a mercaptan with an acyl chloride in pyridine solution.[22a] All of the thiol esters were purified as described previously.[4] The physical constants for nine of the esters agree with previously reported values and the constants for the other 13 previously unreported esters are given in Table V.

TABLE V

PHYSICAL CONSTANTS FOR 13 THIOL ESTERS, RCOSR′[a]

RCOSR′			
R	R′	$n^{25}D$	Bp °C (mm)
n-C_3H_7	CH_3	1.4595^b	142–142.5 (757)
i-C_3H_7	CH_3	1.4559	132–132.1 (757)
n-C_4H_9	CH_3	1.4614^c	165.2–165.4 (757)
i-C_4H_9	CH_3	1.4577	155.4–155.5 (756)
s-C_4H_9	CH_3	1.4585	153.8–154 (756)
t-C_4H_9	CH_3	1.4576	137–137.1 (756)
$C_6H_5CH_2$	CH_3	1.5592	112–112.2 (4)
n-C_4H_9	C_2H_5	1.4576	178–178.1 (757)
n-C_3H_7	t-C_4H_9	1.4505^d	49.5–50 (4.5)
i-C_4H_9	s-C_4H_9	1.4556	77.1–77.2 (6.5)
s-C_4H_9	t-C_4H_9	1.4507	62.5–63.0 (6.0)
t-C_4H_9	t-C_4H_9	1.4695^e	177.5–180 (757)
n-C_4H_9	$C_6H_5CH_2$	1.5347	159.1–159.5 (7.0)

[a] Satisfactory combustion analytical data for C, H, and S (±0.3%) were reported for all of the compounds in this table: Ed. [b] At 26°. [c] At 24°. [d] At 27°. [e] At 23°.

Standard sodium hydroxide solution and 40% aqueous p-dioxane were prepared as described previously.[4]

Determination of Alkaline Hydrolysis Rate Constants.—The apparatus and method of determination of the rate constants were the same as described previously,[4] except that (1) null points were obtained by a null indicator (Leeds and Northrup No. 8067), (2) the initial concentrations in the reaction mixture were 0.005 M thiol ester and 0.01 M sodium hydroxide.

It can be shown from previous studies[4,22b] that the integrated rate equation for this reaction is

$$(a/t)(1/R_0 - 1/R_t) = 2ak(1/R_t) - 2ak/R_\infty \qquad (14)$$

where R_0 and R_t are the resistance readings at time zero and at time t, a is the initial concentration of the thiol ester, k is the second-order rate constant, and R_∞ is the resistance reading after complete reaction (R_∞ is not required in this treatment). An approximate value of R_0 was obtained by measuring the resistance in the *same* conductivity cell of 0.01 M sodium hydroxide in 40% aqueous p-dioxane. Using this value of R_0, the *initial* plot of $(1/t)(1/R_0 - 1/R_t)$ *vs.* $1/R_t$ was always curved to some extent. If the curvature was concave upward, a slightly higher value of R_0 was then tried, and this procedure was repeated until linearity was obtained. If the initial plot was concave downward, slightly lower values of R_0 were tried until linearity resulted. The slope of the regression[6c] of $(1/t)(1/R_0 - 1/R_t)$ on $1/R_t$ was divided by $2a$ to obtain k.

Two or three rate-constant determinations were made on each thiol ester and the average k values are given in Table I. For the 24 thiol esters, the maximum deviation from the mean of replicate k values exceeded 2.0% only in the following four cases: $(CH_3)_2CHCOSCH_3$, 2.2%; $CH_3(CH_2)_3COSCH_3$, 2.9%; $(CH_3)_3CCOSCH_3$, 5.2%; and $CH_3(CH_2)_3COSCH_2CH_3$, 4.1%.

The following alkaline hydrolysis rate constants at 30° in 43 wt % aqueous acetone, determined by the titration method, have been reported previously: ethyl thiolacetate,[22b] 4.39; isopropyl thiolacetate,[22a] 2.42. Under the same conditions, except by the above-described conductivity method, k values of 4.49, 4.61, and 4.30 (av of 4.47) for ethyl thiolacetate and of 2.34 and 2.48 (av of 2.41) for isopropyl thiolacetate were found.

Nmr Spectral Measurements.—Using a Varian A-60 spectrometer, the chemical shifts of the thiol esters (neat), with respect to tetramethylsilane as internal standard, were measured at 37° at 250-Hz chart width and are accurate to about 0.2 Hz. The chemical shifts of methyl protons relative to those of methyl thiolacetate are shown in Table III.

Acknowledgments.—This study was supported in part by a research grant (C. K. H) from the Robert A. Welch Foundation.

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Aromatic Nitration with Nitric Acid and Trifluoromethanesulfonic Acid

CLIFFORD L. COON,* WILLIAM G. BLUCHER, AND MARION E. HILL

Chemistry Laboratory, Stanford Research Institute, Menlo Park, California 94025

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Nitration of aromatic compounds is accomplished by a nitrating reagent not previously reported. Two equivalents of trifluoromethanesulfonic acid (**1**) and one of HNO_3 combine to form a white, crystalline solid that has been identified as a mixture of nitronium trifluoromethanesulfonate (**3**) and the monohydrate of **1**. **3** is an excellent nitrating reagent in inert organic solvents, H_2SO_4, or CF_3SO_3H, and has been used to nitrate toluene, benzene, nitrobenzene, chlorobenzene, m-xylene, and benzotrifluoride. Nitrations with **3** have been carried out over a temperature range of −110 to 30°, yields are consistently >98%, and exceptionally high positional selectivity has been demonstrated. For example, **3** reacts in 1 min with toluene in an inert organic solvent at −110, −90, or −60° to give quantitative yields of mononitrotoluene that contains only 0.23, 0.36, and 0.53% of the meta isomer, respectively. When the mononitration of toluene is carried out at −110, −90, −60, −30, and 0° followed by dinitration at 0°, the combined meta-isomer percentages are 0.33, 0.51, 0.75, 1.08, and 1.33, respectively.

