ether was removed by distillation leaving a liquid from which crystallized 4.2 g. (64.1%) of triethylsilyltriphenylgermane (mixed melting point) melting at 92.5–94.5°.

In another reaction 5.0 g. (0.00823 mole) of hexaphenyldigermane, 1.0 g. (0.00262 mole) of tetraphenylgermane and 2 ml. of 1:5 sodium–potassium alloy were mixed with enough sodium-dried ether (5–10 ml.) to make a slurry. The reaction mixture was stirred and after a few minutes a green color developed which turned to brown after 20 minutes. After stirring 23 hours the excess alloy was amalgamated and the suspension transferred to another flask. To this stirring suspension was added 2.6 g. (0.0169 mole) of triethylchlorosilane in a dropwise fashion. After stirring 1 hour the mixture was hydrolyzed by the dropwise addition of 100 ml. of water. The mixture was filtered, yielding 2 g. (40% recovery) of hexaphenyldigermane (mixed melting point) melting at 343–344°. The ether layer was separated, dried and the ether distilled, yielding a liquid from which separated 2.6 g. (54.2% yield based on 60% cleavage of hexaphenyldigermane) of triethylsilyltriphenylgermane (mixed melting point) melting at 93.5-94.5°. Adding methanol to the remaining liquid precipitated 0.7 g. of material melting at 85–91°; recrystallization of this material from absolute ethanol yielded 0.4 g. (8.4%) of triethylsilyltriphenylgermane melting at 93–94.5°.

In still another reaction 5.0 g. (0.00823 mole) of hexaphenyldigermane and 2 ml. of 1:5 sodium–potassium alloy were mixed with sufficient ether (5–10 ml.) to make a paste. Stirring of the mixture was begun and after a few minutes 50 drops of bromobenzene were added over a period of 2 hours, the color changing from white to green to brown-black. After stirring 24 hours the excess alloy was amalgamated and the suspension transferred to another flask and 10 g. (0.066 mole) of triethylchlorosilane was added dropwise. After stirring 10 minutes the mixture was hydrolyzed by the dropwise addition of 100 ml. of water. The ether layer then was separated, dried and the ether distilled yielding a liquid from which separated 5 g. of solid melting at 90–92°. Recrystallization of this solid from absolute ethanol yielded 3.7 g. (55.3%) of triethylsilyltriphenylgermane melting at 95–96.5°. Mixed melting point and infrared spectra analysis[18] showed the compound to be identical with the triethylsilyltriphenylgermane prepared in previous experiments.

Triphenylgermyllithium.—To 6.0 g. (0.01 mole) of hexaphenyldigermane were added 1.0 g. of lithium wire cut into small pieces and 5 ml. of redistilled ethylene glycol dimethyl ether. This mixture was stirred as rapidly as possible. A brown color appeared after 35 minutes. After stirring 3 hours an additional 45 ml. of solvent was added and the mixture stirred until no more solid settled to the bottom when stirring was stopped, or about 2 hours. The dark solution was pipetted out from under the unreacted lithium into another flask and 3.0 g. (0.02 mole) of triethylchlorosilane was added dropwise. When the addition was complete, the mixture was stirred 17 hours and then hydrolyzed by the addition of 200 ml. of water. This mixture was extracted five times with ether; the combined ether extracts were dried over anhydrous sodium sulfate and distilled leaving an oil from which separated 5.6 g. of material melting over the range 77–90°. Recrystallization of this material from ethanol yielded 3.3 g. (39.8%) of triethylsilyltriphenylgermane (mixed melting point) melting at 97–98°.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for their financial support of this work.

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[18] The authors are indebted to Dr. V. A. Fassel and Mr. M. Margoshes for the infrared spectra of this and other organogermanium compounds.

AMES, IOWA

[CONTRIBUTION OF DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

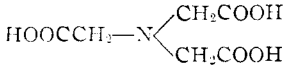
Preparation and Properties of Aminomethylenesulfonic Acids

BY ROGER G. LACOSTE[1] AND ARTHUR E. MARTELL

RECEIVED MAY 6, 1955

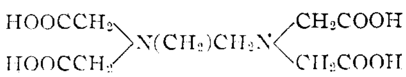
Disodium N,N′-dibutylethylenediamine-N,N′-dimethylenesulfonate, tetrasodium N,N′-ethylenediaminetetramethylenesulfonate, trisodium nitrilomonoacetatedimethylenesulfonate, disodium nitrilohydroxyethyldimethylenesulfonate, trisodium 2-aminobenzoate-N,N-dimethylenesulfonate and trisodium nitrilotrimethylenesulfonate were prepared by the action of the appropriate amine on the bisulfite addition product of formaldehyde. Trisodium nitrilomonomethylenesulfonate diacetate was prepared by the carboxymethylation of aminomethylenesulfonic acid. Acid–base properties and complex formation of these amino acids are discussed.

