Analytica Chimica Acta, 73 (1974) 409–412

SHORT COMMUNICATION

Studies in the tetraarylborates

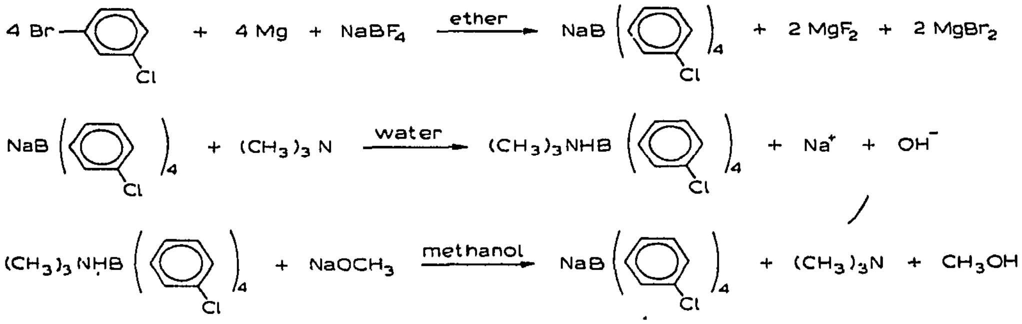
Part VI. The preparation and reagent properties of sodium tetrakis(*m*-chlorophenyl) borate

FRANK JARZEMBOWSKI, FRANK CASSARETTO, HARVEY POSVIC and CARL E. MOORE
Loyola University, Department of Chemistry, 6525 North Sheridan Road, Chicago, Illinois 60626 (U.S.A.)
(Received 25th March 1974)

In a continuation of the study of substituent effects on reagent stability and selectivity[1–5], sodium tetrakis(*m*-chlorophenyl)borate has been synthesized. Sodium tetrakis(*m*-chlorophenyl)borate is similar to sodium tetraphenylborate in selectivity in its reaction with large cations and is superior to tetraphenylborate in respect to stability and precipitate formation.

Synthesis of sodium tetrakis(m-chlorophenyl)borate

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



(1)

(2)

(3)

The reaction apparatus consists of a 1-l three-necked (ground glass) flask equipped with a 125-ml dropping funnel, a 600-ml dropping funnel, a water-cooled reflux condenser, and a teflon-coated magnetic stirring bar. Dry the apparatus by heating gently over a Bunsen flame while blowing nitrogen through the glassware. Place dry magnesium turnings (12.69 g; 0.522 mole) and sodium fluoroborate (14.3 g; 0.131 mole) in the flask. Place 550 ml of anhydrous ethyl ether in the 600-ml funnel. In the 125-ml funnel place 100 g (0.522 mole) of *m*-bromochlorobenzene and 50 ml of anhydrous ethyl ether. Sweep the assembly with dry nitrogen, and then add about 50 ml of the anhydrous ether in order to cover the magnesium turnings.

To initiate the Grignard reaction, add 5 ml of the *m*-bromochlorobenzene solution to the reaction vessel. After reaction begins, quickly add the remaining 500 ml of anhydrous ether and maintain rapid stirring. Partially immerse the flask in an ice water bath and add the remaining *m*-chlorobromobenzene dropwise over a period of about 5 h. Maintain gentle reflux for another hour. Stop the gas flow and rapid stirring. If necessary, allow the reaction mixture to stand overnight in a dry ice–acetone bath before proceeding with isolation and purification.

Transfer the reaction mixture to a 2-l beaker containing 200 ml of water and about 50 g of crushed ice. Add another 200 ml of water containing 4 g of sodium carbonate and 1 g of sodium hydroxide. Saturate the aqueous layer with sodium chloride and separate the ether layer. Extract the aqueous layer three times with 100-ml portions of ether. Add about 900 ml of distilled water to the combined ether solutions (about 1 l) and carefully warm until all the ether has evaporated. Filter the resulting cloudy, aqueous solution containing the required reagent several times through celite until a clear filtrate results. Extract the celite with 500 ml of water, filter and combine the aqueous filtrates (about 1500 ml). Treat this aqueous solution with 300 ml of aqueous 2.5% (w/v) trimethylamine solution while stirring and filter the resulting white precipitate of trimethylammonium tetrakis(*m*-chlorophenyl)borate by suction. Dissolve the precipitate in methanol, filter through celite, and recrystallize from a methanol–water solution. (Yield: 27.8 g.) After a second recrystallization and drying under vacuum at 80°C, the trimethylammonium tetrakis(*m*-chlorophenyl)borate (m.p. 164–165°C) gave the following elemental analysis results (in %): C, 62.64; H, 5.01; N, 2.79; Cl, 27.57. Calculated: C, 62.71; H, 5.07; N, 2.71; Cl, 27.42.

Preparation of sodium tetrakis(m-chlorophenyl)borate

Dissolve 10 g (0.019 mole) of the trimethylammonium salt and 2.05 g (0.038 mole) of sodium methoxide in about 300 ml of anhydrous methanol. Heat and stir until all the trimethylamine has been evolved (*ca.* 3 h); remove the remaining methanol under vacuum. Dissolve the residue in 200 ml of distilled water and filter. Saturate this solution with sodium chloride and extract with ether. Remove the ether under vacuum, leaving a white powder. Dissolve this in anhydrous ether and filter through 10 g of basic alumina. Remove the anhydrous ether under vacuum and air-dry the white residue, sodium tetrakis(*m*-chlorophenyl)borate, at room temperature overnight. Then powder the sodium tetrakis(*m*-chlorophenyl)borate and dry under vacuum at 80°C for 1 h. (Yield: 8.35 g.) Elemental analysis gave the following results (in %): C, 60.09; H, 3.38; Cl, 29.66. Calculated: C, 60.05; H, 3.36; Cl, 29.54.