In the course of work to find a method of reducing meta substitution in the mono- and dinitration of toluene, a study was made on the effect of various strong acids on isomer percentages. The recent availability of trifluoromethanesulfonic acid (**1**), prompted us to determine its effectiveness, relative to other acids, as a nitration solvent and catalyst. **1** is a strong monobasic acid and possesses an acid strength 427 times as great as that of nitric acid and 14 times as great as that of sulfuric acid.[1] This work resulted in the discovery of nitronium trifluoromethanesulfonate and its subsequent use as a reagent to effect aromatic nitration.

The use of nitronium salts for the nitration of aromatic compounds is well known and has recently been reviewed extensively in several articles concerned with the mechanism of aromatic nitration.[2-5] It has long

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TABLE I

MONONITRATION OF TOLUENE WITH 3 IN ORGANIC SOLVENTS[a]

Run	Mole ratio of 3 to toluene	Solvent	Time, min	Temp, °C	Yield, % MNT[b]	Isomer ratios, % *o*-MNT	 *p*-MNT	 *m*-MNT
1	4:1	$CFCl_3$	180	−110	>99	50.52	49.25	0.23
2	4:1	CH_2Cl_2	180	−90	>99	61.32	38.32	0.36
3	4:1	CH_2Cl_2	60	−60	>99	62.13	37.35	0.53
4	2.05:1	CH_2Cl_2	60	−60	>99	61.99	37.49	0.52
5	4:1	$CFCl_3$	1	−60	>99	61.88	37.61	0.51
6	4:1	$CFCl_3$	1	−110	>99	50.78	48.98	0.24

[a] A mixture of 3 and 4 was formed by adding 1 equiv of nitric acid to 2 equiv of 1 dissolved in an organic solvent. About 50 ml of solvent was used for each 10 g of 3 formed. [b] MNT = mononitrotoluene.

TABLE II

PREPARATION OF DINITROTOLUENE IN NITRATING MIXTURES CONTAINING CF_3SO_3H[a]

Run	Composition of nitrating mixture, wt % CF_3SO_3H	 H_2SO_4	 HNO_3	 H_2O	Temp, °C	Yield, %	Isomer distribution 2,6	 2,3–2,5	 2,4	 3,4	Total meta %
1	89.0	0	11.0	0	−5	>98	15.70	0.51	82.84	0.95	1.46
2	45.5	45.5	6.0	3.0	−20	>98	10.19	0.31	88.64	0.86	1.17
3	45.5	45.5	6.0	3.0	−20	99	14.85	0.64	83.42	1.10	1.74
4	22.7	68.3	6.0	3.0	−20	99.5	12.06	0.43	86.37	1.15	1.58
5[b]	0	90.6	6.3	3.1	−25	99	11.77	0.50	86.47	1.26	1.76
6	80	0	10	10	20	99.2	16.79	0.96	81.00	1.25	2.21
7	65	0	5	30	0	100	*o*-/*m*-/*p*-MNT = 58.86/1.96/39.18 *o*/*p* = 1.50				

[a] A 4:1 mole ratio of nitric acid to toluene was used, and reactions were run for 15 min. [b] Run for comparative purposes.

been realized that nitronium salts, such as NO_2HSO_4 and NO_2KSO_4, can be formed *in situ*, and that the attacking species in most nitrating systems is the nitronium ion. The use of stable nitronium salts for aromatic nitration was first mentioned by Goddard, Hughes, and Ingold[6] in 1950 and Olah, Kuhn, and Mlinko[7] in 1956. Subsequently, Olah and coworkers carried out extensive studies on nitration with nitronium salts, such as NO_2BF_4, NO_2PF_6, NO_2ClO_4, NO_2AsF_6, and $NO_2HS_2O_7$.[8–12]

In this paper we report the synthesis of nitronium trifluoromethanesulfonate and its general utility as a nitrating reagent for aromatic compounds, and we briefly examine the mechanism of nitration with this reagent.

Results

Two equivalents of trifluoromethanesulfonic acid (1) and one of anhydrous nitric acid combine to form a white, crystalline solid, 2. This reaction can be carried out between the neat reactants or in solvents such as CH_2Cl_2, CCl_4, H_2SO_4, and excess 1. 2 is very hygroscopic, melts at 60–65°, and partially sublimes at 60–70° (1–2 mm). 2 was shown to be a mixture of nitronium trifluoromethanesulfonate (3) and hydronium trifluoromethanesulfonate (4) by its elemental

$$\underset{\mathbf{1}}{2CF_3SO_3H} + HNO_3 \longrightarrow \underset{\mathbf{3}}{NO_2^+CF_3SO_3^-} + \underset{\mathbf{4}}{H_3O^+CF_3SO_3^-} \qquad (1)$$

analysis and Raman spectrum. Reaction 1 is similar to that described by Goddard, Hughes, and Ingold[1] in which nitric acid reacts with $HClO_4$ to give nitronium perchlorate (5) and the monohydrate of perchloric acid (6).

$$2HClO_4 + HNO_3 \longrightarrow \underset{\mathbf{5}}{NO_2^+ClO_4^-} + \underset{\mathbf{6}}{H_3O^+ClO_4^-} \qquad (2)$$

For the purpose of clarity, 2 will refer to the mixture of nitronium trifluoromethanesulfonate and hydronium trifluoromethanesulfonate, and 3 will refer to nitronium trifluoromethanesulfonate.