In the course of a general program of synthesizing new types of chelating agents, it seemed that the replacement of carboxylate groups of aminopolycarboxylic acids by sulfonate groups would produce an interesting variation in the properties of these substances. The only examples of this type of compound previously reported are an inner complex copper salt of aminomethylenesulfonic acid prepared by Meyer and Taube[2] and the investigation by Schwarzenbach, *et al.*,[3] of the stability of calcium chelates of the isomeric *o*-, *m*-, and *p*-sulfoaniline-N,N-diacetic acids, and of β-aminoethylenesulfonic-N,N-diacetic acid. The results of these investigations indicate that the sulfo group takes part in the coördination of metal ions when its position in the ligand is sterically favorable for the formation of a chelate ring with the metal ion. None of the sulfonato-containing chelating agents previously prepared contained more than one sulfonate group per molecule. The work reported in the present paper involves the preparation and preliminary study of a series of aminosulfonic acids analogous to the well-known chelating agents, ammoniatriacetic acid (I) and ethylenediaminetetraacetic acid (II), and in which all of the carboxyl group are replaced by sulfonic acid groups, as well as compounds containing both carboxyl and sulfonic acid groups.



$$HOOCCH_2{-}N\begin{matrix}\diagup CH_2COOH\\ \diagdown CH_2COOH\end{matrix}$$

I



$$\begin{matrix}HOOCCH_2\diagdown\\ HOOCCH_2\diagup\end{matrix}N(CH_2)CH_2N\begin{matrix}\diagup CH_2COOH\\ \diagdown CH_2COOH\end{matrix}$$

II

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[1] Taken in part from a thesis submitted by Roger G. Lacoste to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Master of Arts.

[2] J. Meyer and W. Taube, *Z. anorg. allgem. Chem.*, **227**, 425 (1936).

[3] G. Schwarzenbach, H. Ackerman and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

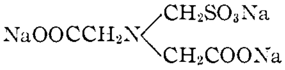
Discussion of Results

Synthetic Methods.—Two general synthetic methods were found useful for the preparation of the desired compounds: 1, the sulfomethylation of the corresponding amine or aminocarboxylic acid with formaldehyde and sodium bisulfite, and 2, carboxymethylation of an aminomethylenesulfonate in alkaline solution. The sulfomethylation proceeded well in most cases when sodium bisulfite taken from a freshly-opened container, was treated with formaldehyde to produce the intermediate hydroxymethylenesulfonate salt which then was treated with the amine without isolation, as is indicated by the general equations

$$\mathrm{CH_2O + NaHSO_3 \longrightarrow HOCH_2SO_3Na}$$

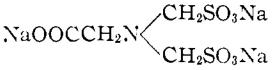
$$\mathrm{HOCH_2SO_3Na + R_2NH \longrightarrow R_2NCH_2SO_3Na + H_2O}$$

Thus trisodium nitrilomonoacetatedimethylenesulfonate (IV), disodium ethanolamine-N,N-dimethylenesulfonate (VI) and trisodium 2-aminobenzoate-N,N-dimethylenesulfonate (VII) and disodium N,N′-dibutylethylenediamine-N,N′-dimethylenesulfonate (IX) were prepared in yields ranging from 65 to 85% of the theoretical value. In the preparation of tetrasodium ethylenediamine-N,N′-tetramethylenesulfonate (VIII) a modification of this general procedure was used in that the intermediate hydroxymethylenesulfonate salt was isolated prior to reaction with the base. An attempt to prepare the tetrasulfonate by the one-step reaction had resulted in the formation of a mixture found to be low in nitrogen and high in sodium and sulfur, and which presumably was contaminated with inorganic salts. A similar result was obtained in the preparation of trisodium nitrilotrimethylenesulfonate. In this case recrystallization resulted in an increase in the proportion of inorganic impurities. The compound finally was prepared in 98% yield by the use of gaseous sulfur dioxide to generate the formaldehyde–bisulfite addition compound directly in the reaction mixture. This modified procedure is considered superior to the general method employed for the other compounds in view of its simplicity, lessened danger of oxidation of the bisulfite, and decreased possibility of side reactions involving the intermediate addition compound.



