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STUDIES IN THE TETRAARYLBORATES

PART III. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE AND SODIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

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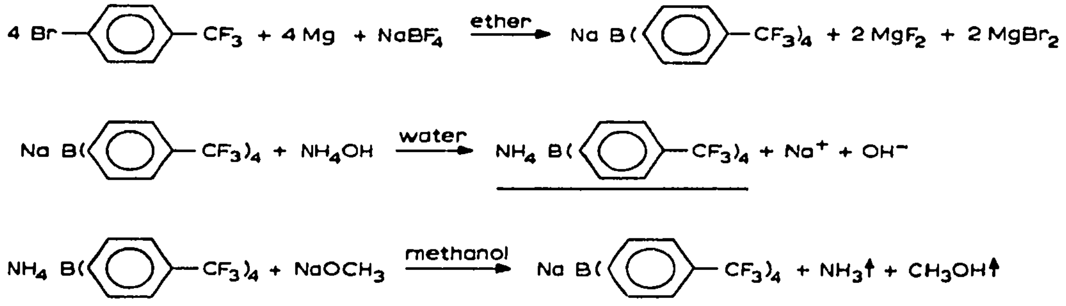
In a continuation of the study of substituent effects on reagent stability and selectivity, two new tetraaryl–boron compounds, sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate, have been prepared via a new experimental *in situ* procedure. Both compounds are more resistant to decomposition in acid media than sodium tetrakis(*p*-chlorophenyl) borate and sodium tetrakis(*p*-fluorophenyl) borate[1,2]. It is felt that electron density in the vicinity of the carbon to boron bonds has been adjusted so that susceptibility to electrophilic attack is reduced. This favorable property is derived from the inductive effect of the highly electronegative fluorine atom in the *m*-position and the strongly deactivating trifluoromethyl group in the *p*-position for the tetrakis(*m*-fluorophenyl) borate and tetrakis(*p*-trifluoromethylphenyl) borate anions, respectively.

EXPERIMENTAL

*Synthesis of sodium tetrakis(*p*-trifluoromethylphenyl) borate*

Sodium tetrakis(*p*-trifluoromethylphenyl) borate is synthesized by the following sequence of reactions:



Distill 400 ml of ether previously dried over sodium into a 500-ml 3-necked flask equipped with a stirrer, water-cooled condenser, thermometer and a dropping funnel. Transfer 100 ml of the freshly distilled ether to the dropping funnel, dissolve 45.0 g (0.2 mole) of *p*-bromobenzotrifluoride and arrange for dropwise addition to the flask. Add 4.9 g (0.2 mole) of dry magnesium turnings and 5.5 g (0.05 mole) of dry sodium fluoroborate to the 500-ml 3-necked reaction flask. Sweep the assembly with dry nitrogen. Add approximately 10 ml of the *p*-bromobenzotrifluoride solution to the flask while rapidly stirring the solution. The reaction generally starts within 20 min. When the reaction starts, immediately cool the reaction flask to 16° and maintain this temperature while the remaining 90 ml of solution is added dropwise over a 3-h period. After completing the addition, stir the reaction mixture for an additional 30 min while the temperature is allowed to rise to 25°.

Immediately pour the contents of the reaction flask onto 300 ml of crushed ice made slightly alkaline with dilute sodium hydroxide solution. Add *ca.* 1 g of sodium carbonate, and stir. A white precipitate of inorganic material forms in the aqueous layer. Separate the ether layer with a separatory funnel. Saturate the aqueous layer with sodium chloride and extract the aqueous phase 3 times with 50-ml portions of ether. Add these to the previously separated ether layer. Add 300 ml of slightly basic distilled water to the ether portion. Evaporate the ether while rapidly stirring the mixture and heating to 45°. Filter the ether-free aqueous solution through a "Celite" analytical filter aid mat and Buchner funnel arrangement. Transfer the filtrate to a 1-l beaker and dilute to 900 ml with distilled water. Heat the solution to 35° and slowly add dropwise a 2.5% ammonium hydroxide solution. Filter the ammonium tetrakis(*p*-trifluoromethylphenyl) borate and air-dry. Recrystallize the white ammonium salt twice from a methanol–water solution, filter and dry under vacuum over phosphorus pentoxide at 80°.

