60706-00-5; **3b**, 60706-01-6; **3c**, 60706-02-7; **3d**, 60706-03-8; **3e**, 60706-04-9; **3f**, 60734-17-0; **3g**, 60706-05-0; **4**, 60706-06-1; 4,7-dichloroisatin, 18711-13-2; ethyl 2-bromopropionate, 535-11-5; 5-bromoisatin, 87-48-9; 5-methylisatin, 608-05-9; 5,7-dichloroisatin, 6374-92-1; 4-chloro-7-methoxyisatin, 60706-07-2; DMAD, 23055-10-9; ethyl propiolate, 105-37-3.

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Ion Radicals. 37. Preparation and Isolation of Cation Radical Tetrafluoroborates by the Use of Nitrosonium Tetrafluoroborate[1,2]

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During the last several years we have reported the preparation of a number of heteroaromatic and aromatic cation radical perchlorates. Methods of oxidation of the organic substrates have varied, e.g., by using $I_2/AgClO_4$, perchloric acid itself, and anodic oxidation in the presence of a perchlorate salt electrolyte. In the case of phenothiazine and 10-methylphenothiazine we have also used disproportionation of the parent heterocycle and its 5-oxide in perchloric acid solution.[3] The preparation of perchlorate salts has been useful not only because of the relative ease of isolating them, but also because the perchlorate ion is an innocuous nucleophile, a desirable feature for our interest in mapping out the reactions of these cation radicals with nucleophilic agents. A hazard that is always present with the cation radical perchlorates (and some of the perchlorate salt products of reaction) is their potential explosiveness,[4] so that their use has always been limited to small amounts. The isolation of solid salts other than perchlorates is attractive, but we have not until now been successful in easily preparing usable ones. Cation radical hexachloroantimonates are very easily obtained,[5] but, in our admittedly limited use of them, they have been troublesome both in interference by chloride ion in nucleophilic reactions and inclusion of antimony in products of reaction.[6] Tetrafluoroborates appear to be attractive alternates to perchlorates. Thianthrene cation radical tetrafluoroborate was prepared by Rundel and Scheffler from the disproportionation reaction in fluoroboric acid,[7] but this preparation requires the use of dry $HF{\cdot}BF_3$. Oxidation by $I_2/AgBF_4$ is suitable in principle, but we have not had encouraging success with this method ourselves.

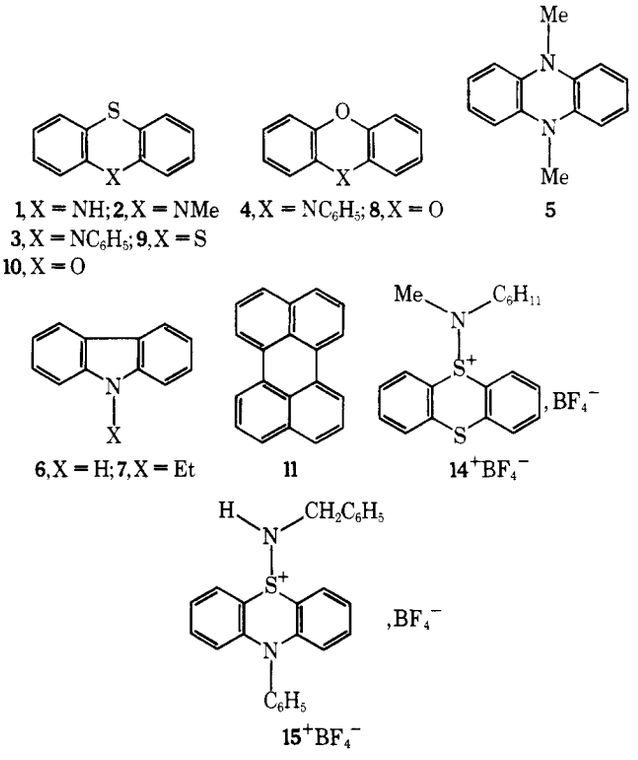
We have found recently that commercially available nitrosonium tetrafluoroborate ($NOBF_4$)[8] is very useful in cleanly oxidizing a number of aromatics and heteroaromatics to the cation radicals (eq 1), and we have isolated a number of crystalline tetrafluoroborates of high purity. Our practice is to carry out the oxidation in, e.g., acetonitrile solution after purging with N_2 and keeping a stream of N_2 bubbling through the solution to carry out the NO that is formed. Unless this is done, complications can arise from the formation of, and subsequent reactions with, NO_2.