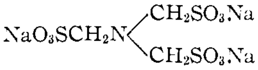
$$\mathrm{NaOOCCH_2N}\Big<\begin{matrix}\mathrm{CH_2SO_3Na}\\ \mathrm{CH_2COONa}\end{matrix}$$

III



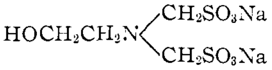
$$\mathrm{NaOOCCH_2N}\Big<\begin{matrix}\mathrm{CH_2SO_3Na}\\ \mathrm{CH_2SO_3Na}\end{matrix}$$

IV



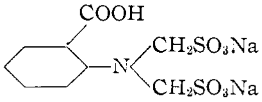
$$\mathrm{NaO_3SCH_2N}\Big<\begin{matrix}\mathrm{CH_2SO_3Na}\\ \mathrm{CH_2SO_3Na}\end{matrix}$$

V

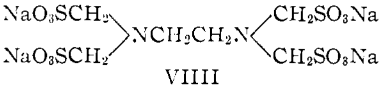


$$\mathrm{HOCH_2CH_2N}\Big<\begin{matrix}\mathrm{CH_2SO_3Na}\\ \mathrm{CH_2SO_3Na}\end{matrix}$$

VI

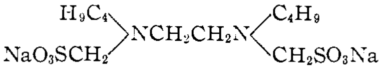


VII



$$\begin{matrix}\mathrm{NaO_3SCH_2}\\ \mathrm{NaO_3SCH_2}\end{matrix}\Big>\mathrm{NCH_2CH_2N}\Big<\begin{matrix}\mathrm{CH_2SO_3Na}\\ \mathrm{CH_2SO_3Na}\end{matrix}$$

VIIII

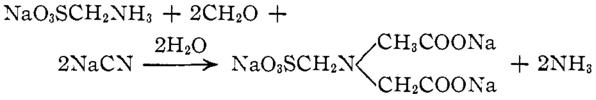


$$\begin{matrix}\mathrm{H_9C_4}\\ \mathrm{NaO_3SCH_2}\end{matrix}\Big>\mathrm{NCH_2CH_2N}\Big<\begin{matrix}\mathrm{C_4H_9}\\ \mathrm{CH_2SO_3Na}\end{matrix}$$

IX

Another method of sulfomethylation investigated is the direct reaction of the amine with sodium chloromethylenesulfonate. This substance, prepared by the interaction of methylene chloride and sodium sulfite[4] was kindly donated by the Dow Chemical Co. Reactions with this compound were discontinued because of relatively low yields, and the difficulty of separating it from sodium chloride, which is usually present in considerable amounts as a contaminant, and which is carried through to the final product.

The carboxymethylation reaction[5] was useful in the preparation of trisodium ammoniadiacetate-N-monomethylenesulfonate (III) from sodium aminomethylenesulfonate, according to the reaction



$$\mathrm{NaO_3SCH_2NH_3 + 2CH_2O +}$$
$$\mathrm{2NaCN \xrightarrow{2H_2O} NaO_3SCH_2N}\Big<\begin{matrix}\mathrm{CH_3COONa}\\ \mathrm{CH_2COONa}\end{matrix} \mathrm{+ 2NH_3}$$

Although the reaction was found to go 97% to completion by measurement of the evolved ammonia, the product was obtained in relatively low yield, 25%, because of difficulties in its isolation and purification.

All of the sodium sulfonate compounds prepared were colorless, crystalline solids with a salt-like appearance, very soluble in water, and insoluble in organic solvents. Most of these substances were found to be very hygroscopic. Like the alkali metal salts of most organic acids, they did not melt under 300°, but began to decompose slowly at temperatures around 200°.

Qualitative information about the basicities and metal-ion affinities—of the functional groups was deduced from titration curves obtained in the presence and in the absence of copper(II) ions.

Acid–Base Properties.—An interesting demonstration of the relative effects of the carboxylate and sulfonate groups on the basicity of the α-amino group can be obtained by comparing the behavior of the simplest amino acid of each series glycine and aminomethylenesulfonic acid. In glycine, with a pK_2 value of 9.8, the basicity of the amino group is nearly as high as in amines. On the other hand, the negative logarithm of the acid dissociation constant of the corresponding sulfonate is approximately 5.7, or about 4 log units more acidic. Apparently the sulfur atom of the sulfonate group is sufficiently more electropositive than the carbon atom of the carboxylate group, that the resulting inductive effect greatly reduces the basicity of the nitrogen atom.