(Analysis: m.p. 185–6°; found, C 55.53%, H 3.50%, N 2.29%; calculated, C 55.25%, H 3.32%, N 2.30%.)

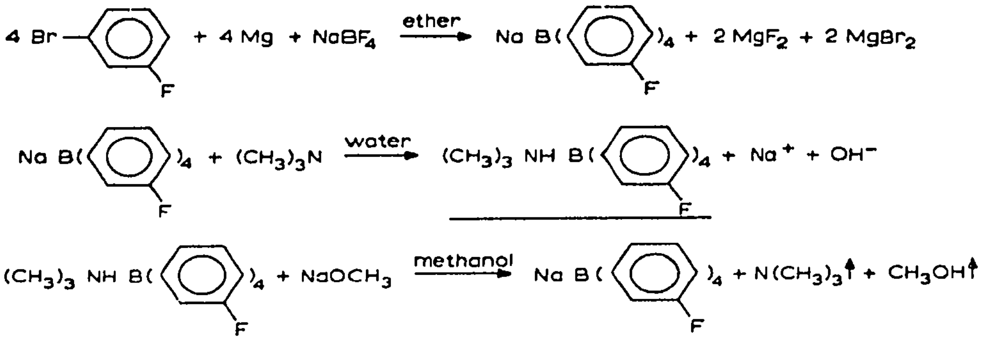
To prepare the pure sodium salt, dissolve 10 g (0.017 mole) of the ammonium salt in 150 ml of anhydrous methanol contained in a 250-ml 3-necked flask equipped with a stirrer, air-cooled condenser and a dropping funnel. Heat the solution to vigorous methanol reflux. Dissolve 1.8 g (0.033 mole) of sodium methylate in 75 ml of anhydrous methanol and add dropwise to the reaction flask. Ammonia gas escapes through the air condenser while the solution is vigorously refluxed for 4 h. Remove the air condenser and evaporate most of the methanol. Remove the remainder under vacuum at 70°. Dissolve the solid sodium salt in 100 ml of anhydrous ether and pass through a basic alumina adsorption column. The ether eluate, which amounts to about 400 ml, is removed using a rotary vacuum evaporator or air evaporation. Any remaining ether is removed under vacuum at 80°. The crystals of the white sodium salt start to appear when most of the ether has been removed. The salt crystallizes as the monohydrate, but the water of hydration can be removed by drying under vacuum and over phosphorus pentoxide at 80°. Yield 17.9 g.

(Analysis: found, C 53.06%, H 2.88%; calculated, C 53.19%, H 2.88%.)

*Synthesis of sodium tetrakis(*m*-fluorophenyl) borate*

Sodium tetrakis(*m*-fluorophenyl) borate is synthesized by the following sequence of reactions:

The procedure for the preparation of sodium tetrakis(*m*-fluorophenyl) borate



is similar to that described for the synthesis of sodium tetrakis(*p*-trifluoromethylphenyl) borate. The reaction assembly is identical. An ether solution of 35 g (0.2 mole) of *m*-fluorobromobenzene is added dropwise to a 500-ml 3-necked flask containing an ether mixture consisting of 4.9 g (0.2 mole) of dry magnesium turnings and 5.5 g (0.05 mole) of sodium fluoroborate. During the addition of the *m*-fluorobromobenzene solution, the temperature of the reaction flask is held at 30°. Extract the aqueous layer, as previously indicated, with ether. Evaporate the ether and dissolve the salt in 300 ml of water made slightly basic. Filter and precipitate the trimethylamine tetrakis(*m*-fluorophenyl) borate salt by dropwise addition of a 2.5% aqueous trimethylamine solution to the diluted tetrakis(*m*-fluorophenyl) borate anion solution. Filter the trimethylamine tetrakis(*m*-fluorophenyl) borate and dry under vacuum at 80°. Recrystallize the white amine salt twice from a methanol–water solution, filter and dry under vacuum and over phosphorus pentoxide at 80°. Yield 15.0 g.