$$Ar + NO^+BF_4^- \rightarrow Ar^+{\cdot}BF_4^- + NO \qquad (1)$$

Nitrosonium salts have been used recently by others. Connelly and co-workers, for example, have pointed out that among the several reactions that are known to occur between $NOPF_6$ and transition-metal complexes are nitrosation and one-electron oxidation.[9] Musker and Wolford have used $NOBF_4$ in making solutions of the cation radical tetrafluoroborates of 1,5-dithiacyclooctane and thianthrene; the salts were not isolated.[10] In our own work, use of $NOBF_4$ has given the solid tetrafluoroborates of phenothiazine (**1**), 10-methylphenothiazine (**2**), 10-phenylphenothiazine (**3**), 10-phenylphenoxazine (**4**), and 5,10-dimethyl-5,10-dihydrophenazine (**5**). The yields varied from 45% (**2**) to 69% (**3** and **5**), while the cation-radical content determined iodimetrically (except with **5**) was 95–99%. No attempts were made to optimize yields. Carbazole (**6**) and *N*-ethylcarbazole (**7**) gave the cation radicals of their dimers, namely 3,3′-dicarbazolyl- and 9,9′-diethyl-3,3′-dicarbazolyl tetrafluoroborates, in 97–98% yield. In contrast, the latter's perchlorate was obtained in 48% yield in solution with $I_2/AgClO_4$.[11] Oxidation of **5** was controlled by the use of less than the stoichiometrically required amount of $NOBF_4$ (i.e., 0.85 equiv), because **5** is easily oxidized also to the dication. Since $5^+{\cdot}$ is not reduced by iodide, the purity of $5^+{\cdot}BF_4^-$ was not assayed; the cation radical was identified by its visible spectrum. Use of an appropriate amount of $NOBF_4$ gave $5^{2+}{\cdot}2BF_4^-$.

Several compounds were easily oxidized to their cation radicals but we could not isolate the solid tetrafluoroborates

Chart of Compounds



without serious loss in purity. Thus, dibenzodioxin (**8**), thianthrene (**9**), phenoxathiin (**10**), and perylene (**11**) gave clean solutions of their cation radicals. Attempts to remove the solvent from $8^{+}\cdot BF_4^-$ and $9^{+}\cdot BF_4^-$, or to precipitate the latter, gave products with poor cation-radical content. We believe that the use of the solutions themselves should be suitable, though, for carrying out cation-radical reactions and have shown that this is so with $9^{+}\cdot BF_4^-$ solution. An example of the use of an isolated cation radical tetrafluoroborate ($3^{+}\cdot BF_4^-$ reacting with benzylamine) is also given.

It may be pertinent to comment briefly at this stage on the competition between one-electron oxidation and nitrosation. One might have anticipated that the electron-rich aromatics which we have used would undergo electrophilic nitrosation rather than one-electron oxidation. In particular, carbazole is easily N-nitrosated with nitrous acid; and, indeed, in aqueous acetonitrile carbazole and $NOBF_4$ gave *N*-nitrosocarbazole (32% yield). Nitrosation appears to occur here through the agency of $H_2{}^+ONO$. One might also wonder if there are connections between nitrosation and one-electron oxidation reactions. For example, where nitrosation does occur with NO^+ is it possible that it is preceded by electron exchange, that is, that a cation radical and NO are formed in close proximity and then unite? This type of question is not new in electrophilic substitutions, and recently proposals for its validity in the alkylation and other reactions of alkyl-substituted phenols have been made.[12] Whether or not nitrosations via this route may be validated too will become a matter of interest. In this connection, too, we note the recent reports that the reaction between nitrous acid and urea in aqueous perchloric acid leads rapidly to the formation of the *S*-nitrosourea cation $[(NH_2)_2CSNO]^+$ (**12**), and this is followed by the slow formation of NO and $[(NH_2)_2CSSC(NH_2)_2]^{2+}$ (**13**), i.e., what is, in principle, the dimer of the urea cation radical.[13] A similar behavior was observed with *N,N'*-tetramethylurea. Precisely how **13** is formed from **12** appears not to be known, but the possibility that the urea cation radical may be involved is intriguing.