The elemental analysis of 2 showed that it was composed of the elements of two molecules of 1 and one of nitric acid. The Raman spectrum gave a strong emission at 1409 cm^{-1}, which is characteristic of the symmetrical stretching vibration for the nitronium ion, and showed the presence of the CF_3– and $-SO_3$– group.

Although our initial work was concerned with the use of 1 as a catalyst and solvent for toluene nitration, the observance of 3 prompted us to investigate its effectiveness as a nitrating agent both in protonic acids and in organic solvents. 3 was found to effect aromatic nitration in a variety of solvents, including sulfuric acid, 1, aqueous 1, CH_2Cl_2, CCl_4, $CFCl_3$, CF_2Cl_2, and pentane, and over a temperature range of −110 to 30°. The

$$ArH + xNO_2CF_3SO_3 \longrightarrow Ar(NO_2)_x + xCF_3SO_3H \qquad (3)$$

nitrating reagent was formed by adding 1 equiv of anhydrous HNO_3 to a solution of 2 equiv of 1 in a suitable solvent. This reaction could be carried out at ambient temperature, and no exotherm was observed. After an aromatic substrate was added and the mixture was stirred from 1 to 60 min, the reaction was quenched on ice and the products were isolated by extraction. Reaction yields were based on weights of isolated products, and isomer proportions were determined by gc. The reactions of 3 with a variety of aromatic compounds and over a wide range of reaction conditions are summarized in Tables I–V.

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TABLE III

DINITRATION OF TOLUENE WITH **3** IN ORGANIC SOLVENTS

Run	Mole ratio of **3** to toluene[a]	Solvent	Time, min	Temp, °C	Yield, % DNT	Isomer content, % 2,6-DNT	 2,4-DNT	 Total meta isomers	2,4-/2,6-DNT ratio
1	4:1	CH_2Cl_2	60	25	>99	16.28	81.96	1.72	5.03
2	4:1	CH_2Cl_2	60	0	>99	16.51	82.16	1.33	4.98
3	4:1	CH_2Cl_2	60	−30	>99	15.75	83.17	1.08	5.28
			60	0					
4	4:1	CH_2Cl_2	60	−60		17.18	82.07	0.75	4.78
			60	0	100				
5	4:1	CH_2Cl_2	180	−90		17.67	81.82	0.51	4.63
			180	0					
6	4:1	$CFCl_3$	180	−110	>99	12.66	87.01	0.33	6.87
			60	0					
7	2.05:1	CH_2Cl_2	60	0	99	16.38	82.87	1.35	5.02
8	4:1	CCl_4	60	0	96[b]	15.98	82.82	1.20	5.52
9	4:1	$CFCl_3$	60	0	>99	16.47	82.36	1.17	5.00
10	4:1	CF_2Cl_2	60	−30[c]	[c]	[c]	[c]	[c]	
11	4:1	Pentane	60	0	[d]				
12	4:1	Pentane	60	25	98	16.72	81.54	1.74	4.88

[a] A mixture of **3** and **4** was formed by adding 1 equiv of nitric acid to 2 equiv of **1** dissolved in an organic solvent. About 50 ml of solvent was used for each 10 g of **3** formed. [b] Small amount of MNT present. [c] Reaction run at reflux temperature of CF_2Cl_2 (Freon 12). Product contained 80% MNT and 20% DNT. [d] Product contained 10% toluene, 69% MNT, and 21% DNT; isomer ratios not determined.

TABLE IV

NITRATION OF COMPOUNDS OTHER THAN TOLUENE WITH **3**

Run	Compd, mmol	Registry no.	CF_3SO_3H, mmol	HNO_3, mmol	CH_2Cl_2, ml	Temp, °C	Time, hr	Products
1	PhH, 43	71-43-2	345	172	500	0	2	98% $PhNO_2$, 2% $C_6H_4(NO_2)_2$
2	$PhNO_2$, 8	98-95-3	40	20	60	25	5	84.8% $C_6H_4(NO_2)_2$ ($o/m/p$ = 9.0/88.7/2.3), 15.2% $PhNO_2$
3	$PhNO_2$, 8		40	20	60	30	3	96.9% $C_6H_4(NO_2)_2$ ($o/m/p$ = 10.0/87.4/2.5), 3.1% $PhNO_2$
4	PhCl, 8	108-90-7	40	20	60	25	2.5	56% $C_6H_4ClNO_2$, 44% $C_6H_3Cl(NO_2)_2$
5	PhCl, 20		42	21	63	25	2.5	97% $C_6H_4ClNO_2$ ($o/m/p$ = 30.5/0.1/69.4%), 3% $C_6H_3Cl(NO_2)_2$
6	m-$C_6H_4(CH_3)_2$, 10	108-38-3	42	21	63	25	1	61.5% 4,6-dinitro-*m*-xylene, 37.4% 2,4-dinitro-*m*-xylene, <0.5% each of four other products
7	$PhCF_3$, 5	98-08-8	40	20	60	25	16	85.6% m-$C_6H_4CF_3NO_2$, 14.3% o-$C_6H_4CF_3NO_2$, 0.1% p-$C_6H_4CF_3NO_2$