(Analysis: m.p. 150–1°; found, C 71.78%, H 5.82%, N 3.12%; calculated, C 71.85%, H 5.82%, N 3.10%.)

To prepare the pure sodium salt, add dropwise a solution of 2.4 g (0.044 mole) of sodium methylate in 75 ml of anhydrous methanol to the previously described flask assembly containing 10 g (0.022 mole) of trimethylamine tetrakis(*m*-fluorophenyl) borate in 150 ml of anhydrous methanol at vigorous reflux. After addition of the sodium methylate solution, remove the air condenser to speed evaporation of the trimethylamine. Heat the reaction solution until there is no further liberation of trimethylamine. Remove the remaining methanol under vacuum at 70°. Dissolve the solid sodium salt in anhydrous ether and pass through a basic alumina adsorption column. The ether eluate is removed as before using a rotary vacuum evaporator or air evaporation. Any remaining ether or water is removed by drying under vacuum over phosphorus pentoxide at 80°. Yield 13.7 g.

(Analysis: found, C 69.43%, H 3.88%, F 18.00%; calculated, C 69.59%, H 3.90%, F 18.35%.)

*Reagent properties of the tetrakis(*p*-trifluoromethylphenyl) borate anion*

Qualitative testing was done with a 1% solution of the sodium salt. Approximately 1 ml of the reagent was added to 1 ml of a 0.1 *M* solution of the ion to be tested. The following ions gave heavy precipitates: potassium, ammonium, silver and thallium(I). However, the silver and thallium(I) ions appeared to be slightly reduced. The following ions tested gave slight precipitates: rubidium and cesium.

No precipitates were obtained with copper, nickel, cobalt, calcium, barium or magnesium.

The reagent was tested for its ability to precipitate compounds containing a basic nitrogen atom which had been protonated and quaternary ammonium compounds. These compounds were dissolved in distilled water and precipitated with a 1% solution of the reagent. A few of the precipitates were filtered, recrystallized, dried and analyzed for nitrogen, and melting points were taken on a melting point block. The results are summarized in Table I. Quinidine, cinchonine, quinine and 1-phenylethylamine also gave heavy precipitates.

TABLE I

SOME BASIC NITROGEN COMPOUNDS FORMING SALTS WITH TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE ANION

Material tested	*M.p. (°)*	*% Nitrogen*	
		Found	*Calc.*
Tetrabutylammonium iodide	145–6	1.70	1.68
N-Butylamine	107–9	2.38	2.10
Benzidine	188–191 (not sharp)	2.27 (di-substituted salt)	2.05
Ethylamine	121–3	2.17	2.20
N-Ethylaniline	113–4	1.94	1.96
β-Alanine	>300	2.20	2.06
Ammonium hydroxide	185–6	2.29	2.30

The reagent was tested for its ability to precipitate potassium ion by mixing 2 ml of a 0.03 *M* reagent solution with 2 ml of the test solution. For a comparison, sodium tetraphenylborate, sodium tetrakis(*p*-fluorophenyl) borate, sodium tetrakis-(*p*-chlorophenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate were used in a similar series of tests. The results are summarized in Table II.

*Sodium tetrakis(*p*-trifluoromethylphenyl) borate as a reagent for potassium*

The procedure described by GLOSS[3] in the determination of potassium with sodium tetraphenylborate was selected but slightly modified for the study of the precipitation of potassium with sodium tetrakis(*p*-trifluoromethylphenyl) borate.