Experimental Section

Oxidations with $NOBF_4$. The general procedure is illustrated with **phenothiazine** (**1**). Nitrogen was bubbled vigorously into a solution of 466 mg (2.34 mmol) of **1** in 15 ml of dry CH_3CN for 30 min. To this was added next, dropwise, a solution of 279 mg (2.38 mmol) of $NOBF_4$ in 20 ml of CH_3CN. After addition, N_2 bubbling was continued for 15 min, and the solution was poured into 500 ml of ether. The precipitated $1^{+}\cdot BF_4^-$ was filtered, washed with ether, and dried under vacuum to give 370 mg (1.29 mmol, 55%). Iodimetric assay showed the product to have 98.2% of $1^{+}\cdot$.

From 426 mg (2.00 mmol) of **10-methylphenothiazine** (**2**) in 20 ml of CH_3CN and 234 mg (2.00 mmol) of $NOBF_4$ in 20 ml of CH_3CN was obtained 270 mg (0.90 mmol, 45%) of $2^{+}\cdot BF_4^-$, 99.6% assay. From 450 mg (1.63 mmol) of **10-phenylphenothiazine** (**3**) and 190 mg (1.62 mmol) of $NOBF_4$ was obtained 405 mg (1.12 mmol, 68.7%) of $3^{+}\cdot BF_4^-$, 99.9% assay. From 225 mg (0.868 mmol) of **10-phenylphenoxazine** (**4**) in 10 ml of CH_2Cl_2 and 112 mg (0.96 mmol) of $NOBF_4$ in 8 ml of CH_2Cl_2 was obtained by pouring into 100 ml of dry petroleum ether, bp 30–60 °C, 180 mg (0.52 mmol, 60%) of $4^{+}\cdot BF_4^-$, 97% assay. From 420 mg (2.0 mmol) of **5,10-dimethyl-5,10-dihydrophenazine** (**5**) in 40 ml of dry CH_3CN and 198 mg (1.69 mmol) of $NOBF_4$ in 20 ml of CH_3CN was obtained 410 mg (1.38 mmol, 69%) of $5^{+}\cdot BF_4^-$, λ_{max} (CH_3CN) and 10^{-3} ϵ 446 nm, 7.0; 454 nm, 7.0; 601 nm, 1.25; 649 nm, 1.82; and 719 nm, 1.63. From 504 mg (3.02 mmol) of **carbazole** (**6**) in 40 ml of CH_3CN and 576 mg (4.92 mmol) of $NOBF_4$ in 20 ml of CH_3CN was obtained 542 mg (1.29 mmol, 86%) of **3,3'-dicarbazolyl cation radical tetrafluoroborate,** assay 97.3%, mass spectrum parent peak 332.1 (calcd for the cation radical, $6^{+}\cdot$, 332.1). From 1.04 g (5.33 mmol) of ***N*-ethylcarbazole** (**7**) in 30 ml of CH_3CN and 1.0 g (8.54 mmol) of $NOBF_4$ in 30 ml of CH_3CN was obtained by pouring into 600 ml of dry ether 1.24 g (2.6 mmol, 98%) of **9,9'-diethyl-3,3'-dicarbazolyl cation radical tetrafluoroborate,** 94.5% assay.

Preparation of $5^{2+}\cdot 2BF_4^-$. From a solution of 420 mg (2.0 mmol) of **5** in 30 ml of dry CH_3CN and 579 mg (4.95 mmol) of $NOBF_4$ in 40 ml of CH_3CN was obtained by pouring into 500 ml of dry ether 625 mg (1.63 mmol, 81.5%) of $5^{2+}v12BF_4^-$. Iodimetric assay constituted reduction to $5^{+}\cdot$ and showed 84% content of 5^{2+}.