TABLE V

EFFECT OF VARIOUS SULFONIC ACIDS ON THE NITRATION OF TOLUENE IN METHYLENE CHLORIDE[a]

Run	Nitrating mixture Acid, mmol	 Registry no.	 HNO_3, mmol	Toluene, mmol	Time, min	Yield, MNT, %	Comments
1	CF_3SO_3H, 40	1493-13-6	20	5	60	100	$o/m/p$ = 62.13/0.53/37.35
2	FSO_3H, 40	7789-21-1	20	5	120	89	$o/m/p$ = 62.76/0.72/36.52
3	CH_3SO_3H, 104	75-75-2	52	13	150	20	Toluene recovered[b]
4	H_2SO_4, 40	7664-93-9	20	5	120	9	Toluene recovered[b]

[a] Reaction temperature −65 to −60°. [b] MNT isomer ratio not determined.

Discussion

Nitronium trifluoromethanesulfonate (**3**) proved to have excellent nitrating properties in each reaction medium investigated in this work. Product yields were nearly quantitative in a variety of solvent systems including sulfuric acid, **1**, aqueous **1**, methylene chloride, and $CFCl_3$, thus indicating the absence of side reactions. In sulfuric acid or mixtures of sulfuric acid and **1**, dinitration of toluene occurred to give high yields of DNT. In aqueous **1**, as in aqueous sulfuric acid, either mono- or dinitration could be made to occur depending on the concentration of the acid.

Although it is not surprising that **3** is an effective nitrating reagent in sulfuric acid, **1**, or aqueous solutions of these acids, the use of **3** as a nitrating reagent in inert organic solvents has proven to be an exceptionally good nitrating system. In organic solvents, mono- or dinitration of toluene could be controlled by reaction temperature, as shown in Tables I and III. At −110 to −60° in methylene chloride, mononitration oc-

TABLE VI
NITRATION OF TOLUENE WITH NITRONIUM SALTS IN METHYLENE CHLORIDE

Run No.	Nitronium salt	Registry no.	Mmol	Toluene, mmol	Temp, °C	Time, min	Yield, %	MNT isomer ratio		
								o-	*m*-	*p*-
1	NO_2BF_4	13826-86-3	14.85	3.47	−65	150	70.2	56.55	0.65	42.80
2	NO_2PF_6	19200-21-6	10.39	2.60	−65	150	88.5	46.44	0.81	52.75
3	$NO_2CF_3SO_3$	42262-35-1	19.99	4.99	−60	1	>99	62.18	0.54	37.28

curred accompanied by only a trace of DNT products; at 0° or higher, quantitative yields of DNT were obtained. At −30° mixtures of MNT and DNT were formed.

3 proved to be a slightly less effective nitrating agent in carbon tetrachloride at 0°. In pentane **3** reacted with toluene to give mixtures of MNT and DNT after 1 hr at 0°. At 25° the reaction of **3** with toluene in pentane gave a 98% yield of DNT (see runs 11–12, Table III).

The mononitration of toluene with **3** is very fast, as shown by the fact that in methylene chloride at temperatures from −110 to −60° mononitration of toluene is complete within 1 min. The dinitration step, that is, the nitration of nitrotoluenes, carried out at 0°, is somewhat slower; after 15 min it is 50% complete and requires about 30 min for completion. Although these results show that **3** is not as strong a nitrating agent as the H_2SO_4–HNO_3–0–5% H_2O, oleum–HNO_3, or oleum–metal nitrate systems in which the dinitration step is very fast, **3** in an inert solvent is a very strong nitrating system and one of the few that will convert toluene to DNT at 0°. Although oleum and sulfuric acid nitration systems are stronger than **3** in an organic solvent, these systems freeze and are impractical as nitration media much below −25°. The lowest temperature limit for the effective use of **3** as a nitrating agent is still under investigation.

Complete mono- or dinitration of toluene is possible without the use of excess nitrating reagent. For example, 2.05 equiv of **3** reacts with 1 equiv of toluene at 0° in CH_2Cl_2 to give a 99% yield of DNT after 1 hr (run 7, Table III). In addition, at −60° only a slight excess of **3** is needed for rapid mononitration of toluene.

3 shows a high degree of positional selectivity as a reagent for aromatic nitration. As with all other nitrating systems the amount of meta isomer produced in toluene nitration is directly dependent upon reaction temperature. At −60, −90, and −110° the reaction of **3** with toluene gives MNT that contains 0.53, 0.36, and 0.23% *m*-MNT, respectively (see Table I). The last value is the lowest that has been reliably recorded for a MNT synthesis. Since most meta substitution takes place in the mononitration stage, the final meta-isomer content in DNT can be greatly influenced by running the mononitration step at low temperatures followed by dinitration at 0–25°. Thus, when mononitration was carried out at −110, −90, −60, −30, 0, and 25° followed by dinitration at 0 or 25°, the resulting DNT products contained 0.33, 0.51, 0.75, 1.08, 1.33, and 1.72% meta isomers, respectively. The value 0.33% is the lowest that has been reliably recorded for meta isomers in a DNT synthesis. A similar relationship between reaction temperature and meta-isomer content was noted in nitrations carried out in a mixture of sulfuric acid and **1** shown in Table II.