TABLE II

COMPARATIVE SENSITIVITIES OF SOME TETRAARYLBORATES AS PRECIPITANTS FOR POTASSIUM

K taken (mg/ml)	$NaB(C_6H_5)_4$	$NaB(C_6H_4\text{p-}F)_4$	$NaB(C_6H_4\text{p-}Cl)_4$	$NaB(C_6H_4\text{m-}F)_4$	$NaB(C_6H_4\text{p-}CF_3)_4$
2.0	Heavy, immed.	None	Heavy, immed.	Heavy, immed.	Heavy, immed.
0.2	Heavy, immed.	None	Heavy, immed.	Slight, slow	Heavy, immed.
0.1	Medium, immed.	None	Medium, immed.	None	Heavy, immed.
0.05	Medium, immed.	None	Medium, slow	None	Heavy, immed.
0.02	Slight, immed.	None	Slight, slow	None	Medium, slow
0.01	Slight, immed.	—	Trace, slow	None	Medium, slow
0.005	Trace, slow	—	None	—	Slight, slow
0.002	None	—	None	—	Trace, slow

The preparation of the reagent for the quantitative study was performed as described by GLOSS, except that the aqueous reagent solution was filtered through a basic alumina adsorption column before use. A 2% solution of the reagent in water, pH 8, was used. The sample containing the potassium ion was adjusted to 50 ml and heated to 70°. The reagent which usually amounted to 30 ml was added dropwise from a buret. The sample was allowed to stand at room temperature for 1 h immersed in an ice bath for 1 h, transferred to a tared fine sintered-glass filter crucible and washed with three 5-ml portions of ice water. The crucible was dried at 110° for 1 h, cooled in a desiccator and weighed, and the recovery of potassium was calculated from the theoretical gravimetric factor 0.06203. The results are shown in Table III.

TABLE III

RECOVERY OF POTASSIUM FROM PURE POTASSIUM SOLUTIONS

K taken (mg)	*K found (mg)*	*% Recovery*	*K taken (mg)*	*K found (mg)*	*% Recovery*
20.38	20.30	99.6	4.98	4.80	96.4
20.38	20.28	99.5	4.98	4.87	97.8
12.46	12.29	98.6	4.98	4.92	98.8
12.46	12.31	98.8	4.98	4.91	98.6
12.46	12.49	100.2	4.98	4.89	98.2
12.46	12.40	99.5		$\sigma = \pm 0.05$	
12.46	12.34	99.0			
12.46	12.31	98.8			
	$\sigma = \pm 0.08$[a]				

[a] σ = standard deviation.

TABLE IV

SOLUBILITY OF POTASSIUM TETRAKIS(*p*-TRIFLUOROMETHYLPHENYL) BORATE

pH	*Temperature (°)*	*Time (h)*	*Solubility (g/l)*
3.3	25	68	0.163
6.3	25	68	0.168
10.2	25	68	0.176
7.0	0	48	0.145

The solubility of the pure potassium salt was determined at 25° and at 0°. At 25° the solubility is unaffected by pH in the range 3.3 to 10.2. The solubilities, which were computed from flame photometric data on the potassium ion in solution, were taken after 68 h (Table IV). Since this salt possesses good stability at various pH values, relatively long equilibration times were employed. Solubility values obtained immediately following precipitation were essentially the same as shown in Table IV.

*Reagent properties of the tetrakis(*m*-fluorophenyl) borate anion*

A 1% solution of the sodium salt was used for qualitative testing. About 2 ml of the reagent was added to 2 ml of a 0.1 *M* solution of the ion to be tested. Heavy precipitates were given with cesium, silver and thallium(I) ions. However, reduction seemed to be occurring in the silver and thallous solutions during the precipitation.

The rubidium ion gave a medium precipitate while potassium and ammonium ions gave slight precipitates. No precipitates were obtained with copper, nickel, cobalt, barium, calcium and magnesium.

Some quaternary ammonium compounds and other compounds containing a basic nitrogen atom were precipitated with the tetrakis(*m*-fluorophenyl) borate anion. The protonated nitrogen-compound was dissolved in water and precipitated with a 1% solution of the reagent. Some of the precipitates were filtered, recrystallized, dried and analyzed for nitrogen, and melting points were obtained on a melting point block. The results are shown in Table V. In addition, N-butylamine, benzidine, N-ethylaniline, quinidine and quinine gave heavy precipitates.

