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STUDIES IN THE TETRAARYLBORATES

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

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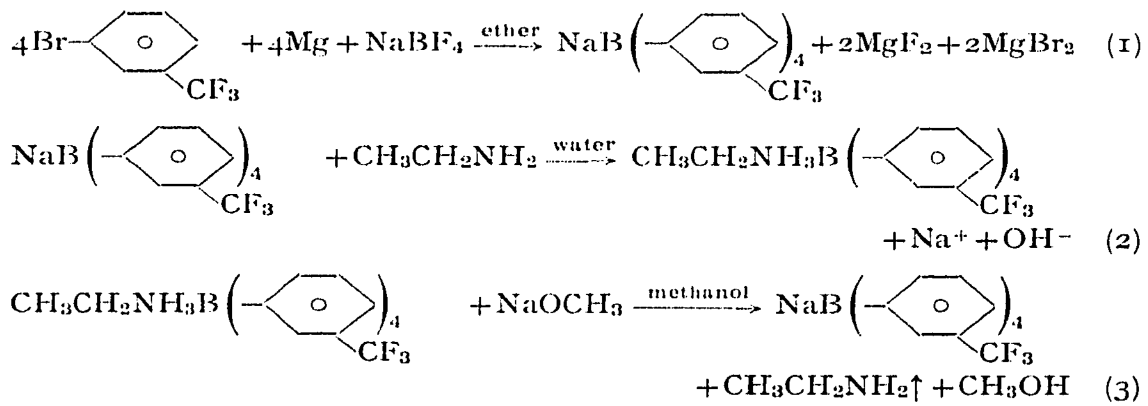
In a continuation of the study of substituent effects on reagent stability and selectivity, sodium tetrakis(*m*-trifluoromethylphenyl)borate has been synthesized. This compound selectively precipitates cesium in the presence of rubidium or potassium, and is comparable in acid stability to the other tetraarylborates which have strongly electronegative substituents in *para* or *meta* positions on the phenyl rings[1-3].

EXPERIMENTAL

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

The following sequence of reactions was employed in the preparation of sodium tetrakis(*m*-trifluoromethylphenyl)borate:



Distil *ca.* 400 ml of ether dried over sodium into a 3-necked 500-ml flask fitted with a reflux condenser, dropping funnel and magnetic stirrer. Transfer a 100-ml portion of the ether to the dropping funnel, and to this add 45.0 g (0.2 mole) of *m*-bromobenzotrifluoride. Then place 4.9 g (0.2 mole) of dry magnesium turnings in the flask, add a few crystals of iodine to catalyze the Grignard reaction, and start the stirrer. Add *ca.* 10 ml of the solution in the dropping funnel to the flask, and sweep the entire apparatus with dry nitrogen. Raise the temperature to 35° and hold until the reaction begins. Then add 5.5 g (0.05 mole) of finely-ground and dried sodium fluoroborate, cool to 14°, and add the *m*-bromobenzotrifluoride in ether solution dropwise over a 3-h period. Finally, maintain the mixture at 25° for 1 h.

Pour the reaction mixture slowly, with stirring, into 400 ml of ice-cold water containing several g of sodium carbonate which precipitates the inorganic salts from the solution. Separate the ether and aqueous layers in a large separatory funnel, saturate the aqueous phase with sodium chloride and extract three times with 50-ml portions of ether. Combine the ether solutions and pour over 500 ml of water adjusted to pH 8 with dilute sodium hydroxide in a large beaker. Stir this solution vigorously, warm and evaporate all the ether at 35°. Filter the aqueous solution through a "Celite" mat to remove any insoluble material.

Dilute the filtrate to 3 l and stir, while adding an aqueous 7% ethylamine solution dropwise to form the ethylamine tetrakis(*m*-trifluoromethylphenyl)borate salt. Addition of the amine should be discontinued immediately after the white flocculent amine salt ceases to form. If excess amine is added, brown reaction by-products precipitate from the solution and contaminate the desired precipitate. These impurities have solubility characteristics which are similar to those of the amine salt and cannot easily be removed through recrystallization. If the precipitation is carried out carefully, however, powdery white ethylamine tetrakis(*m*-trifluoromethylphenyl)-borate is obtained; m.p. 124–126°, 9.04 g yield.

