timized interlocked geometries with X–C_α–C_β–C_γ = 0°, X-C_α-C_β-C_γ = 180° and 1.34 Å (C=CH_2), 1.28 Å (C=NH), 1.22 Å (C=O), 1.56 Å (C=S) bond distances.

Registry No. 1, 5857-68-1; 2, 29097-52-7; 3, 815-24-7; 4, 54396-69-9; 5, 56956-23-1.

Preparation of Solid Thianthrene Cation Radical Tetrafluoroborate

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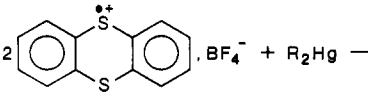
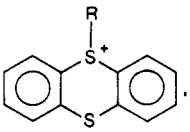
For some years we have used thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) for studying the reactions of $Th^{\bullet+}$ in solution. $Th^{\bullet+}ClO_4^-$ was chosen for use because it is easily prepared in the crystalline state and its counter ion is not nucleophilic. However, use of solid $Th^{\bullet+}ClO_4^-$ can be hazardous. A warning about its use was issued in 1969 after a sample exploded when being transferred from a filter funnel.[2] Because of this hazard, $Th^{\bullet+}ClO_4^-$ should be (and has been in all of our work) made in small quantities, handled carefully, and used soon after preparation. Because of the potential for explosion, we tried on a number of occasions to prepare other isolable salts. Hexachloro- and hexafluoroantimonates can be made by reaction of Th with antimony pentachloride or pentafluoride. However, we found the use of these salts to be troublesome because of the difficulties of removing antimony compounds from products and, in the case of $Th^{\bullet+}SbCl_6^-$, because of the presence of nucleophilic chloride ion in solution. The tetrafluoroborate ($Th^{\bullet+}BF_4^-$) was an obvious, attractive alternative. Some years ago, attempts were made to prepare solid cation radical tetrafluoroborates by reactions of Th and analogues with nitrosonium tetrafluoroborate ($NOBF_4$). Success was achieved with some cation radicals, for example, those of phenothiazine and 10-methyl- and 10-phenylphenothiazine. However, we were unable to prepare solid $Th^{\bullet+}BF_4^-$. We were able to prepare solutions of $Th^{\bullet+}BF_4^-$ and to use them successfully soon after preparation, but the solutions were not stable for storage during a day or two.[3] Therefore, use of $Th^{\bullet+}BF_4^-$ solutions was discontinued. $Th^{\bullet+}BF_4^-$ had, in fact, been prepared earlier by disproportionation of Th and its 5-oxide (ThO) in fluoboric acid, but the preparation required the use of dry $HF{\cdot}BF_3$.[4] We have now found that solid $Th^{\bullet+}BF_4^-$ can be prepared in good yield and quality by a simple control of the method of reaction between Th and $NOBF_4$. The brown, solid salt can be prepared in large quantities as compared with preparations of $Th^{\bullet+}ClO_4^-$. In order to validate the usefulness of the salt, we used it quantitatively in some reactions that in the past had given excellent results with $Th^{\bullet+}ClO_4^-$, namely, reaction with water, dimethylmercury, and diphenylmercury.[5] Reaction with water gave equal and quantiative yields (by GC) of Th and ThO (eq 1). Reaction with the mercurials gave the expected 5-thianthreniumyl tetrafluoroborates (eq 2) in good yields.

$$2Th^{\bullet+} + H_2O \longrightarrow Th + ThO + 2H^+ \quad (1)$$



$$2\,\cdot BF_4^- + R_2Hg \longrightarrow$$



$$\cdot BF_4^- + Th + RHgBF_4 \quad (2)$$

We found, again,[3] that when solutions of $Th^{\bullet+}BF_4^-$ in acetonitrile were made in situ by reaction of Th with $NOBF_4$, the concentration of $Th^{\bullet+}$ diminished with time, as judged visually by the color of the solution, lasting no more than a day or two. The reason for this instability is not known, but it may be because NO from reduction of NO^+ remained in solution and, after air oxidation to NO_2, led to decomposition of $Th^{\bullet+}$. On the other hand, solutions of $Th^{\bullet+}BF_4^-$ made by dissolving the solid salt in dry acetonitrile were stable for weeks.

Thus, $Th^{\bullet+}BF_4^-$ should serve as a useful, safe substitute for $Th^{\bullet+}ClO_4^-$.