TABLE V

SOME BASIC NITROGEN COMPOUNDS FORMING SALTS WITH TETRAKIS(*m*-FLUOROPHENYL) BORATE ANION

Material tested	*M.p. (°)*	*% Nitrogen*	
		Found	*Calc.*
Trimethylamine	150–1	3.12	3.10
Tetrabutylammonium iodide	176–7	2.13	2.21
Brucine	141–2	3.64	3.55
Ethylamine	124–5	3.18	3.20
1-Phenylethylamine	122–3	2.86	2.73

A sensitivity test was performed on the reagent for its ability to precipitate cesium ion by mixing 2 ml of a 0.03 *M* reagent solution with 2 ml of the test solution. To make a comparison, a similar series of tests were done with sodium tetraphenylborate, sodium tetrakis(*p*-fluorophenyl) borate, sodium tetrakis(*p*-chlorophenyl) borate and sodium tetrakis(*p*-trifluoromethylphenyl) borate (Table VI).

*Sodium tetrakis(*m*-fluorophenyl) borate as a reagent for cesium*

The gravimetric studies on the sodium tetrakis(*m*-fluorophenyl) borate were performed by the procedure described above for sodium tetrakis(*p*-trifluoromethylphenyl) borate. The recovery of cesium was calculated from the theoretical gravimetric factor 0.2536 (Table VII).

TABLE VI

COMPARATIVE SENSITIVITIES OF SOME TETRAARYLBORATES AS PRECIPITANTS FOR CESIUM

Cs taken (mg/ml)	$NaB(C_6H_5)_4$	$NaB(C_6H_4p\text{-}F)_4$	$NaB(C_6H_4p\text{-}Cl)_4$	$NaB(C_6H_4m\text{-}F)_4$	$NaB(C_6H_4p\text{-}CF_3)_4$
2.0	Heavy, immed.	Heavy, immed.	Heavy, immed.	Heavy, immed.	Medium, immed.
0.2	Heavy, immed.	Medium, immed.	Heavy, immed.	Heavy, immed.	Slight, immed.
0.1	—	Slight, slow	—	Heavy, immed.	Trace, immed.
0.05	—	Trace, slow	—	Medium, immed.	Trace, immed.
0.02	Light, immed.	None	Slight, immed.	Slight, immed.	Trace, immed.
0.01	Slight, immed.	None	Slight, immed.	Trace, immed.	None
0.005	Trace, immed.	None	Slight, immed.	Trace, immed.	None
0.002	None	None	None	None	None

The solubility of the pure cesium salt was determined at 25° and 0°. At 25° the solubility is essentially unaffected by pH in the range 3.5 to 10.0. The solubilities were calculated from flame photometric data and are listed in Table VIII.

Additional solubility values were determined for potassium tetrakis(*m*-fluorophenyl) borate and rubidium tetrakis(*m*-fluorophenyl) borate salts (Table IX).

TABLE VII

RECOVERY OF CESIUM FROM PURE CESIUM SOLUTIONS

Cs taken (mg)	*Cs found (mg)*	*% Recovery*	*Cs taken (mg)*	*Cs found (mg)*	*% Recovery*
70.52	70.50	100.0	23.51	23.48	99.9
70.52	69.79	99.0	23.51	23.38	99.4
			23.51	23.28	99.0
47.02	46.99	99.9		$\sigma = \pm 0.09$	
47.02	46.94	99.8			
47.02	46.92	99.8	9.40	9.26	98.5
47.02	46.97	99.9	9.40	9.23	98.2
47.02	46.99	99.9	9.40	9.36	99.6
	$\sigma = \pm 0.03$		9.40	9.33	99.3
			9.40	9.43	100.3
23.51	23.33	99.2	9.40	9.46	100.6
23.51	23.26	98.9		$\sigma = \pm 0.09$	
23.51	23.46	99.8			

TABLE VIII

SOLUBILITY OF CESIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

pH	*Temperature (°)*	*Time (h)*	*Solubility (g/l)*
3.5	25	68	0.057
6.5	25	68	0.061
10.0	25	68	0.079
7.0	0	48	0.047