Comparison of the titration curves of tetrasodium N,N′-ethylenediaminetetramethylenesulfonate and tetrasodium N,N′-ethylenediaminetetraacetate leads to a similar conclusion. The titration of the tetraacetic acid indicates two inflections corresponding to the formation of the di- and trialkali metal salts as stable entities in solution. The basicities of the amino groups are indicated by values of 6.16 and 10.26 for pK_3 and pK_4, respectively. For the tetrasulfonate, it was found that a single inflection occurs when 3 moles of base have been

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[4] J. Head, private communication.

[5] R. Smith, J. L. Bullock, F. C. Bersworth and A. E. Martell, *J. Org. Chem.*, **14**, 355 (1949).

added per mole of the amino acid. Hence, there is considerable overlapping in the first three dissociation steps, and only one amino group retains any degree of basicity. The dissociation of even the last ammonium group takes place at a lower *p*H than normal, it being half converted to the neutral amino group at *p*H of about 8.3.

Further verification of the assumption that the addition of a sulfonate group greatly reduces the basicity of the nitrogen atom may be demonstrated by a comparison of the titration curves of trisodium ammoniatriacetate with trisodium ammoniadiacetatemonomethylenesulfonate, trisodium ammoniamonoacetatedimethylenesulfonate and trisodium ammoniatrimethylenesulfonate. The pK_3 value of the triacetate is 9.7, whereas the pK_3 values for the monosulfonatediacetate, disulfonatemonoacetate and trisulfonate are approximately 8.9, 8.2 and 3.3, respectively. Potentiometric titrations of the other aminosulfonates prepared indicate little or no basicity of the amino group.

Complex Formation with Copper.—Upon addition of an equimolar amount of copper to aqueous solutions of the compounds prepared in this investigation, it was found that, in nearly all cases the copper ion was precipitated as the hydroxide, in the *p*H range where the hydroxide normally precipitates in the absence of complexing agent. The only exceptions were trisodium nitrilomonomethylenesulfonatediacetate, and trisodium nitrilomonoacetatedimethylenesulfonate. In the latter case precipitation took place above a *p*H of 6.7, while in the former no precipitation took place even when the *p*H was raised to values above 10. When qualitative titrations were carried out with aminomethylenesulfonic acid, hydroxyethyliminodimethylenesulfonic acid and ethylenediaminetetramethylenesulfonic acid, in the presence of an equimolar amount of copper, little or no acidification or lowering of the acid buffer regions occurred, and when the *p*H was raised above 5, the copper precipitated.

It is apparent, therefore, that the substitution of sulfonate groups in place of carboxylate groups in α-amino acids greatly reduces the tendency to bind metal ions, and that this effect correlates with the fact that the sulfonate group also greatly lowers the basicity of the amino group toward hydrogen ions. Thus the sulfonate analogs of the powerful chelating agents nitrilotriacetic acid and ethylenediaminetetraacetic acid seem to have little affinity for transition metal ions. In compounds containing both aminoacetate and aminomethylenesulfonate groups, the metal ion affinity seems to decrease as the proportion of sulfonate groups increases.

Experimental

Disodium N,N′-Dibutylethylenediamine-N,N′-dimethylenesulfonate.—To 55 g. of sodium bisulfite, dissolved in 73 ml. of water, was added 41 g. of a 37% solution of formaldehyde. The reaction mixture was heated to between 60 and 65° for 30 minutes with continual stirring. Then 43 g. of dibutylethylenediamine, dissolved in 75 ml. of 95% ethanol, was added dropwise and the temperature was raised to between 70 and 75°. The reaction was allowed to run at this temperature and with constant stirring for 3 hours. When the reaction mixture was cooled to room temperature, a colorless solid precipitated. This precipitate was filtered and washed with 160 ml. of absolute alcohol. It was then slurried with 400 ml. of benzene, filtered and dried in a vacuum desiccator. The yield represented 70% of the theoretical amount.

The product was recrystallized from a hot solution of 70% alcohol. It is a colorless, crystalline solid, which is soluble in cold water, slightly soluble in hot water, and insoluble in organic solvents.

Anal. Calcd. for $C_{12}H_{26}O_6N_2S_2Na_2$: N, 6.94; Na, 11.38; mol. wt., 404. Found: N, 6.6; Na, 11.33; mol. wt., 406.