Preparation of *N*-Nitrosocarbazole. To a solution of 2.0 g (17.1 mmol) of $NOBF_4$ in 19 ml of CH_3CN, containing 1 ml of water, was added a solution of 500 mg (3.00 mmol) of carbazole. After 2 h of stirring the solution was concentrated and poured into 300 ml of water. Following extraction with 3 × 75 ml of CH_2Cl_2, concentration, and preparative scale TLC of the CH_2Cl_2 solution, with petroleum ether (bp 30–60 °C) as developer, there was obtained 185 mg (0.944 mmol, 31.4%) of *N*-nitrosocarbazole, mp 79–80.5 °C (from petroleum ether), lit. mp 82 °C.[14] Five other bands were removed from the TLC plates, giving 283 mg of products which were not investigated further.

Reaction of Thianthrene$^{+}\cdot BF_4^-$ with Cyclohexylmethylamine. To a solution of 927 mg (7.92 mmol) of $NOBF_4$ in 30 ml of dry CH_3CN was added a solution of 1.9 g (8.79 mmol) of thianthrene, while N_2 was bubbled vigorously continuously. After 1 h of standing the purple solution was added to a stirred solution of 3 ml (~23.0 mmol) of cyclohexylmethylamine in 10 ml of CH_3CN. Reaction was immediate. The solution was concentrated, poured into 300 ml of water, and extracted with CH_2Cl_2, and the dried, concentrated CH_2Cl_2 solution was chromatographed on a column of silica gel (Merck, 30–70 mesh). Benzene elution gave 1.07 g (4.95 mmol, 56% conversion) of thianthrene; ether elution gave 234 mg (1.01 mmol, 11%) of thianthrene 5-oxide; acetone elution gave 540 mg (1.31 mmol, 15%) of 5-(cyclohexylmethylamino)thianthrenium tetrafluoroborate ($14^+BF_4^-$), mp 183–184.5 °C (from CH_2Cl_2–ether).

Conversion of $14^+BF_4^-$ into $14^+ClO_4^-$. A solution of 340 mg (0.82 mmol) of $14^+BF_4^-$ and 2.0 g (18.8 mmol) of $LiClO_4$ in 75 ml of CH_3CN was stirred overnight, concentrated, and poured into 300 ml of water. Extraction with CH_2Cl_2 gave 272 mg (0.64 mmol, 78%) of $14^+ClO_4^-$, mp 170–172 °C (from CH_2Cl_2–ether). Authentic $14^+ClO_4^-$ prepared by the reaction of $9\cdot{}^+ClO_4^-$ with cyclohexylmethylamine had mp 170–172 °C.

Reaction of $3^{+}\cdot BF_4^-$ with Benzylamine. Benzylamine was added dropwise to a solution of 2.0 g (5.52 mmol) of $3^{+}\cdot BF_4^-$ in 30 ml of dry CH_3CN until reaction was complete (disappearance of $3^{+}\cdot$ color). After stirring for 10 min the solution was poured into 400 ml of water. Extraction with 5 × 75 ml of petroleum ether (bp 30–60 °C) gave 778 mg (2.83 mmol, 102% yield) of **3.** Extraction with 3 × 75 ml of CH_2Cl_2 gave 610 mg (1.30 mmol, 47%) of 5-(benzylimino)-5,5-dihydro-10-phenylphenothiazine tetrafluoroborate ($15^+BF_4^-$), mp 166–168 °C (from CH_2Cl_2–ether).

Reaction of 5-Benzylimino-5,5-dihydro-10-phenylphenothiazine with Methyl Iodide. A solution of 345 mg (0.737 mmol) of $15^+BF_4^-$ in 20 ml of ethanol was made alkaline with a few drops of 50% aqueous NaOH. The solution was concentrated at room temperature and water was added. The precipitated solid [5-(benzylimino)-5,5-dihydro-10-phenylphenothiazine] was extracted with ether and to this were added several milliliters of methyl iodide. The solution was evaporated after 1 h and the residue was crystallized from CH_2Cl_2–ether, giving 334 mg (0.692 mmol, 94%) of (5-benzylmethylimino)-5,5-dihydro-10-phenylphenothiazine iodide (**16**), mp 149–150 °C, lit. mp 149–150 °C.[3a]

Elemental Analyses. Although iodimetric titrations were in agreement with the anticipated structures of the solid cation radical fluoroborates, two were selected as representative for elemental analysis.