Dry the ethylamine salt under vacuum and then dissolve in 100 ml of anhydrous methanol. Pour this solution into a 3-necked 250-ml flask equipped with an air condenser, small dropping funnel, stirrer and heating mantle. Bring the mixture to a vigorous methanol reflux and slowly add a solution containing 2.3 g of sodium methoxide in 100 ml of anhydrous methanol from the dropping funnel. Continue heating and stirring until all the ethylamine has been evolved (*ca.* 6 h). Remove methanol under vacuum, yielding a white, powdery residue.

Dissolve the salt in ether, and chromatograph the resulting solution through a column containing 25 g of basic alumina. Collect the chromatographed ether solution (*ca.* 300 ml) and add 75 ml of alkaline (pH 10) water. Evaporate the ether by stirring and heating, and filter the resulting aqueous solution through a fine sintered-glass crucible containing a layer of basic alumina. Saturate the filtrate with sodium chloride and extract 4 times with 50-ml portions of ether. Evaporate the combined ether extracts, with heating and stirring, until they become viscous. Finally, dry the sample under vacuum and over P_2O_5 at 80° for 24 h.

The sodium tetrakis(*m*-trifluoromethylphenyl)borate initially forms a glass which must be powdered to increase the surface area for drying. The total yield was 6.83 g. An NMR spectrum indicated the presence of 0.75 molecule of water per molecule of salt. Elemental analysis gave the following results (in %): C 53.86, H 2.70; calculated: C 53.57, H 2.81. This salt is very hygroscopic and difficult to analyze.

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

A 1% solution of the sodium salt was prepared and approximately 1 ml of this reagent was added to 1 ml of a 0.1 *M* solution of the ion to be tested. The following ions gave heavy precipitates: cesium, thallium(I) and silver. Rubidium formed a precipitate only after 2 ml of the reagent were added. No precipitates were obtained with copper, cobalt, nickel, calcium, magnesium, barium, lithium or potassium.

The reagent was tested for sensitivity with 1-ml aliquots of cesium, rubidium and potassium ions in the concentration range from 0.002 to 0.2 mg/ml. An equal volume of 0.03 *M* reagent solution, with pH adjusted to *ca.* 8, was added. Cesium formed precipitates throughout the range of concentrations, but both potassium and rubidium failed to precipitate even in the most concentrated solutions.

The reagent was also tested as a possible precipitant for amines and other compounds containing protonated nitrogen. The compound was dissolved in water, with 0.1 *N* hydrochloric acid added, if necessary, to solubilize it. An equal volume of 1% reagent solution was added. This test was carried out with a series of amines, amino acids and alkaloids. Many compounds formed no precipitates, and those which did form were too colloidal to be useful in qualitative or quantitative analysis.

*The tetrakis(*m*-trifluoromethylphenyl)borate anion as a precipitant for cesium*

A quantity of pure cesium tetrakis(*m*-trifluoromethylphenyl)borate was obtained by adding a 2% reagent solution dropwise to a solution of cesium chloride. The cesium salt was recrystallized twice from a methanol–water mixture and dried under vacuum and over P_2O_5 at 80°. An elemental analysis gave the following results (in %): C 46.32, H 2.41; calculated: C 46.44, H 2.23.

The rubidium salt was obtained by adding a large excess of the reagent to a solution of rubidium chloride. It was recrystallized from methanol–chlorobenzene and dried under vacuum and over P_2O_5 at 80°. No potassium salt could be precipitated.

Solubilities of the cesium and rubidium salts were obtained. The values were calculated from flame photometric data on the cations in solution after equilibration for 48 h. These figures are listed in Table I and show that both the cesium and the rubidium salts are more soluble in basic than in acidic solutions. The rubidium salt is approximately 100 times more soluble than the cesium salt. Furthermore, the cesium salt is significantly more soluble at 25° than at 0°.

TABLE I

SOLUBILITIES OF CESIUM TETRAKIS (*m*-TRIFLUOROMETHYLPHENYL)BORATE AND RUBIDIUM TETRAKIS (*m*-TRIFLUOROMETHYLPHENYL)BORATE

(Equilibration time, 48 h)

Salt	*pH*	*Temp. (°)*	*Solubility (g/l)*
$CsB(C_6H_4m\text{-}CF_3)_4$	2.6	25	0.123
	6.5	25	0.131
	10.5	25	0.228
	2.6	0	0.078
	6.5	0	0.141
	10.5	0	0.144
$RbB(C_6H_4m\text{-}CF_3)_4$	2.7	25	8.442
	10.6	25	10.778

The precipitation of cesium from pure cesium ion solutions was carried out in the following manner. A sample of cesium solution was adjusted to 50 ml. This solution was heated to 90° and 25 ml of a 2% reagent solution, pH 8, which had previously been filtered through alumina, were added dropwise. The sample was allowed to stand at room temperature for 1 h, transferred to an ice-bath for 1 h, and collected on a previously tared fine sintered-glass filtering crucible. It was washed with three 5-ml portions of cold water and dried at 110° for 1 h. Finally, it was cooled in a desiccator and weighed. The quantity of cesium recovered was calculated by multiplying the weight of the precipitate times the gravimetric factor 0.1835. These results are given in Table II.