Tetrasodium N,N′-Ethylenediaminetetramethylenesulfonate.—An aqueous solution containing 55 g. of sodium bisulfite was added to 45 g. of a 37% solution of formaldehyde and heated to 75°, with stirring, for 45 minutes. The reaction mixture then was allowed to cool to room temperature and a small amount of ethanol was added. When the reaction mixture was shaken, the product crystallized out within a short time. The yield of colorless, crystalline sodium hydroxymethylenesulfonate was 89%.

To 67 g. of sodium hydroxymethylenesulfonate, dissolved in 125 ml. of water, was added 9 g. of ethylenediamine dissolved in 75 ml. of water. The resulting solution was heated with stirring, for 3 hours. The product precipitated out of the reaction mixture upon the addition of a small amount of methanol. It was filtered, washed with methanol and dried in a vacuum desiccator. The yield represented 55%.

The crude product was recrystallized from a hot 71% aqueous methanol solution. The purified salt was found to be a colorless hygroscopic crystalline solid, very soluble in water, and insoluble in organic solvents.

Anal. Calcd. for $C_6H_{12}O_{12}N_2S_4Na_4$: N, 5.35; S, 24.4; Na, 17.5. Found: N, 5.16; S, 23.4; Na, 16.8.

Trisodium Nitrilomonoacetatedimethylenesulfonate.—To 55 g. of sodium bisulfite, dissolved in 75 ml. of water, was added 41 g. of a 37% solution of formaldehyde and the reaction mixture was heated, with stirring, to 65° for 30 minutes. An alcoholic solution containing 7 g. of sodium hydroxide and 13.2 of glycine was added to the reaction mixture and the resulting solution was heated at 80° for 3 hours. The reaction mixture then was allowed to cool and a small amount of methanol was added. A gelatinous substance crystallized after standing overnight in the aqueous methanol solution. The colorless solid was filtered and dried in a vacuum desiccator. The yield represented 84.7%.

The product was recrystallized from a water-alcohol solution. In order to recover a large fraction of the product remaining in the mother liquor, it was necessary to concentrate the filtrate under vacuum and to recrystallize the material obtained in this manner. These steps were repeated several times before the majority of the product was recovered in crystalline form. The colorless solid thus obtained is very soluble in water, insoluble in organic solvents and hygroscopic.

Anal. Calcd. for $C_4H_6O_8NS_2Na_3 \cdot H_2O$: N, 4.02; Na, 19.9. Found: N, 4.5; Na, 20.7.

Disodium Ethanolamine-N,N-dimethylenesulfonate.—To 55 g. of sodium bisulfite, dissolved in 75 ml. of water, was added 41 g. of a 37% solution of formaldehyde and the resulting solution was heated to 65° for 30 minutes. Then 10.2 g. of ethanolamine, dissolved in 70 ml. of alcohol, was added, and the reaction mixture was heated to 75° for 3 hours. It then was cooled to room temperature, a little methanol was added, and the resulting solution was allowed to stand overnight. The precipitate which formed was filtered and dried in a vacuum desiccator. The yield represented 66.5%.

Recrystallization of the product was very difficult. It partially crystallized from a water–alcohol solvent only after the solution was concentrated to a viscous liquid. The recrystallized product thus obtained is a colorless solid which is very soluble in water, insoluble in organic solvents and very hygroscopic.

Anal. Calcd. for $C_4H_9O_7NS_2Na_2 \cdot H_2O$: S, 20.35; Na, 14.8. Found: S, 20.35; Na, 15.0.

Trisodium Nitrilodiacetatemonomethylenesulfonate.—One hundred four grams of sodium bisulfite was added to 116.7 g. of a 37% solution of formaldehyde and heated to 70° for 15 minutes. Then 135 ml. of commercial ammonium hydroxide was added dropwise and the temperature was maintained at 75° for 30 minutes. The reaction mixture was placed in an ice-bath and treated with concentrated sulfuric acid, whereupon the product quickly crystallized. The yield of colorless aminomethylenesulfonic acid represented 83% of the theoretical amount. It is slightly soluble in cold water, very soluble in hot water and insoluble in organic solvents. It melts with decomposition between 190 and 194°. The molecular weight was found by titration to be 111, in good agreement with the theoretical value of 114.