TABLE IX

SOLUBILITY VALUES OF POTASSIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE AND RUBIDIUM TETRAKIS(*m*-FLUOROPHENYL) BORATE

Salt	*pH*	*Temperature (°)*	*Time (h)*	*Solubility (g/l)*
$RbB(C_6H_4m\text{-}F)_4$	6.4	25	68	0.169
$KB(C_6H_4m\text{-}F)_4$	3.5	25	68	0.540
	6.7	25	42	0.607
	10.4	25	42	0.660

DISCUSSION

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate have been synthesized by a new *in situ* procedure. Ammonium ion and trimethylamine have been used in purification steps of these salts by forming precipitates with the tetrakis(*p*-trifluoromethylphenyl) borate and tetrakis(*m*-

fluorophenyl) borate anions, respectively. Extension of this procedure should be possible by employing amines selective for certain tetraarylborate compounds.

The data in Tables III and VII indicate that potassium and cesium can be gravimetrically determined with tetrakis(*p*-trifluoromethylphenyl) borate and tetrakis(*m*-fluorophenyl) borate anions, respectively. Neither anion is a specific reagent for the above cations. Both precipitates separate as white crystalline compounds with desirable analytical properties. They are easily filterable and attain constant weight rapidly at 110°. A prolonged heating of 16 h caused no further weight loss or sign of decomposition with either salt.

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate should be excellent reagents for use in quantitative analysis where interference from coprecipitation is absent. Aqueous solutions of these soluble salts are stable and very active at pH 8 when tested over a 6-month period.

In addition, these tetraarylborate anions form insoluble salts with various protonated amine, alkaloid and amino acid compounds. This should allow qualitative or quantitative analyses to be performed with these salts.

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SUMMARY

Sodium tetrakis(*p*-trifluoromethylphenyl) borate and sodium tetrakis(*m*-fluorophenyl) borate were synthesized by a new *in situ* method. Both salts formed precipitates with potassium, rubidium and cesium ions, quaternary ammonium and protonated basic nitrogen compounds. Potassium tetrakis(*p*-trifluoromethylphenyl) borate was more insoluble than potassium tetraphenylborate while cesium tetrakis-(*m*-fluorophenyl) borate was less soluble than cesium tetrakis(*p*-fluorophenyl) borate. The salts formed with nitrogen-containing compounds offer possibilities for qualitative and quantitative analyses.

RÉSUMÉ

On décrit un nouveau procédé pour la synthèse de tétrakis(*p*-trifluométhylphényl)borate de sodium et de tétrakis(*m*-fluophényl)borate de sodium. Ces deux sels donnent des précipités avec les ions potassium, rubidium et césium, l'ammonium quaternaire, et les composés azotés protoniques basiques. Le tétrakis(*p*-trifluométhylphényl)borate de potassium est moins soluble que le tétraphénylborate de potassium, tandis que tétrakis(*m*-fluophényl)borate de césium est moins soluble que le tétrakis-(*p*-fluophényl)borate de césium. Les sels formés avec des composés azotés permettent des analyses qualitatives et quantitatives.

ZUSAMMENFASSUNG

Natriumtetrakis(*p*-trifluoromethylphenyl)borat und Natriumtetrakis(*m*-

fluorophenyl)borat wurden mit einer neuen *in situ*-Methode synthetisiert. Beide Salze bilden Niederschläge mit Kalium-, Rubidium- und Cäsium-Ionen, quaternären Ammonium- und protonisierten basischen Stickstoffverbindungen. Kaliumtetrakis-(*p*-trifluoromethylphenyl)borat war unlöslicher als Kaliumtetraphenylborat, während Cäsiumtetrakis(*m*-fluorophenyl)borat weniger löslich als Cäsiumtetrakis-(*p*-fluorophenyl)borat war. Die Salze, welche mit stickstoffhaltigen Verbindungen gebildet werden, bieten Möglichkeiten für die qualitative und quantitative Analyse.

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