The *o*-/*p*-MNT and 2,4-/2,6-DNT ratios of the reaction products from Tables I–III are of interest because they illustrate a trend that has not heretofore been noted. In the low-temperature nitration studies in Table I, we noted that at −110° the *o*-/*p*-MNT ratio was substantially different from those obtained at −90 and −60°. *E.g.*, the ortho/para ratios at −90 and −60° are 1.60 and 1.66, respectively, which are typical of *o*-/*p*-MNT ratios obtained from many other nitration systems. At −110° this ratio changes suddenly to 1.03, indicating that a greater selectivity for the para position occurs in the temperature range between −90 and −110°. In the series of reactions shown in Table III in which mononitration was carried out at low temperature followed by dinitration at a higher temperature, the 2,4-/2,6-DNT ratio varies only slightly between 4.63 and 5.28 except for the reaction in which mononitration is carried out at −110°. In this case the 2,4-/2,6 ratio is 6.87, indicating that the mononitration step gave an unusually low *o*-/*p*-MNT ratio. The significant point of these experiments is that in the temperature range from −90 to 25° the *o*-/*p*-MNT ratio appears to decrease slightly as the nitration temperature is lowered, but at −110° the *o*-/*p*-MNT ratio changes suddenly and para substitution predominates.

The positional selectivity of **3** in aromatic nitration (see Table IV) is slightly different from that of other nitrating systems. In general **3** tends to give less meta and more ortho substitution than other nitrating systems. For each aromatic substrate investigated, less meta substitution occurred than was obtained from other nitrating systems at comparable temperatures. In the case of toluene, in which mononitration with 1 equiv of **3** could not be carried out at 25° without formation of some DNT, a direct comparison could not be made. However, since meta isomers from DNT prepared at 25° total only 1.74%, the *m*-MNT percentage can be no larger than this. This decrease in meta substitution occurs for both ortho-, para- and meta-directing aromatic substrates and results in increased ortho, rather than para, substitution. This is especially true in the cases of nitrobenzene and benzotrifluoride, in which exceptionally high values for ortho substitution were recorded. The amounts of ortho substitution obtained for the nitration of toluene and chlorobenzene with **3** were comparatively high but typical of other nitrating reagents.

A short study was conducted to compare the effectiveness of **3** with NO_2BF_4 and NO_2PF_6 as nitrating agents for toluene in methylene chloride at −65° (see Table VI).

The results of this study show that **3** is a far more effective nitrating reagent in methylene chloride than either NO_2BF_4 or NO_2PF_6. Whereas **3** converts toluene to MNT in 1 min, nitrations with NO_2BF_4 and NO_2PF_6 give 70.2 and 85.5% yields, respectively, after 2.5 hr. In addition, **3** shows a higher positional selectivity than either NO_2BF_4 or NO_2PF_6, at least with regard to meta substitution. A meta-isomer percentage of 0.54 was formed with **3**, whereas NO_2BF_4 and NO_2PF_6 gave 0.65 and 0.81% *m*-MNT, respectively. At higher temperatures, **3** also appears to be more reactive than NO_2BF_4. Whereas Ciaccio and Marcus[13] have shown that excess NO_2BF_4 mononitrates nitrobenzene at 24° to give conversions of about 100, 75, and 50% after 30 min in sulfuric acid, methanesulfonic acid, and acetonitrile, respectively, a fourfold excess of $NO_2CF_3SO_3$ in CH_2Cl_2 gave a 100% conversion to DNT after 30 min.

The *o-/p*-MNT ratio obtained from the nitration of toluene with NO_2PF_6 (see Table V) was 0.88, one of the lowest values recorded. Others have reported the nitration of toluene with NO_2PF_6 in organic solvents, such as tetramethylene sulfone (TMS) at 25°, and found the ortho/para ratio to be 2.18.[10] It is not known if there is a gradual reduction in the ortho/para ratio in the mononitration of toluene with NO_2PF_6 as the temperature decreases and then a sudden change occurs to predominantly para substitution near $-65°$. This point will be the subject of additional research.

The reaction of **3** with an aromatic hydrocarbon is one of the few examples in which a reagent that is insoluble in the reaction medium is used to effect nitration. At most, only minute quantities of **3** are dissolved in methylene chloride. When **1** and nitric acid react in methylene chloride to form a mixture of **3** and **4**, the supernatant liquid, when separated by filtration, possesses no nitrating capabilities. If fresh methylene chloride is added to the mixture of **3** and **4**, the nitration of aromatic compounds proceeds in the expected manner. Olah, Kuhn, and Mlinko first reported heterogeneous nitrations involving a solid nitronium salt in ether.[7] Bachman and coworkers[14-16] also reported a heterogeneous nitration system in which the solid products from the reaction of BF_3 with N_2O_4 or N_2O_5 are used as nitrating agents in organic solvents such as $CHCl_3$, CCl_4, benzene, or nitromethane. Whereas in Bachman's work heating and long reaction times are necessary to obtain moderate yields, nitrations effected by **3** in inert solvents are very fast even at temperatures as low as $-110°$.