Reagent properties of the tetrakis(m-chlorophenyl)borate anion

Some of this reagent was dissolved in distilled water and subsequently used to precipitate the potassium ion. The potassium salt after recrystallization from a methanol–water solution and drying for 1 h at 100°C, gave the following elemental analysis (in %): C, 58.40; H, 3.31; Cl, 28.85. Calculated: C, 58.10; H, 3.25; Cl, 28.58.

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. Silver gave a heavy flocculant precipitate. Cesium, rubidium, potassium and ammonium gave heavy, dense precipitates. Lead and copper showed a trace of precipitate formation, and no precipitates were observed for cadmium, manganese, barium, and nickel. The alkali metals were detectable at the concentrations 0.01 mg K ml^{-1}, 0.002 mg Rb ml^{-1}, and 0.002 mg Cs ml^{-1}.

The reagent was investigated for its ability to precipitate "onium" compounds by testing several compounds containing a basic nitrogen atom and a few quaternary ammonium salts. A number of these compounds dissolved in either distilled water or dilute hydrochloric acid, gave precipitates with the reagent. Typical analytical results are summarized in Table I.

TABLE I

PROPERTIES OF PRECIPITATES FORMED WITH TETRAKIS(*m*-CHLOROPHENYL) BORATE

Material tested	*M.p. (°C)*	*% Nitrogen*	
		Found	*Calc.*
Ammonium chloride	198–204 Decomposes	3.04	2.95
Trimethylamine	164–165	2.79	2.71
Tetramethylammonium bromide	222.5	2.56	2.64
Dimethylaminoethanol	128	2.60	2.56
1-Ethylpyridinium bromide	210	2.74	2.48
Methylene blue chloride	201–205	5.49	5.67

Sodium tetrakis(m-chlorophenyl)borate as a reagent for potassium

The precipitation of potassium from a pure potassium chloride solution was carried out in the following manner. Samples containing 33.44 mg, 16.35 mg, and 8.36 mg K ml^{-1} were prepared, diluted to 50 ml, and heated to about 70°C. A 2% solution of the reagent was filtered through a column containing 2 g of basic alumina and added dropwise to the samples. A calculated 15% excess of the reagent was used in each case. After cooling to room temperature, the precipitates were placed in an ice bath for 1 h. The fine, dense precipitate was then transferred to a tarred medium-porosity crucible and washed with three 5-ml portions of distilled water cooled to about 5°C. The crucible was dried at 100°C for 2 h and the recovery of potassium was calculated from the theoretical gravimetric factor of 0.07882. The results are shown in Table II.

The solubility of potassium tetrakis(*m*-chlorophenyl)borate in water was found by atomic absorption to be 0.0992 g l^{-1}; the sample was held at a constant temperature of 24°C for 138 h before the determination. Sodium tetrakis(*m*-chlorophenyl)borate forms sparingly soluble precipitates with K^+, Rb^+, and Cs^+. It appears to be a suitable gravimetric reagent for potassium. The reagent forms a fine, dense precipitate similar in appearance to that of barium sulfate, which is readily filterable through both medium- and fine-porosity crucibles. The reagent appears to have greater stability in aqueous solution than sodium tetraphenylborate. It also has possible utility as a reagent for "onium" compounds with which it forms well-defined crystalline precipitates. A 1% solution of sodium tetrakis(*m*-chloro-

TABLE II

RECOVERY OF POTASSIUM FROM PURE POTASSIUM CHLORIDE SOLUTIONS

K Taken (mg)	*K found[a] (mg)*	*Average recovery (%)*
33.44	33.32±0.08[b]	99.7
16.35	16.09±0.14	98.5
8.36	8.14±0.05	97.4

[a] Average of 5 results.
[b] Standard deviation.

phenyl)borate has remained active for a period of seven months with no visible appearance of decomposition.

Conclusions

Sodium tetrakis(*m*-chlorophenyl)borate has been synthesized and shown to be suitable as a gravimetric reagent for potassium, being in some ways superior to sodium tetraphenylborate. The salts formed with nitrogen-containing compounds offer possibilities for both qualitative and quantitative analysis.

REFERENCES

1 F. P. Cassaretto, J. J. McLafferty and C. E. Moore, *Anal. Chim. Acta*, 32 (1965) 376.
2 C. E. Moore, F. P. Cassaretto, H. Posvic and J. J. McLafferty, *Anal. Chim. Acta*, 35 (1966) 1.
3 J. T. Vandeberg, C. E. Moore, F. P. Cassaretto and H. Posvic, *Anal. Chim. Acta*, 44 (1969) 175.
4 M. Meisters, C. E. Moore and F. P. Cassaretto, *Anal. Chim. Acta*, 44 (1969) 287.
5 M. Meisters, J. T. Vandeberg, F. P. Cassaretto, H. Posvic and C. E. Moore, *Anal. Chim. Acta*, 49 (1970) 481.