to a solution of 0.4 mole of aromatic in 30 ml. of tetramethylene sulfone, keeping the temperature of the mixture around 10-15°. After the addition was completed, the mixture was allowed to come to room temperature, was stirred for another 30 minutes, then poured into cold water, the organic layer separated, washed twice more with water and treated as under (a).

**Nitration of Aromatics with NO<sub>2</sub>Cl + SbCl<sub>5</sub>.**—NO<sub>2</sub>Cl (0.1 mole) and 0.1 mole of SbCl<sub>5</sub> were dissolved in 100 ml. of tetramethylene sulfone and this solution was added dropwise to a stirred solution of 0.2 mole of aromatic in 50 ml. of tetramethylene sulfone. The temperature of the reaction mixture was kept at 10-15° during the addition. After the addition was completed, the reaction mixture was allowed to come to room temperature and was stirred for another 30 minutes. It then was poured into cold water, the organic layer separated, washed twice with water and treated as previously.

**Nitration of Aromatics with NO<sub>2</sub>F + Lewis Acid Fluorides.**—NO<sub>2</sub>F (0.1 mole) was dissolved in 100 ml. of tetramethylene sulfone and the solution was saturated with the Lewis acid fluoride (BF<sub>3</sub>, PF<sub>5</sub>, AsF<sub>5</sub>) by keeping the temperature around 10°. The solution was then added dropwise to a stirred solution of 0.2 mole of aromatic in 50 ml. of tetramethylene sulfone, keeping the temperature between 10-15°. After the addition was completed the mixture was allowed to come to room temperature, stirred for an additional 30 minutes and then treated as in previous experiments.

**Nitration of Aromatics with NO<sub>2</sub>Cl + AgBF<sub>4</sub>.** (a) **Excess Aromatic as Solvent.**—Anhydrous silver tetrafluoroborate (0.1 mole) was dissolved in 0.5 mole of the aromatic (alkylbenzene or halobenzene) and into the stirred solution, 0.1 mole of NO<sub>2</sub>Cl gas was introduced while keeping the temperature of the mixture at 0° with external cooling. Precipitated silver chloride was filtered, the reaction mixture washed twice with 30-30 ml. of water. After drying the organic layer with calcium chloride, the excess unchanged aromatic was distilled off and the nitro product isolated as previously.

(b) In Tetramethylene Sulfone Solution.—Anhydrous silver tetrafluoroborate (0.1 mole) was dissolved in 200 g. of tetramethylene sulfone, and into this solution 0.1 mole of nitryl chloride was introduced. The temperature of the mixture was kept around 20-25°. Precipitated silver chloride was filtered and the clear solution obtained, containing NO<sub>2</sub>BF<sub>4</sub>, was used as described under nitrations with pre-prepared nitronium salts.

(c) In Nitromethane Solution.—Anhydrous silver tetrafluoroborate (0.1 mole) and 0.5 mole of the aromatic to be nitrated were dissolved in 100 g. of nitromethane. Into the stirred solution, 0.1 mole of nitryl chloride dissolved in 25 g. of nitromethane was dropped, while maintaining the temperature of the reaction mixture around 25°. After the addition was completed, the mixture was stirred for another 15 minutes. Precipitated silver chloride was filtered, the solution washed twice with 25-25 ml. water, the organic layer dried with calcium chloride and the product isolated as in previous experiments.

**Nitration of Aromatics with N<sub>2</sub>O<sub>5</sub> + Lewis Acid Catalyst in Tetramethylene Sulfone Solution.**—Dinitrogen tetroxide

(24) F. Seel and I. Nogrady, *Z. anorg. allgem. Chem.*, **269**, 188 (1952).

(25) R. Kaplan and H. Schechter, "Inorganic Syntheses," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 52.

(26) A. V. Faloon and W. B. Kinna, *J. Am. Chem. Soc.*, **73**, 2937 (1951).

(27) G. A. Olah and H. W. Quinn, *J. Inorg. Nucl. Chem.*, **14**, 295 (1960).

(28) N. S. Gruchut, M. Goldfrank, M. L. Cushing and G. V. Caesar, "Inorganic Syntheses," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 78.



(0.1 mole) was dissolved in 200 g. of tetramethylene sulfone, 0.1 mole of the Lewis acid halide ( $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{TiCl}_4$ ) was then introduced into the solution while the temperature was kept around  $15^\circ$ . The  $\text{N}_2\text{O}_5$  catalyst solution thus obtained was added dropwise to a stirred solution of 0.5 mole of the aromatic to be nitrated in 50 ml. of tetramethylene sulfone. After the addition was completed, the reaction mixture was heated slowly under reflux condenser, generally to  $100^\circ$  and kept there for an hour. After cooling, the reaction mixture was poured on crushed ice, the organic layer separated, washed twice with water, dried with calcium chloride and distilled. The products obtained were analyzed by gas-liquid chromatography.

**Nitration of Aromatics with  $\text{N}_2\text{O}_5$  + Lewis Acid Catalyst in Tetramethylene Sulfone Solution.**—Dinitrogen pentoxide (0.1 mole) was dissolved in 200 g. of tetramethylene sulfone; 0.1 mole of the Lewis acid halide ( $\text{BF}_3$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$ ,  $\text{TiCl}_4$ ) was introduced, while keeping the temperature between  $10$ – $20^\circ$ . The  $\text{N}_2\text{O}_5$ -catalyst solution obtained then was added to a well-stirred solution of 0.5 mole of the aromatic to be nitrated in 50 ml. of tetramethylene sulfone, and kept at  $10$ – $15^\circ$ . The nitration takes place very fast and is practically completed after the addition is finished. The mixture was stirred at room temperature for another 15 minutes, then poured on crushed ice. The organic layer was separated, washed twice with water and the nitro product isolated as previously.

