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TECHNICAL NOTE

The Synthesis, Characterization, and Testing of a Reagent for the Selective Removal of Dichromate and Perchlorate from Aqueous Solution

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ABSTRACT

N-4-Vinylbenzyl-*N'*-benzyl-1,4-diazabicyclo[2.2.2]octane was synthesized and tested to determine its ability to selectively precipitate anions. Fifty-one common anions were tested. The reagent reacted only with nine: dichromate, dithionate, ferricyanide, tetrafluoroborate, iodide, nitroferricyanide, perchlorate, persulfate, and picrate.

INTRODUCTION

A serendipitous discovery was made when the preparation of a reagent to selectively remove phosphate from water was undertaken. While *N*-4-vinylbenzyl-*N'*-benzyl-1,4-diazabicyclo[2.2.2]octane does not precipitate phosphate, it does selectively remove dichromate and perchlorate from aqueous solution. Cr(VI) has been found to be harmful to the human population as well as the environment. It has been found to be toxic to aquatic life forms (1) and to be a carcinogen and mutagen (2, 3). A reagent which can separate dichromate from waste streams would be extremely beneficial. The removal of perchlorate from the laboratory environment would also be very useful when procedures employing perchloric acid are done. Pure HClO₄ is a colorless mobile, shock-sensitive liquid, while the anhydrous form is an extremely powerful oxidizing agent which reacts explosively with most organic materials (4). Figure 1 shows the structure of the compound prepared, characterized, and tested.

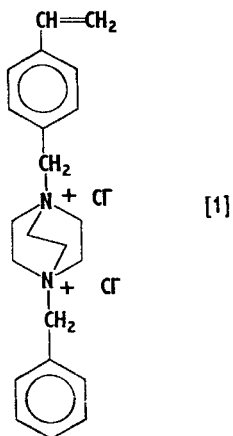


FIG. 1 Compound synthesized and tested: *N*-4-vinylbenzyl-*N'*-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride.

EXPERIMENTAL

All reagents used in testing were reagent grade and used as received. Solutions were prepared from the following: lithium fluoride, picric acid, and stannous titanate; potassium or sodium salts of acetate, aluminate, arsenate, arsenite, bicarbonate, bismuthate, bisulfate, bisulfite, borate, bromate, bromide, carbonate, chlorate, chloride, chromate, citrate, cyanate, cyanide, dichromate, dithionate, dithionite, ferricyanide, ferrocyanide, tetrafluoroborate, hydroxide, iodate, iodide, metaborate, molybdate, nitrate, nitrite, nitroferricyanide, oxalate, perchlorate, periodate, persulfate, selenate, selenite, silicate, sulfate, sulfite, thiocyanate, thiosul-

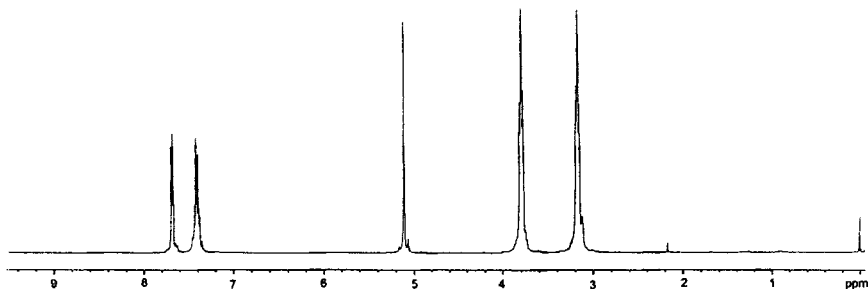


FIG. 2 NMR spectrum of *N*-benzyl-1,4-diazabicyclo[2.2.2]octane chloride in CDCl_3 .

fate, tungstate, vanadate, tribasic phosphate, dibasic phosphate, and monobasic phosphate. All water was distilled and deionized.

The synthesized compounds were characterized with a Varian 400 MHz NMR Spectrometer, Hewlett-Packard model 5859A Mass Spectrometer, and a Perkin-Elmer model 1310 IR Spectrometer. All melting points were obtained without correction using a Fisher-Johns melting point apparatus. Elemental Analyses were done at Galbraith Laboratories, Knoxville, TN 37950-1610.

