Synthesis of Methylene-bis(trimethylammonium iodide)

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The previously unknown methylene-bis(trimethylammonium iodide), $CH_2[N(CH_3)_3I]_2$, was synthesized by the reaction of tetramethyldiaminomethane and methyl iodide in water. The compound is unstable in aqueous solution above 40° C. and forms tetramethylammonium iodide as one of the decomposition products.

THE synthesis of methylenediamine bis-quaternary ammonium salts has been explored relatively little although they were reported as early as 1902 (*4–7, 9–14*). The preparations of all salts reported prior to 1951, except two (*9, 11, 12*), were shown to be erroneous (*6*).

Three attempts were made to prepare methylene-bis(trimethylammonium) salts. Tsatsas and Damiens (*14*) isolated only tetramethylammonium iodide. Böhme and Lehners (*2*) came to the conclusion that the synthesis of methylene-bis(trimethylammonium) salts was unlikely since they could be formed only in solvents in which the mono-salts were soluble. The insolubility of the latter in organic solvents would tend to terminate the quaternization reaction at the mono-salt stage. They also demonstrated that the presence of trace quantities of acidic materials in diethyl ether and ethanol would cleave the mono-salt at the methylene-nitrogen bond, while the presence of dilute base prevented this decomposition. The third attempt resulted in a mixture of the bis-iodide and dimethylaminomethyltrimethylammonium iodide which was not separated (*13*).

When the synthesis of methylene-bis(trimethylammonium iodide) was run with a 25% excess of methyl iodide in carefully dried ethanol, only impure bis-salt was isolated. Attempts to purify this material resulted in decomposition. However, the synthesis was successful in water using a slight excess of the diamine. The analytical data for the white, crystalline solid are listed in Table I.

The methylene diamines have been reported to cleave at the methylene-nitrogen linkage, both with hydrochloric acid (*3*) and with 50% aqueous sodium hydroxide (*2*), and they are temperature-sensitive in aqueous solution and when distilled (*1*). Thus, there is always the possibility that the product might not be the bis-salt but a mixture of cleavage products. In the presence of methyl iodide, the reaction shown in Equation 1 could occur.

$$\underset{}{(CH_3)_2NCH_2N(CH_3)_2} + 2CH_3I \rightarrow \underset{I}{(CH_3)_4NI} + \underset{II}{(CH_3)_2NCH_2I} \qquad (1)$$

However, II is water-sensitive and decomposes according to Equation 2 to give formaldehyde and dimethylammonium iodide (*3*).

$$\underset{II}{(CH_3)_2NCH_2I} + H_2O \rightarrow \underset{III}{(CH_3)_2NH_2I} + CH_2O \qquad (2)$$

The formaldehyde would be removed on drying in a vacuum and an equimolar mixture of I and III would result. The elemental analysis for such a mixture is significantly different from that obtained for the bis-salt (Table I). In addition, III has a melting point considerably lower than that found for the bis-salt, and the infrared spectrum of the bis-salt did not show the presence of either tetramethylammonium iodide or dimethylammonium iodide.

The thermal instability of the diamine and its bis-salt was demonstrated when, in scaling up the preparation, the quantity of water used was reduced by 50%. On addition of the diamine solution to the methyl iodide suspension, the mixture heated up sufficiently to cause the methyl iodide to reflux. The white, crystalline solid which precipitated on cooling was identified as tetramethylammonium iodide by its elemental analysis and by comparison with an authentic sample.

EXPERIMENTAL

Preparation of Methylene-bis(trimethylammonium iodide). To a chilled suspension of 2.84 grams (0.020 gram-mole) of methyl iodide in 13 ml. of water was added a solution of 1.22 grams (0.012 gram-mole) of *N,N,N′,N′*-tetramethyldiaminomethane in 12 ml. of water. The mixture was stirred

Table I. Elemental Composition and Properties of Quaternary Ammonium Iodides

	Calculated for					
	$(CH_3)_4NI$ (I)	$(CH_3)_2NCH_2I$ (II)	$(CH_3)_2NH_2I$ (III)	Equimolar Mixture of I + III	$CH_2[N(CH_3)_3I]_2$	Found for $CH_2[N(CH_3)_3I]_2$
C	23.89	19.48	13.89	19.26	21.78	21.50
H	6.02	4.36	4.66	5.39	5.22	5.50
N	6.97	7.57	8.10	7.49	7.26	6.80
I	63.12	68.59	73.35	67.86	65.75	65.60
M.p., C.	dec. > 230°	. . .	147°[a]; 155°[b]	. . .	. . .	232–5°(dec.)
Stability in H_2O	Stable	Decomposes	Stable	Stable	. . .	Stable to 40° C.