Experimental Section

Preparation of Solid $Th^{\bullet+}BF_4^-$. Thianthrene (Th, 510 mg, 2.36 mmol) and nitrosonium tetrafluoroborate (Aldrich, 290 mg, 2.48 mmol) were placed side by side in a two-necked, round-bottom 250-mL flask. The flask was kept flushed with argon while 40 mL of dry acetonitrile was added. The mixture turned dark blue very quickly and was stirred under gently flowing argon for 1 h, after which 120 mL of dry ether was added gradually with continued stirring. The dark precipitate that formed was filtered, washed with dry ether, and finally dried under vacuum for 5 h, giving 528 mg (1.74 mmol, 75.5%) of $Th^{\bullet+}BF_4^-$.

The product was assayed twice by dissolving a sample in 10 mL of acetonitrile and 10 mL of carbon tetrachloride to which was added 1 g of sodium iodide. The liberated iodine was titrated with standard sodium thiosulfate. Assays were 100.5% and 98.6% of $Th^{\bullet+}$.

Preparation was repeated on the scale of 2 g of Th (1.07 g of $NOBF_4$, 80 mL of acetonitrile, 240 mL of ether) and 5 g of Th (2.7 g of $NOBF_4$, 150 mL of acetonitrile, 550 mL of ether), giving respectively 2.0 g (73%) and 5.4 g (77%) of product. Again, assays of $Th^{\bullet+}$ content were 96.7% and 96.3%, respectively. After 3 months of storage at room temperature, the assay was 85.4%.

The isolated $Th^{\bullet+}BF_4^-$ had mp 175–180 °C, and the dark melt decomposed very quickly. Anal. Calcd for $C_{12}H_8S_2BF_4$: C, 47.5; H, 2.64; S, 21.1. Found: C, 47.7; H, 2.58; S, 21.1.[6]

Reaction of $Th^{\bullet+}BF_4^-$ with Water. A sample of 303 mg (1.0 mmol) of $Th^{\bullet+}BF_4^-$ was dissolved in 10 mL of acetonitrile. To the solution was added 1.5 mL of water, which caused the rapid disappearance of the dark blue color of $Th^{\bullet+}$. The solution was evaporated to dryness, and the residue was treated with 10 mL of water and extracted with methylene chloride. Workup gave 217 mg (96.7%) of a mixture of Th and ThO. Analysis by GC showed quantitative yields of Th and ThO. Separation by preparative-scale TLC gave 99 mg (0.46 mmol, 92%) of Th, mp 154–155.5 °C, and 83 mg (0.36 mmol, 72%) of ThO, mp 139–140 °C.

Reaction of $Th^{\bullet+}BF_4^-$ with Dimethylmercury. Dimethylmercury was added dropwise from a syringe to a stirred solution of 612 mg (2.02 mmol) of $Th^{\bullet+}BF_4^-$ in 10 mL of acetonitrile until the color of $Th^{\bullet+}$ disappeared. A small amount of solid had formed. The solvent was removed by rotary evaporation at room temperature. To the residue was added 20 mL of water, and the mixture was extracted with 2 × 30 mL of methylene chloride. The dried ($MgSO_4$) solution was evaporated to 5 mL, to which was added 40 mL of dry ether. The precipitated salt was washed several times with dry ether and dried in air to give 244 mg (0.767 mmol, 76%) of product, mp 186–191 °C. The

(1) On leave from the Institute of Organic and Physical Chemistry, Technical University, Wroclaw, Poland.
(2) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.
(3) Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561.
(4) Rundel, W.; Scheffler, K. *Tetrahedron Lett.* **1963**, 993.
(5) Bandlish, B. K.; Porter, W. R.; Shine, H. J. *J. Phys. Chem.* **1978**, *82*, 1168.
(6) Analyses by Desert Analytics, Tucson, AZ.

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product was purified by reprecipitating from methylene chloride with ether, giving 5-methylthianthreniumyl tetrafluoroborate (eq 2, R = Me): mp 194–196 °C dec; ^{1}H NMR ($CDCl_3$–CD_3CN) δ 8.22 (d, 2 H, J = 7.6 Hz), 7.69–7.92 (m, 6 H), 3.25 (s, 3 H, CH_3). Anal. Calcd for $C_{13}H_{11}S_2BF_4$: C, 49.1; H, 3.46; S, 20.1. Found: C, 49.2; H, 3.46; S, 20.5.