Synthetic Procedures

Preparation of *N*-benzyl-1,4-diazabicyclo[2.2.2]octane chloride was achieved via a nucleophilic substitution reaction. To a 500-mL beaker, equipped with a magnetic stir bar, was added 33.65 g (0.30 mol) of diazabicyclo[2.2.2]octane and 37.98 g (0.30 mol) of benzyl chloride to 300 mL acetone. After 5 seconds the white crystalline precipitate of the product

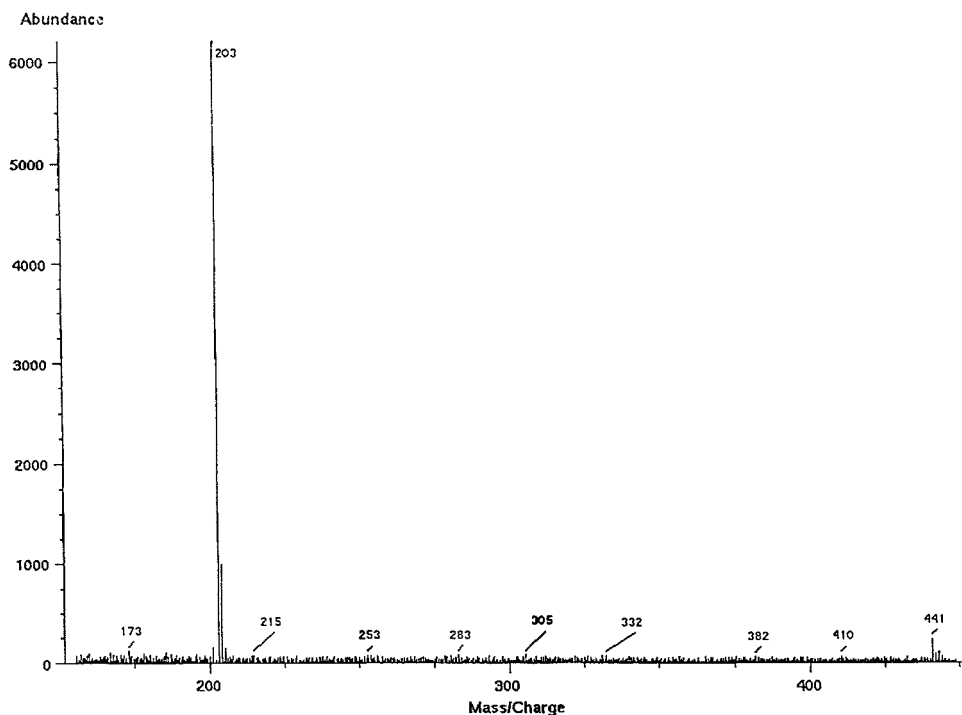


FIG. 3 MS (fast atom bombardment ionization) of *N*-benzyl-1,4-diazabicyclo[2.2.2]octane chloride.

was collected, recrystallized two times from acetone, and dried under vacuum. 61.54 g (85.91% yield) of *N*-benzyl-1,4-diazabicyclo[2.2.2]octane chloride was obtained with a melting point of 150°C (hardens at 166°C). NMR (Fig. 2): 3.2 ppm: (N—CH₂—), 3.8 ppm: (N⁺—CH₂—), 7.4 and 7.7 ppm: (aromatic). MS (Fig. 3): 203 (M⁺—Cl). IR (Fig. 4).

Preparation of *N*-4-vinylbenzyl-*N*'-benzyl'-1,4-diazabicyclo[2.2.2]octane dichloride was also achieved via a nucleophilic substitution reaction. To a 250-mL 3-necked round bottom flask, equipped with a thermometer, magnetic stir bar, water condenser, and nitrogen atmosphere, was added 4.92 g (0.013 mol) *N*-benzyl-1,4-diazabicyclo[2.2.2]octane chloride and 1.92 g (0.013 mol) *p*-vinylbenzyl chloride to 125 mL chloroform. The temperature was maintained at 57°C for 22 hours. The white precipitate was recrystallized from chloroform and then dissolved in methanol, filtered, and dried under vacuum. 3.73 g (75.55% yield) of *N*-4-vinylbenzyl-*N*'-benzyl'-1,4-diazabicyclo[2.2.2]octane dichloride was obtained with a melting point of 200°C (decomposes to light yellow), 247°C (dark yellow). Elemental analysis: 64.62% C, 7.52% H, 6.71% N, 17.71% Cl. Theoretical: 67.5% C, 7.2% H, 7.2% N, 17.9% Cl. NMR (Fig. 5): 3.9 ppm (—N⁺—CH₂—CH₂—N⁺—), 4.95 ppm (CH₂), 5.39 and 5.95 ppm (CH₂=), 6.8 ppm (CH=), 7.4–7.65 ppm (aromatic). MS (Fig. 6): 355 (M⁺—Cl). IR (Fig. 7).