Anal. Calcd for $C_{13}H_{11}NSBF_4$($2^{+}\cdot BF_4^-$): C, 52.0; H, 3.70; F, 25.3. Found: C, 52.7; H, 3.78; F, 24.9.

Anal. Calcd for $C_{18}H_{13}NSBF_4$($3^{+}\cdot BF_4^-$): C, 59.7; H, 3.62; N, 3.87; S, 8.84; F, 21.0. Found: C, 60.0; H, 4.31; N, 3.77; S, 8.59; F, 20.8.

It was found that if the solid fluoroborates were heated (boiling benzene) under vacuum or pumped under vacuum for long periods for preanalysis drying they tended to lose BF_3. Analyses were carried out, therefore, on solids which were dried under vacuum for a short time only.

Registry No.—**1,** 92-84-2; $1^{+}\cdot BF_4^-$, 60896-29-9; **2,** 1207-72-3; $2^{+}\cdot BF_4^-$, 54014-68-5; **3,** 7152-42-3; $3^{+}\cdot BF_4^-$, 60896-30-2; **4,** 37832-25-0; $4^{+}\cdot BF_4^-$, 60896-31-3; **5,** 15546-75-5; $5^{+}\cdot BF_4^-$, 60896-32-4; $5^{2+}\cdot 2BF_4^-$, 60896-33-5; **6,** 86-74-8; **7,** 86-28-2; **9,** 92-85-3; $9^{+}\cdot BF_4^-$, 60896-34-6; $9^{+}\cdot ClO_4^-$, 35787-71-4; $14^+BF_4^-$, 60896-36-8; $14^+ClO_4^-$, 60896-37-9; $15^+BF_4^-$, 60920-64-1; **16,** 55223-15-9; $NOBF_4$, 14635-75-7; 3,3'-dicarbazolyl$^{+}\cdot BF_4^-$, 60896-39-1; 9,9'-diethyl-3,3'-dicarbazolyl$^{+}\cdot BF_4^-$, 60920-63-0; *N*-nitrosocarbazole, 2788-23-0; cyclohexylmethylamine, 100-60-7; benzylamine, 100-46-9.

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Fluorotrinitromethane as an Alkaline Nitrating Agent. Preparation of α,2,4,6-Tetranitrotoluene from 2,4,6-Trinitrotoluene

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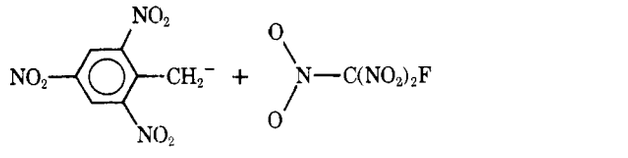
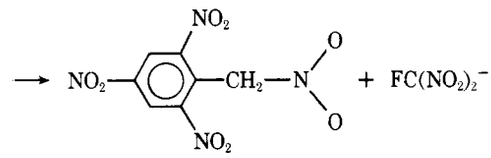
Although alternative synthetic methods for α,2,4,6-tetranitrotoluene (**1**) have been reported,[2,3] they are relatively cumbersome. We have therefore investigated the possibility that alkaline nitration of 2,4,6-trinitrotoluene (**2**) might offer a more convenient route to **1**. In contrast with more usual alkaline nitrating agents (alkyl nitrates, tetranitromethane), which did not give the desired tetranitrotoluene, we found that **1** can be prepared in excellent yield by the reaction of **2** with fluorotrinitromethane in alkaline THF–methanol.



3



1

Alkaline nitration of **2** with fluorotrinitromethane apparently proceeds by nucleophilic attack of 2,4,6-trinitrobenzyl anion **3**[4] on a nitro nitrogen, resulting in displacement of fluorodinitromethide carbanion; the latter, however, was not isolated.[5] This is in marked contrast to the manner in which certain other nucleophiles ($OC_2H_5^-$, $OCH_2CF_3^-$, N_3^-, F^-) attack fluorotrinitromethane resulting in formal substitution on carbon, with displacement of one of the nitro groups.[6]

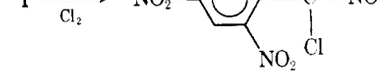
$$B^- + FC(NO_2)_3 \rightarrow FC(NO_2)_2B + NO_2^-$$

The fact that **3** attacks fluorotrinitromethane on nitrogen rather than carbon is probably due to the greater steric requirements of **3** over the other nucleophiles. The nitrogen atoms in fluorotrinitromethane are sterically more accessible than the carbon atom.