Reaction of $Th^{\cdot+}BF_4^-$ with Diphenylmercury. Reaction was carried out by adding 10 mL of acetonitrile to a mixture of 610 mg (2.01 mmol) of $TH^{\cdot+}BF_4^-$ and 370 mg (1.05 mmol) of diphenylmercury. Workup as described for reaction with Me_2Hg gave 327 mg (0.86 mmol, 86%) of 5-phenylthianthreniumyl tetrafluoroborate (eq 2, R = Ph), mp 244–246 °C, after reprecipitation: ^{1}H NMR ($CDCl_3$–CD_3CN) δ 8.39 (d, 2 H), 7.90 (m, 6 H), 7.49 (m, 3 H), 7.09 (m, 2 H). Anal. Calcd for $C_{18}H_{13}S_2BF_4$: C, 56.8; H, 3.42; S, 16.8. Found: C, 56.8; H, 3.45; S, 17.7.

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Registry No. $Th^{\cdot+}BF_4^-$, 60896-34-6; $NOBF_4$, 14635-75-7; Th, 92-85-3; ThO, 2362-50-7; Me_2Hg, 593-74-8; Ph_2Hg, 587-85-9; 5-methylthianthreniumyl tetrafluoroborate, 32593-00-3; 5-phenylthianthreniumyl tetrafluoroborate, 32593-01-4.

Preparation of 2-Aryladamantanes and 3-Aryldiamantanes by Improved Ionic Hydrogenation of the Corresponding Tertiary Alcohols with Sodium Borohydride–Triflic Acid or Formic Acid–Triflic Acid[1]

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Introduction

In the expanding chemistry of hydrocarbon derivatives of adamantane and adamantane analogues, the preparation of tertiary derivatives is accomplished more readily than that of secondary derivatives.[2,3] The number of secondary substituted adamantanes is limited since their synthesis could formerly be achieved only by ring-closure reactions in low yield.[2] While preparative procedures for certain secondary derivatives of adamantane are available,[3] many have not yet been prepared.

Preparation of several tertiary alkyl and aryl derivatives (e.g., methyl, ethyl, benzyl) of adamantane has been reported by Schleyer et al. by a Grignard coupling method under rigorous conditions.[4] The method was also found to be useful in the preparation of other alkyl and aryl tertiary derivatives of adamantanes.[5] The Grignard and the organolithium coupling method were found to be ineffective for the preparation of alkyl and aryl secondary derivatives of adamantane and diamantane.[6]

Preparation of 2-phenyladamantane and isomeric 2-tolyladamantanes was reported in 50–70% yield by Wynberg et al. using dehydroadamantane (tetracyclo[3.3.1.1^{3,7}.0^{2,4}]decane) and $AlCl_3$ or BF_3·OEt_2 in benzene and toluene, respectively.[7] The method is involved since the synthesis of the precursor dehydroadamantane is a multistep process.[8] We now report an efficient method for the preparation of 2- and 3-aryl derivatives of adamantane and diamantane, respectively, using improved ionic hydrogenation of the corresponding tertiary alcohols.

Table I. Percent Yield of 2-Aryladamantanes and 3-Aryldiamantanes Obtained by $NaBH_4$ Reduction of Aryladamantanols (Diamantanols)

2-aryladamantanes and 3-aryldiamantanes	% yield (isolated) $NaBH_4$–CF_3COOH	% yield (isolated) $NaBH_4$–CF_3SO_3H	% yield (isolated) HCO_2H–CF_3SO_3H	mp, °C (bp)
1a	81	98	94	30–31
1b	72	95	94	57–58
1c	70	96	94	(120–121 [1.2 Torr])
1d	74	99	98	58–59
2a	80	97	94	73–74
2b	70	94	95	76–77
2c	77	98	95	56–57
2d	75	99	96	87–88

Results and Discussion

The reduction of different functional groups with sodium borohydride in carboxylic acids has been used over the years.[9] Thus, $NaBH_4$ in neat carboxylic acid media sequentially reduces and alkylates N-heterocycles to give the corresponding *N*-alkyl compounds.[10] The reagent combination was further used for the alkylation of amines,[10a,11] reduction of oximes,[12] nitrimine,[13] amide,[14] and nitrile.[15] Diaryl ketones and di- and triarylmethyl alcohols were found to give corresponding hydrocarbons in high yield with $NaBH_4$–CF_3COOH.[16,17] Under certain conditions, this reagent system was found to convert arenes to 1,1,1-trifluoro-2,2-diarylethanes in moderate yield.[18] In the case of arylalkylmethyl alcohols only partial reduction to hydrocarbons was observed. Thus, in the reduction of 2-phenyl-2-propanol with $NaBH_4$–CF_3COOH, only 45%