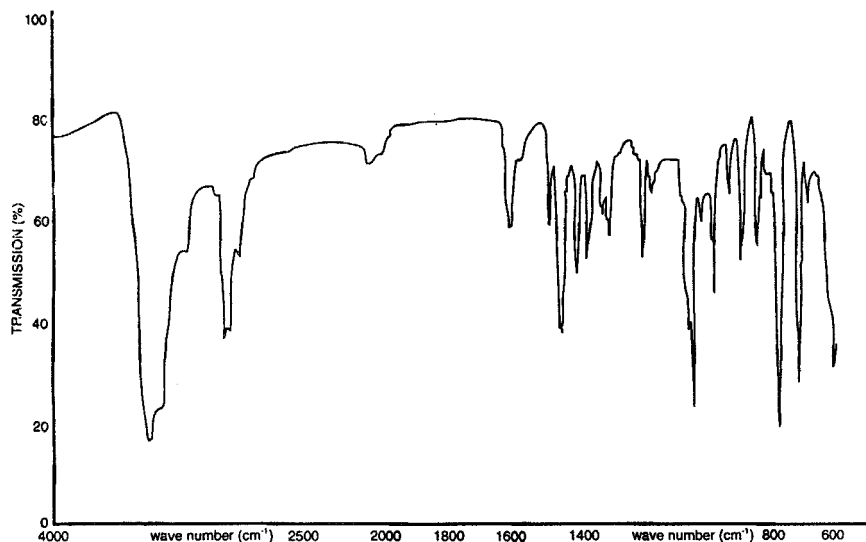


FIG. 4 IR spectrum of *N*-benzyl-1,4-diazabicyclo[2.2.2]octane chloride.

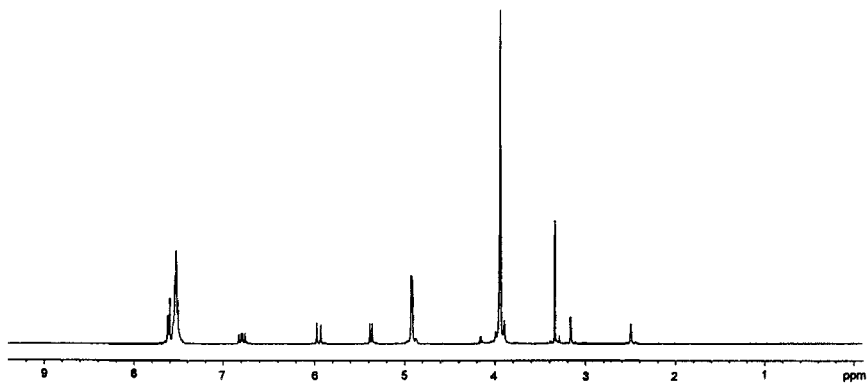


FIG. 5 NMR spectrum of *N*-4-vinylbenzyl-*N*'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride in DMSO.