Precipitations of cesium in the presence of rubidium or potassium ions were carried out under somewhat different conditions. In the case of cesium in the presence of rubidium, a solution containing both ions was adjusted to 50 ml. This mixture was heated to 70° with constant stirring, and the 2% reagent solution was added dropwise. Addition was discontinued when no further precipitation was visible. The sample was cooled for 1 h at room temperature and for 1 h in an ice-bath. The precipitate was transferred to a tared fine sintered-glass filtering crucible, washed with three 5-ml portions of cold water, dried at 110° for 1 h, cooled in a desiccator and weighed. The presence of rubidium was checked by dissolving the weighed sample in 95% ethanol and carrying out a standard additions determination on the flame photometer. No

TABLE II

RECOVERY OF CESIUM FROM PURE CESIUM SOLUTIONS

Cs taken (mg)	*Cs found (mg)*	*% Recovery*
24.78	24.39	98.4
24.78	24.34	98.2
24.78	24.32	98.1
24.78	24.37	98.3
24.78	24.59	99.2
24.78	24.56	99.1
	S.D. = ±0.12	
9.91	9.38	94.6
9.91	9.14	92.2
9.91	9.34	94.3
9.91	9.16	92.4
9.91	9.25	93.3
9.91	9.30	93.8
	S.D. = ±0.10	

TABLE III

RECOVERY OF CESIUM IN THE PRESENCE OF RUBIDIUM

Cs taken (mg)	*Rb taken (mg)*	*Rb found (mg)*	*Cs found (mg)*	*% Cs recovery*
24.95	24.99	0.00	24.20	97.0
24.95	24.99	0.00	24.48	98.1
24.95	24.99	0.00	24.65	98.8
24.95	24.99	0.00	24.90	99.8
24.95	24.99	0.00	24.45	98.0
24.95	24.99	0.00	24.25	97.2
			S.D. = ±0.26	

TABLE IV

RECOVERY OF CESIUM IN THE PRESENCE OF POTASSIUM

Cs taken (mg)	*K taken (mg)*	*K found (mg)*	*Cs found (mg)*	*% Cs recovery*
24.95	30.00	0.00	24.61	98.6
24.95	30.00	0.00	24.52	98.3

rubidium was detected in these samples, with the flame photometer's detection limit of *ca.* 2 p.p.m. The results are given in Table III.

Several cesium precipitations in the presence of potassium ion were carried out in an analogous manner. No potassium was detected in these precipitates (Table IV).

DISCUSSION

Sodium tetrakis(*m*-trifluoromethylphenyl)borate has been synthesized. Tables III and IV show that this compound is a highly selective reagent for the cesium ion, even in the presence of equivalent quantities of rubidium or potassium ions.

The compound does not appear suitable for precipitating amines or other basic nitrogen-containing compounds.

This reagent, when in solution at pH 8, has remained clear and coloress and is still effective in precipitating cesium after standing for 4 months. An equivalent solution of sodium tetraphenylborate shows visible signs of decomposition after the same length of time.

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SUMMARY

Sodium tetrakis(*m*-trifluoromethylphenyl)borate has been synthesized and shown to be a highly selective reagent for cesium ion even in the presence of other alkali metal ions. Equivalent amounts of rubidium or potassium do not interfere.

RÉSUMÉ

Le tétrakis (*m*-trifluorométhylphényl) borate de sodium a été synthétisé; c'est un réactif très sélectif pour l'ion césium même en présence d'autres ions de métaux alcalins. Des quantitées équivalentes de rubidium ou de potassium n'interfèrent pas.

ZUSAMMENFASSUNG

Natrium-Tetrakis(*m*-trifluoromethylphenyl)-borat wurde synthetisiert und erwies sich als ein hoch selektives Reagenz für Cäsiumionen, auch in Gegenwart anderer Alkalimetallionen. Äquivalente Gehalte von Rubidium oder Kalium stören nicht.

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