(1) Synthetic Methods and Reactions 134. For Part 133, see: Olah, G. A.; Wu, A.-h.; Farooq, O.; Prakash, G. K. S. *Synthesis*, in press.
(2) Fort, R. C.; Schleyer, P. v. R. *Chem. Rev.* **1964**, *64*, 277.
(3) Fort, R. C. In *Adamantane, the Chemistry of Diamond Molecules*; Marcell Dekker: New York, 1976.
(4) Osawa, E.; Majerski, Z.; Schleyer, P. v. R. *J. Org. Chem.* **1971**, *36*, 205.
(5) Farooq, O. Ph.D. Thesis, University of Southern California, Los Angeles, CA, Dec 1984.
(6) Olah, G. A.; Farooq, O., unpublished results.
(7) Udding, A. C.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1968**, 1345.
(8) Udding, A. C.; Strating, J.; Wynberg, H.; Schlatmann, J. L. M. A. *Chem. Commun.* **1966**, 657.
(9) (a) Marshall, J. A.; Johnson, W. S. *J. Org. Chem.* **1963**, *28*, 421. (b) Marshall, J. A.; Johnson, W. S. *J. Org. Chem.* **1963**, *28*, 595. (c) Klein, E.; Rojahn, W.; Henneberg, D. *Tetrahedron* **1964**, *20*, 2025. (d) Uzarewicz, I.; Uzarewicz, A. *Rocz. Chem.* **1975**, *49*, 1113. (e) Hach, V. *Synthesis* **1974**, 340. (f) Djerassi, C.; Monteiro, H. J.; Walser, A.; Durham, L. J. *J. Am. Chem. Soc.* **1966**, *88*, 1792. (g) Gribble, G. W. *Eastman Org. Chem. Bull.* **1979**, *51*(1).
(10) (a) Gribble, G. W.; Lord, P. D.; Skotnicki, J.; Dietz, S. E.; Eaton, J. T.; Johnson, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7812. (b) Kucherova, N. F.; Novikova, N. N.; Sharkova, N. M.; Silenko, I. D.; Zagorevskii, V. A. *Khim. Geterotsikl. Soedin.* **1977**, *No. 7*, 995. (c) For $NaBH_3CN$–CF_3CO_2H, see: Berger, J. G.; Davidson, F.; Langford, G. E. *J. Med. Chem.* **1977**, *20*, 600. (d) Gribble, G. W.; Hoffman, J. H. *Synthesis* **1977**, 859. (e) Gribble, G. W.; Heald, P. W. *Synthesis* **1975**, 650. (f) Gribble, G. W.; Lord, P. D., unpublished results. (g) Maki, Y.; Suzuki, M.; Ozeki, K. *Tetrahedron Lett.* **1976**, 1199.
(11) (a) Marchini, P.; Liso, G.; Reho, A.; Liberatore, F.; Moracci, F. M. *J. Org. Chem.* **1975**, *40*, 3453. (b) Miyake, A.; Kuriki, H.; Itoh, K.; Nishikawa, M.; Oka, Y. *Chem. Pharm. Bull.* **1977**, *25*, 3289. (c) Gribble, G. W.; Jasinski, J. M.; Pellicone, J. T.; Panetta, J. A. *Synthesis* **1978**, 766. (d) Gribble, G. W.; Leese, R. M., unpublished results.
(12) Gribble, G. W.; Leiby, R. W.; Sheehan, M. N. *Synthesis* **1977**, 856.
(13) Haire, M. J. *J. Org. Chem.* **1977**, *42*, 3446.
(14) Umino, N.; Iwakuma, T.; Itoh, N. *Tetrahedron Lett.* **1976**, 763.
(15) Umino, N.; Iwakuma, T.; Itoh, N. *Tetrahedron Lett.* **1976**, 2875.
(16) Gribble, G. W.; Leese, R. M.; Evans, B. E. *Synthesis* **1977**, 172.
(17) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* **1978**, 763.
(18) Gribble, G. W.; Nutaitis, C. F. *Synthesis* **1985**, 756.

0022-3263/88/1953-5143$01.50/0