[a] Reference *8*. [b] Reference *15*.

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and kept cold until all of the methyl iodide had disappeared (approximately 1.5 hours) and the clear solution was then evaporated to dryness in vacuo at room temperature, followed by drying in a high vacuum for six hours at room temperature. The white, crystalline solid, 3.68 grams, melted at 232–235° C. with decomposition and represented a 95.5% yield. The elemental analysis is listed in Table I.

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Preparation and Characterization of Several Unsaturated Amines and Quaternary Ammonium Salts

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Twelve previously unreported unsaturated secondary or tertiary amines and nine previously unreported unsaturated quaternary ammonium salts have been prepared and characterized. An unsaturated quaternary ammonium salt containing an asymmetric nitrogen atom and one containing an asymmetric carbon atom were resolved to obtain the dextrorotatory isomer in each case.

DURING the course of an unsuccessful attempt to prepare optically active quaternary ammonium ion exchange resins, a number of previously unreported amines and quaternary ammonium salts were prepared. The physical properties and pertinent data on these new compounds along with the experimental details for resolution and isolation of one optically active antipode from each of two classes of asymmetric quaternary ammonium salts are reported. One class studied contained an asymmetric quaternary nitrogen atom while the other class contained an asymmetric carbon atom.

The amines were prepared in most cases by reaction of the appropriate alkenyl halide with the appropriate amine in presence of a proton acceptor (*2*). The physical properties, yields, and analytical data are reported in Table I.

The quaternary ammonium salts were prepared by reaction of the appropriate alkyl halide or alkenyl halide with the appropriate tertiary amine in a polar solvent such as acetone, according to well established procedures (*1*). The physical properties, yields, and analytical data in these quaternary ammonium salts are reported in Table II.

The *dl*-allylmethallylmethylphenylammonium bromide was resolved to obtain the dextrorotatory isomer in an optically pure state by use of *d*-camphor-10-sulfonic acid. The procedure used was a modified form of that reported by Pope and Peachey (*6*). The *d*-*d*-allylmethallylmethylphenylammonium camphor-10-sulfonate, after purification and determination of its optical properties was converted to *d*-allylmethallylmethylphenylammonium iodide by treating with an aqueous solution of potassium iodide from which the quaternary ammonium iodide precipitated. After purification and drying, its optical properties were determined. The molecular rotation of the iodide was found to be +26.6°. This value is in good agreement with the value of +27.36°, obtained from the maximum rotation obtained for the *d*-camphor-10-sulfonate after correction for the contribution of the camphor moeity (*4, 5*) (77.95° − 50.59° = 27.36°). *d*-Triallyl-2-octylammonium *p*-bromobenzenesulfonate was obtained by heating triallyamine with *d*-2-octyl *p*-bromobenzenesulfonate, and purification of the product. The physical properties, yields, and analytical data for these compounds are recorded in Table III.

As an intermediate for the preparation of *d*-triallyl-2-octylammonium *p*-bromobenzenesulfonate, *d*-2-octanol was prepared by the method of Cary, Vitcha, and Shriner (*3*). The product had a specific rotation of +6.50°, and was estimated to be 65% optically pure. This alcohol was converted to the *p*-bromobenzenesulfonate ester by reaction with the sulfonyl chloride. The purified ester had a specific rotation of +4.26° indicating it to be 60.2% optically pure. The analytical data and other physical properties for this compound are reported in the experimental section.

The resolution of *dl*-triallyl-*sec*-butylammonium bromide was also attempted by use of silver salts of *d*-camphor-10-sulfonic acid, *d*-3-bromocamphorsulfonic acid, and *d*-tartaric acid without success. The products were invariably viscous oils which could not be induced to crystallize. An attempt to resolve *dl*-diallyl-*sec*-butylamine was also unsuccessful.

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