Since **3** proved to be an excellent nitrating reagent for toluene, several reactions were run to determine if less acidic sulfonic acids, such as fluorosulfonic acid (**7**), methanesulfonic acid (**8**), or sulfuric acid would react in the same manner. The conditions and results for these experiments are summarized in Table V. These systems were substantially different from those of HNO_3 and **1** in CH_2Cl_2 in that a solid, stable, nitronium salt did not form. The combination of HNO_3 and **7** in CH_2Cl_2, which formed a cloudy suspension, is an effective nitrating reagent giving an 89% yield of MNT after 1 hr at $-60°$. The combinations of HNO_3 and **8** or H_2SO_4 were somewhat less effective and formed only low yields of MNT. These low yields were probably due to poor mixing between a viscous second phase with the CH_2Cl_2 solution of toluene.

From the data presented in this paper it is difficult to determine the mechanism by which aromatic nitration with **3** in organic solvents occurs. The facts that **3** can be used as a suspended solid in organic solvents and that the nitrations are essentially between solid **3** and a dissolved aromatic compound set this reagent apart from other much-studied nitration systems. This heterogeneity makes comparisons of our observed data on relative reaction rates and isomer distributions with data from homogeneous systems difficult to interpret. In addition, the presence of **4** in the reaction mixture and the role it might take in the nitration processes are not known.

The major difference between aromatic nitration with **3** and other nitronium salts is reaction rate. The rate of nitration of toluene by **3** at -60 and $-110°$ compared with that using NO_2BF_4 or NO_2PF_6 at $-60°$ convincingly illustrates differences in the nitrating species involved. Because it must be assumed that the nitronium ion is present in the attacking species, the difference in reactivity must arise from the accompanying anion. Whether this difference can be attributed to solubility difference in the NO_2^+-containing species in CH_2Cl_2, the formation of a reactive complex between **3** and **4**, or the inherent reactivity of **3** will be a subject of future research.

Experimental Section

General.—Elemental analyses were determined by the Stanford University Microanalytical Laboratory. Infrared spectra were run on a Perkin-Elmer 237 spectrophotometer and Raman spectra on a Specs Ramalog 1401 Double Monochromator, Coherent Radiation Model 52, Mixed Gas Argon Krypton Laser. Vpc analyses were run on an Aerograph 1520 gas chromatograph equipped with a flame ionization detector. Mononitrotoluene, nitrochlorobenzene, dinitrobenzene, and nitrated xylene mixtures were analyzed on a 12 ft × 0.125 in., 4% QF-1 on 100/120 mesh Chromosorb G, acid-washed, DMCS-treated column. Dinitrotoluene and nitrobenzotrifluoride mixtures were analyzed on a 12 ft × 0.125 in. column packed with 4% poly-*m*-phenyl ether (six ring) on 80/100 mesh Chromosorb G, acid washed, DMCS treated. Base-line separation of all DNT isomers was obtained except for the 2,3 and 2,5 isomers, which had the same retention time. Each vpc analysis was compared with that of a standard that contained approximately the same isomer distribution.

Starting Materials.—Trifluoromethanesulfonic acid was obtained from the 3M Co. under the name of trimsylate acid (FC-24). It was analyzed as ~99% pure by preparation of its aniline salt and was used without further purification. Toluene was obtained from usual commercial sources and was distilled before use to obtain fractions that were pure by vpc analysis. Benzene (Matheson Coleman and Bell), nitrobenzene (Curtin Chemical Co.), chlorobenzene (Baker Chemical Co.), *m*-xylene (Matheson Coleman and Bell), and benzotrifluoride (Pierce Chemical Co.) were of sufficient purity for use as received.

Reaction of CF_3SO_3H with HNO_3. Method A.—Under an atmosphere of N_2, a 6.00-g sample (40 mmol) of trifluoromethanesulfonic acid was placed in a 50-ml flask equipped with a mechanical stirrer, N_2 inlet tube, and dropping funnel. To this stirred liquid was added dropwise 1.26 g (20 mmol) of anhydrous nitric acid. As the nitric acid was added a white, crystalline solid was continually formed. The resulting solid was allowed to stir for 1 hr to assure complete mixing and reaction. The product was shown to contain approximately the original weights of starting material by elemental analysis. It melted at 60-65° and sublimed at 60-70° (1-2 mm): ir (KCl pellet) 525 (m), 590 (m), 640 (s), 765 (m, very sharp), 830 (w), 850 (w), 880 (w), 1030 (w), 1150-1180 (vs), and 1230-1300 cm^- (s); Raman (crystalline) 321 (C-S), 351 (SO_3) 520 (CF_3), 580 (NO_2^+), 776 (CF_3), 1038 (SO_3), 1160, 1188 (SO_3), 1228 (CF_3), 1323, and 1409 cm^- (NO_2^+).

Anal. Calcd for $C_2H_3NO_9F_6S_2$: C, 6.61; H, 0.83; F, 31.39; N, 3.06; S, 17.66. Found: C, 6.59; H, 1.31; F, 34.9; N, 3.48; S, 16.44.

Method B.—Under an atmosphere of N_2, 6.00 g (40 mmol) of trifluoromethanesulfonic acid was dissolved in 100 ml of CH_2Cl_2 in a 200-ml flask equipped with a mechanical stirrer, N_2 inlet tube,

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[13] L. L. Ciaccio and R. A. Marcus, *J. Amer. Chem. Soc.*, **84**, 1838 (1962).