**Nitration of Aromatics with  $\text{NO}_2\text{BF}_4$  in Tetramethylene Sulfone Solution.**—The aromatic (0.5 mole) was dissolved in 100 ml. of tetramethylene sulfone and a solution of 20 g. (0.15 mole) of nitronium tetrafluoroborate in 300 ml. of tetramethylene sulfone (0.5 molar solution) was added to the stirred solution with external cooling at a rate such as to allow the temperature to remain between  $15$ – $25^\circ$ . After the addition was completed, the reaction mixture was stirred at room temperature for another 10 minutes. In the case of deactivated aromatics, longer reaction times and higher temperatures are needed. The reaction mixture then was diluted with 500 ml. of water, the organic layer separated, washed twice with water, dried with  $\text{CaCl}_2$  and the excess aromatic removed by distillation. The nitro products now were isolated either by fractionation or crystallization. For details of the reaction times, temperatures and yields obtained, see Tables I–V.

**Picryl Fluoride.**—A mixture of 60 g. of 100%  $\text{H}_2\text{SO}_4$ , 0.15 mole of  $\text{NO}_2^+\text{HS}_2\text{O}_7^-$  and 9.3 g. (0.05 mole) of 2,4-dinitrofluorobenzene was heated to  $110$ – $120^\circ$  and kept at this temperature for 12 hours. After cooling, the reaction mixture was poured on crushed ice. The organic material was extracted with 120 g. of a 1:1 mixture of toluene and Freon 113 and diluted with ligroin until separation of crystals started. The mixture then was left standing overnight in a refrigerator. The separated crystals were filtered and dried in a vacuum desiccator; m.p.  $128$ – $130^\circ$ , yield 4.6 g., 40% of the theoretical. *Anal.* Calcd.: C, 31.17; H, 0.84; N, 18.18; F, 8.21. Found: C, 31.12; H, 0.90; N, 18.02; F, 8.11.

Previously<sup>20</sup> we reported the melting point of picryl fluoride as  $35^\circ$ . In a personal communication Dr. R. E. Parker of the University of Southampton, England, called our attention to the fact that picryl fluoride prepared under conditions similar to those used by us previously, gives, after repeated recrystallization, a product with a melting point of  $+130^\circ$ . This was found entirely correct and the previous low melting point could have been due to impurities of 2,4-dinitrofluorobenzene present.

The infrared spectrum (obtained as a mixed Nujol-Fluorolube mull on a Perkin-Elmer model 221-G spectrophotometer) showed the bands at 3117m, 3090sh, 1715w, 1618s, 1547s, 1410m, 1335s, 1310w, 1176m, 1078s, 940m, 924m, 910m, 776m, 730m, 720s, 695m  $\mu$  (s = strong, m = medium, w = weak). The spectrum agrees well with that of picryl chloride, the 1078 band being obviously a C–F stretching frequency.

Identical results were obtained in nitrations using  $\text{NO}_2\text{BF}_4$  dissolved in 100%  $\text{H}_2\text{SO}_4$ .  $\text{BF}_3$  evolution is observed,  $\text{BF}_4^-$  being obviously replaced by  $\text{HSO}_4^-$  or  $\text{HS}_2\text{O}_7^-$ .

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## Aromatic Substitution. VIII.<sup>1</sup> Mechanism of the Nitronium Tetrafluoroborate Nitration of Alkylbenzenes in Tetramethylene Sulfone Solution. Remarks on Certain Aspects of Electrophilic Aromatic Substitution<sup>2</sup>

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Ingold's method of competitive nitration has been used in order to determine relative reactivities of alkylbenzenes and benzene in homogeneous mononitrations with nitronium tetrafluoroborate in tetramethylene sulfone solutions. Relative reactivities and isomer distributions were determined by gas-liquid chromatography. The obtained relative rates show a good correlation with relative  $\pi$ -complex stabilities of alkylbenzenes ( $\text{Ag}^+$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{ICl}$ , picric acid,  $\text{HCl}$ ,  $\text{HF}$ ), but not with  $\sigma$ -complex stabilities ( $\text{HF} + \text{BF}_3$ ). The reaction mechanism is considered to involve oriented (or localized)  $\pi$ -complex formation between  $\text{NO}_2^+$  and the aromatics as the main rate-determining step. This is in accordance with the fact that partial rate factors and empirical selectivity factors are not applicable to present systems (primary competition is between donor molecules as such and not individual positions of those). The nitration of benzene- $d_6$  and toluene- $d_3$  shows a small secondary reverse kinetic isotope effect (the heavy compound reacting faster). The mechanism of the investigated nitration of alkylbenzenes with nitronium tetrafluoroborate is discussed in the light of the obtained experimental data.

### Introduction

The idea that the actual nitrating agent in aromatic nitrations under certain conditions might be the nitronium ion was first suggested by von Euler as early as 1903<sup>3</sup> and has since been supported by numerous other authors.<sup>4</sup>

(1) Part VII, *J. Am. Chem. Soc.*, **83**, 4554 (1961).

(2) Partly presented as a paper at the 140th National Meeting of the American Chemical Society in Chicago, Ill., September, 1961.

In a series of fundamental papers, Ingold, Hughes and co-workers<sup>5,6</sup> investigated the kinetics and

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(6) C. K. Ingold, E. D. Hughes, *et al.*, ref. 5, also E. D. Hughes, C. K. Ingold and R. B. Pearson, *J. Chem. Soc.*, 4357 (1958).