The reasons for failure with alkyl nitrates and tetranitromethane are not clear and cannot be rationalized on the basis of the relative stabilities of the leaving groups since fluorodinitromethide carbanion is very much less stable than trinitromethide carbanion.[6] Other factors to be considered are the relative rates of the competing reactions of tetranitromethane with **3** and the excess of hydroxide ion used to convert **2** to **3**. Another possibility is O-nitration as a competing reaction. However, by TLC analysis we detected no trinitrobenzyl alcohol, trinitrobenzyl nitrite, or trinitrobenzaldehyde, which would be likely products of O-nitration.

The pK_a of **1** in methanol–water (75:25) was found to be 5.93 (the midpoint in the titration with sodium hydroxide). The potassium salt of **1** can be formed from **1** and potassium hydroxide in tetrahydrofuran–methanol solution and precipitated by the addition of ether (Caution! The potassium salt is highly sensitive to impact and heat.) Addition of the deep red potassium salt to aqueous acid regenerates **1**.

Chlorination of **1** in the presence of sodium hydroxide yields α,α-dichloro-α,2,4,6-tetranitrotoluene (**4**).



4

Experimental Section[7]

General. (Caution!) The compounds described herein are explosives and should be handled with care. Fluorodinitro compounds show varying degrees of toxicity and may cause painful burns when brought into contact with the skin.

α,2,4,6-Tetranitrotoluene. A well-stirred solution of 11.5 g (0.05 mol) of 2,4,6-trinitrotoluene and 17 g (0.1 mol) of fluorotrinitromethane[8] in 150 ml of tetrahydrofuran and 75 ml of methanol was immersed in a dry ice–acetone bath. When the temperature of the solution reached 0 °C, an ice-cold solution of 9.6 g (0.15 mol) of potassium hydroxide (87%) in 50 ml of water and 75 ml of methanol was quickly added. The temperature immediately rose to about 5 °C and then began to fall. When the temperature of the deep red solution again reached 0 °C, the reaction was quenched by pouring the solution into 1500 ml of water containing 25 ml of concentrated hydrochloric acid. The total reaction time was approximately 1.5 min. The precipitated yellow solid was removed by filtration, washed well with water, and dried. The yellow solid (12.0 g, 89%) showed only one spot on a thin layer chromatogram (no starting TNT remained). Crystallization from benzene–hexane gave 10.0 g, mp 114–116 °C. An additional crystallization from methanol–water raised the melting point to 116.5–118 °C; NMR (CD_3COCD_3) δ 9.24 (s, 2, aromatic H), 6.30 (s, 2, CH_2); mass spectrum *m/e* 226 ($M^+ - NO_2$); mol wt calcd 272, found 270.

Anal. Calcd for $C_7H_4N_4O_8$: C, 30.89; H, 1.48; N, 20.58. Found: C, 30.76; H, 1.26; N, 20.45.

α,α-Dichloro-α,2,4,6-tetranitrotoluene. To a solution of 0.54 g (0.002 mol) of α,2,4,6-tetranitrotoluene in 15 ml of tetrahydrofuran and 5 ml of water was added 0.4 ml of 5 N sodium hydroxide. Chlorine gas was bubbled into the red solution until the solution was light yellow in color and then 50 ml of water containing 5 ml of concentrated hydrochloric acid was added. A yellow oil separated which solidified upon standing to give 0.65 g, mp 126–129 °C dec. Crystallization from methanol–water gave 0.5 g of pale yellow needles: mp 133–134 °C dec; NMR (CD_3COCD_3) δ 9.18 (s); mass spectrum *m/e* 294, 296, 298 ($M^+ - NO_2$, chlorine isotopes).

Anal. Calcd for $C_7H_2N_4O_8Cl_2$: C, 24.65; H, 0.59; N, 16.43; Cl, 20.79. Found: C, 24.45; H, 0.48; N, 16.25; Cl, 20.41.

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Registry No.—**1**, 35113-75-8; **2**, 118-96-7; **4**, 60789-52-8; fluorotrinitromethane, 1840-42-2.