[14] G. B. Bachman, H. Feuer, B. R. Bluestein, and C. M. Vogt, *J. Amer. Chem. Soc.*, **77**, 6188 (1955).

[15] G. B. Bachman and J. L. Dever, *J. Amer. Chem. Soc.*, **80**, 5871 (1958).

[16] G. B. Bachman and C. M. Vogt, *J. Amer. Chem. Soc.*, **80**, 2987 (1958).

thermometer, and addition funnel. To this solution was added dropwise at 25° 1.26 g (20 mmol) of anhydrous nitric acid; no exotherm was noted. The solution was stirred for 15 min and then filtered under N_2 to collect a white, crystalline solid. Not all of the solid was collected, since some adhered to the sides of the flask. The solid, 6.67 g, was dried under vacuum over P_2O_5 and NaOH, mp 60-64°. The ir spectrum of this product was identical with that obtained from the product from method A.

Anal. Calcd for $C_2H_3NO_9F_6S_2$: C, 6.61; H, 0.83; N, 3.06. Found: C, 6.58; H, 1.21; N, 3.29.

Preparation of Mononitrotoluene.—A solution containing 6.00 g (40 mmol) of trifluoromethanesulfonic acid dissolved in 100 ml of CH_2Cl_2 was placed in a 200-ml flask equipped with a mechanical stirrer, addition funnel, and thermometer. A 1.26-g sample (20 mmol) of anhydrous HNO_3 was added to this solution, causing a white, crystalline solid to separate from solution. The temperature of the mixture was lowered to −60° by means of a Dry Ice–acetone bath, and 0.46 g (5 mmol) of toluene was added in one portion. The mixture was stirred at −60° for 1 hr and then quickly poured onto 100 g of crushed ice. The resulting mixture was extracted with three 100-ml portions of CH_2Cl_2. These were combined and dried ($MgSO_4$), and the solvent was removed under vacuum, leaving 0.69 g (100%) of mononitrotoluenes. A gc analysis of this product showed that it contained 62.12% *o*-nitrotoluene, 0.53% *m*-nitrotoluene, and 37.35% *p*-nitrotoluene; a trace (<0.1%) of dinitrotoluene was present.

Preparation of Dinitrotoluene. Method A.—A nitrating mixture consisting of 42.63 g (284 mmol) of CF_3SO_3H, 42.75 g of 96% H_2SO_4, and 7.91 g (126 mmol) of anhydrous HNO_3 was prepared in a 100-ml flask equipped with a mechanical stirrer, addition funnel, and thermometer. The solution was cooled to −24° and 2.02 g (22 mmol) of toluene was added dropwise in 50 min. As the toluene was added, a solid product was formed and the nitrating mixture became partially frozen. Stirring was continued for 1 hr at −24 to −20° and the reaction mixture was poured onto 1200 g of crushed ice. The resulting mixture was extracted with three 250-ml portions of CH_2Cl_2; there were combined and dried ($MgSO_4$) and the solvent was evaporated, leaving 3.83 g (97%) of a light yellow solid that was identified as a mixture of dinitrotoluene isomers by its ir spectrum and elemental analysis. Gc analysis showed that this product contained 12.20% 2,6-DNT, 0.45% 2,3- and 2,5-DNT, 86.31% 2,4-DNT, and 1.04% 3,4-DNT. Total meta-isomer content was 1.49%.

Anal. Calcd for $C_7H_6N_2O_4$: C, 46.16; H, 3.32; N, 15.38. Found: C, 46.12; H, 3.33; N, 15.25.

Method B.—A nitrating mixture consisting of 50.0 g (333 mmol) of CF_3SO_3H and 6.30 g (100 mmol) of anhydrous HNO_3 was prepared in a 100-ml, three-necked flask equipped with a mechanical stirrer, addition funnel, and thermometer. The mixture consisted of an insoluble complex of $2CF_3SO_3H/HNO_3$ in CF_3SO_3H. The mixture was cooled to 0° and 4.00 g (43 mmol) of toluene was added over a 10-min period. The reaction mixture was stirred at 0° for 1 hr and quenched on 500 g of crushed ice. The resulting mixture was extracted with three 100-ml portions of CH_2Cl_2, which were combined and dried ($MgSO_4$). Removal of solvent left 7.75 g (98%) of a light yellow solid that was identified as a mixture of dinitrotoluene isomers by ir spectrum. A gc analysis of this product showed that it contained 15.70% 2,6-DNT, 0.51% 2,3- and 2,5-DNT, 82.84% 2,4-DNT and 0.95% 3,4-DNT.

Method C.—A mixture containing 6.00 g (40 mmol) of trifluoromethanesulfonic acid and 100 ml of $CFCl_3$ was prepared in a 200-ml flask equipped with a mechanical stirrer, addition funnel, and thermometer. A 1.26-g sample (20 mmol) of anhydrous HNO_3 was added at 25°, forming the $2CF_3SO_3H/HNO_3$ complex. The temperature of the reaction was lowered to 0° and 0.46 g (5.0 mmol) of toluene was added in one portion. The mixture was stirred for 1 hr at 0° and poured onto 100 g of crushed ice. Three 100-ml CH_2Cl_2 extractions were combined and dried over $MgSO_4$. The solvent was removed, leaving 0.90 g (99%) of a light yellow solid that was identified as a mixture of dinitrotoluene isomers by its ir spectrum. A gc analysis of this product showed that it contained 16.47% 2,6-DNT, 0.45% 2,3- and 2,5-DNT, 82.36% 2,4-DNT, and 0.72% 3,4-DNT. Total meta-isomer content was 1.17%.