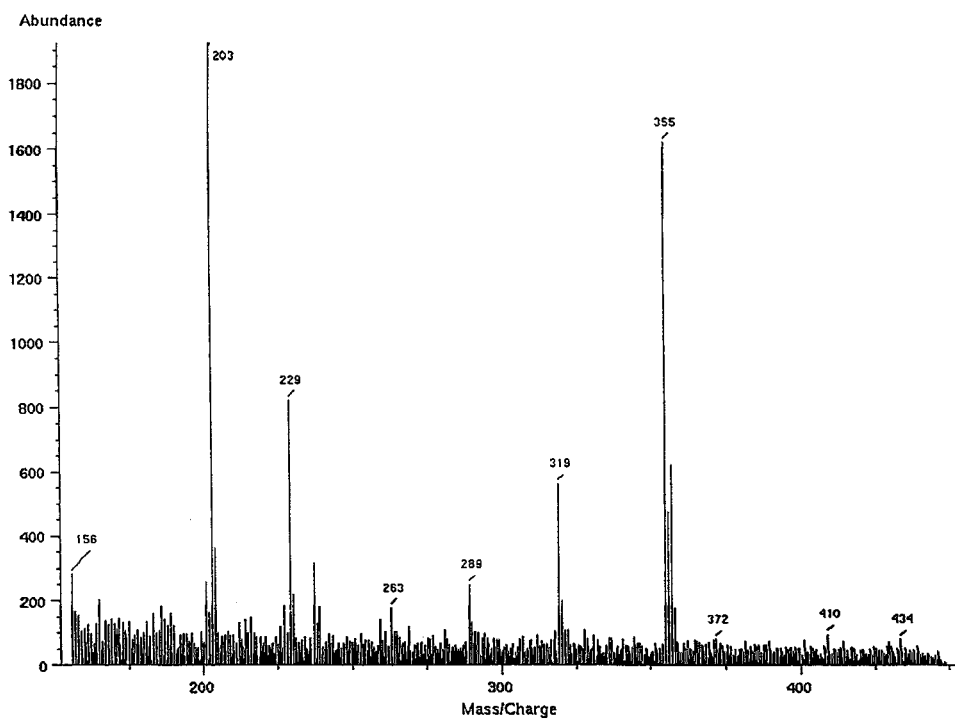


FIG. 6 MS (fast atom bombardment ionization) of *N*-4-vinylbenzyl-*N*'-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride.

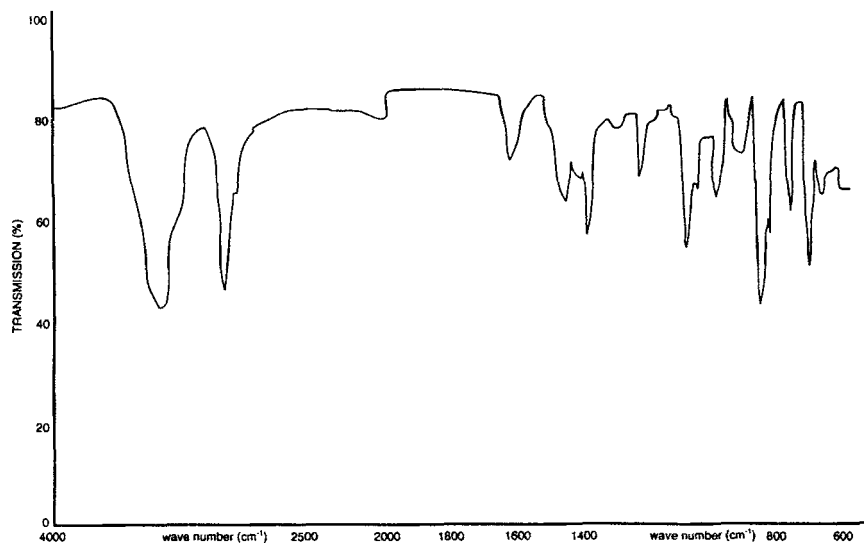


FIG. 7 IR spectrum of *N*-4-vinylbenzyl-*N'*-benzyl-1,4-diazabicyclo[2.2.2]octane dichloride.

Analytical Tests

A 0.100 *M* solution of [1] was prepared by dissolving 3.918 g in 100 mL water. A solution (0.1 *M*) of each anion was prepared. An anion solution (10 mL) was placed in a test tube, and the reagent solution (2 mL) added. Observations were made immediately on any reactions and again at 2 and 24 hours.

RESULTS AND DISCUSSION

The results of the reactions between the reagent and the anions are summarized in Table 1. Fifty-one anions were tested. In general, one of three results were observed: no reaction, immediate precipitation, precipitation at 2 hours. In general, the precipitates were white, crystalline, and easy to filter and recover.

TABLE I
Anion Tests with *N*-4-Vinylbenzyl-*N'*-benzyl-1,4-
diazabicyclo[2.2.2]octane Dichloride

<i>No Reaction</i>		
Acetate	Chromate	Periodate
Aluminate	Citrate	Selenate
Arsenate	Cyanate	Selenite
Arsenite	Cyanide	Silicate
Bicarbonate	Dithionite	Sulfate
Bismuthate	Ferrocyanide	Sulfite
Bisulfate	Fluoride	Thiocyanate
Bisulfite	Hydroxide	Thiosulfate
Borate	Iodate	Titanate
Bromate	Metaborate	Tungstate
Bromide	Molybdate	Vanadate
Carbonate	Nitrate	Tribasic Phosphate
Chlorate	Nitrite	Dibasic Phosphate
Chloride	Oxalate	Monobasic Phosphate
<i>Formation of an Immediate Precipitate</i>		
	Dichromate	
	Ferricyanide	
	Nitroferricyanide	
	Perchlorate	
	Persulfate	
	Picrate	
<i>Formation of a Precipitate at 2 Hours</i>		
	Dithionate	
	Tetrafluoroborate	
	Iodide	

CONCLUSIONS

1. The reagent under investigation, [1], is selective toward a limited number of anions: dichromate, dithionate, ferricyanide, tetrafluoroborate, iodide, nitroferricyanide, perchlorate, persulfate, and picrate.
2. The selected anions are generally large and either multivalent or easily polarized.
3. Generally those anions which were going to react did so quickly.

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