Method D.—A solution containing 6.00 g (40 mmol) of trifluoromethanesulfonic acid in 100 ml of CH_2Cl_2 was prepared in a 200-ml, three-necked flask equipped with a mechanical stirrer, addition funnel, and thermometer. The addition of 1.26 g (20 mmol) of anhydrous HNO_3 caused the precipitation of the white, crystalline $2CF_3SO_3H/HNO_3$ complex. The temperature of the mixture was lowered to −60° by means of a Dry Ice–acetone bath and 0.46 g (5.0 mmol) of toluene was added in one portion. After the mixture was stirred at −60° for 1 hr, the reaction temperature was raised to 0° over a 10-min period and the mixture was stirred at 0° for 1 hr. The reaction mixture was poured onto 100 g of crushed ice, and the organic products were extracted into CH_2Cl_2 (3 × 100 ml). The CH_2Cl_2 extracts were combined and dried ($MgSO_4$), and the solvent was removed, leaving 0.91 g (100%) of a light yellow solid that was identified as a mixture of dinitrotoluenes by its ir spectrum. A gc analysis of this product showed that it contained 17.18% 2,6-DNT, 0.28% 2,3- and 2,5-DNT, 82.07% 2,4-DNT, and 0.47% 3,4-DNT. Total meta-isomer content was 0.75%.

Relative Reaction Rates of Toluene and Benzene toward 3.—A nitrating mixture was prepared from 4.80 g (32 mmol) of CF_3SO_3H and 1.01 g (16 mmol) of anhydrous HNO_3 in 40 ml of CH_2Cl_2. The resulting slurry was kept at −65° and added in portions over a 10-min period to a solution of 1.84 g (20.0 mmol) of toluene and 1.56 g (20.0 mmol) of benzene in 10 ml of CH_2Cl_2. During the mixing of the reactants and for an additional 1 hr, a stirring rate of ~2000 rpm was maintained. The reaction mixture was poured onto 200 g of ice water, and the organic products were extracted with three 50-ml portions of CH_2Cl_2. The extracts were combined and dried ($MgSO_4$) and the products were analyzed by gc without removing the solvent. Gc analysis showed a nitrotoluene to nitrobenzene ratio of 1.94; no dinitro products were present. Based on our work with toluene and benzene described above, we assumed that all of the nitric acid was consumed. Therefore, the amount of toluene and benzene remaining would be 9.5 and 14.5 mmol, respectively. A relative rate factor using the equation $k_t/k_b = (\log t - \log t_0)/(\log b - \log b_0)$ was found to be 2.3 (t, t_0, b, and b_0 equal final and initial concentrations of toluene and benzene).

Nitration of Chlorobenzene—Chlorobenzene was nitrated according to method C The reaction was run at 25° for 2.5 hr using 6.30 g (42 mmol) of CF_3SO_3H, 1.32 g (21 mmol) of anhydrous HNO_3, and 2.25 g (20 mmol) of chlorobenzene in 63 ml of CH_2Cl_2; product weight was 3.21 g (100% based on HNO_3). Gc analysis showed 3% dinitrochlorobenzene. The *o*-, *m*-, and *p*-nitrochlorobenzene percentages were 30.5, 0.1, and 69.4%, respectively

Nitration of Nitrobenzene—Nitrobenzene was nitrated according to method C. The reaction was run at 25° for 5 hr using 6.0 g (40 mmol) of CF_3SO_3H, 1.26 g (20 mmol) of anhydrous HNO_3, and 0.98 g (8.0 mmol) of nitrobenzene in 60 ml of CH_2Cl_2. Product weight was 1.25 g (84.8%). Gc analysis showed 8.96, 88.75, and 2.29% of *o*-, *m*-, and *p*-dinitrobenzene, respectively.

Nitration of Benzotrifluoride—Benzotrifluoride was nitrated according to method C. The reaction was run at 25° for 16 hr; reaction times of 1–5 hr were not sufficient for complete nitration. The reaction was run using 6.00 g (40 mmol) of CF_3SO_3H, 1.26 g (20 mmol) of anhydrous HNO_3, and 0.73 g (5 mmol) of benzotrifluoride in 60 ml of CH_2Cl_2. Product weight was 0.98 g (theoretical weight of nitrobenzotrifluorides is 0.96 g). A gc analysis showed that the product contained 7.6, 92.3, and <0.1% of *o*-, *m*-, and *p*-nitrobenzotrifluoride, respectively.

Nitration of *m*-Xylene.—*m*-Xylene was nitrated according to method C. The reaction was run at 25° for 1 hr using 6.30 g (42 mmol) of CF_3SO_3H, 1.32 g (21 mmol) of anhydrous HNO_3, and 1.06 g (10 mmol) of *m*-xylene in 63 ml of CH_2Cl_2. The product weight was 1.98 g [the theoretical weight of dinitroxylene (DNX) is 1.96]. Gc analysis showed that the product contained 61.5% 2,6-DNX, 37.4% 2,4-DNX, and <0.5% each of 2,5- and 4,5-DNX and an unknown.

Registry No.—HNO_3, 7697-37-2; toluene, 108-88-3.