The aminomethylenesulfonic acid thus obtained was converted to the sodium salt by adding 33.25 g. of the acid to a solution containing 10 g. of sodium hydroxide. The resulting solution was placed in a three-necked, round-bottom flask fitted with a mercury-seal stirrer, a reflux condenser and two dropping funnels. The reaction mixture was heated to water-bath temperature and one-third of an aqueous solution of 50.5 g. of sodium cyanide, was added. Of the total required amount of formaldehyde (43 g. of 37% solution), one-third was added, dropwise, over a period of 45 minutes. The second and third portions of these reagents were added in a similar manner and the reaction was allowed to proceed for 24 hours at the same temperature. The course of the reaction was followed by trapping the ammonia given off and titrating it with standard sulfuric acid. Approximately 97% of the theoretical amount of ammonia was evolved from the reaction mixture.

The product was isolated as a semi-solid material by evaporation of the solution under reduced pressure. It was obtained in a dry form by repeated vacuum distillation of alcoholic solutions. The crude material finally was recrystallized from a water-alcohol solution and dried in a vacuum desiccator. The final product is a colorless, crystalline very hygroscopic material.

Anal. Calcd. for $C_5H_6O_7NS_2Na_3$: N, 4.77; S, 10.9. Found: N, 4.57; S, 11.45.

Trisodium 2-Aminobenzoate-N,N-dimethylenesulfonate.—A solution consisting of 55 g. of sodium bisulfite, 73 ml. of water and 41 g. of a 37% formaldehyde solution was heated to 65° for 30 minutes. Next, a solution of 34.25 g. of anthranilic acid and 10 g. of sodium hydroxide in 200 ml. of water and 150 ml. of alcohol was added, and the reaction mixture was heated to 75° for 4 hours. The reaction solution was allowed to cool to room temperature and then was treated with ethanol, whereupon the product precipitated from the alcoholic solution.

Proper conditions for recrystallization were not found. The compound would not crystallize from water or water-alcohol solutions. The uncrystallized product is a colorless solid which is soluble in water, insoluble in organic solvents.

Anal. Calcd. for $C_9H_8O_8NS_2Na_3 \cdot H_2O$: N, 3.14; S, 14.4. Found: N, 3.0; S, 14.3.

Trisodium Nitrilotrimethylenesulfonate—An aqueous solution containing 55.2 g. of sodium hydroxide, 51 g. of aminomethylenesulfonic acid and 75.4 g. of a 37% solution of formaldehyde was prepared. The resulting mixture then was cooled down to room temperature and 58.8 g. of gaseous sulfur dioxide was added over a period of 8 hours. The reaction solution then was heated to 70° for 3 hours. After the reaction mixture had been cooled to room temperature, the product was precipitated out by the addition of a little methanol. After recrystallization from a water-alcohol solution the nitrilotrimethylenesulfonate salt was obtained as a colorless, crystalline trihydrate.

Anal. Calcd. for $C_3H_6O_9NS_3Na_3 \cdot H_2O$: N, 3.4; S, 23.07; Na, 16.5. Found: N, 3.8; S, 22.7; Na, 16.2.

Determination of Neutral Equivalent.—A weighed sample of amino acid (20 to 40 mg.) was dissolved in 250 ml. of distilled water and standard sodium hydroxide was added in small quantities to the stirred solution. After each addition of base, the *p*H was measured with a glass electrode and a saturated calomel reference electrode used in conjunction with a Beckman *p*H meter. After the *p*H reached a value of about 10, a standard solution of hydrochloric acid was added in order to bring the *p*H back to its original value. Then the sample was titrated with standard hydrochloric acid in a similar manner. After each addition the *p*H of the solution was recorded. Observation of inflections in the titration curve thus obtained made it possible to calculate a neutral equivalent in certain cases where inflections were found at positions other than that corresponding to the starting material. In such cases the neutral equivalent could be interpreted in terms of molecular weight in view of the nature of the known functional groups in the substance being studied.

Determination of Copper Complex Formation.—To the acid solution obtained in the determination of neutral equivalent was added a stoichiometric amount of copper(II) nitrate. In most cases the amount of metal added was calculated on the basis of a 1:1 molar ratio of ligand to copper salt, although in the case of ligands having a small number of functional groups, the molar equivalent of copper salt used was reduced to one-half of this value. The resulting solution was then titrated potentiometrically with small increments of standard sodium hydroxide until the *p*H reached a value above 10 or until a precipitate formed.

Acknowledgment.—The authors are indebted to F. C. Bersworth of Versenes, Inc., for financial support of this research, and for helpful suggestions and continued interest in the problem.

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Synthesis of Methyl-d_3 Alcohol and Methyl-d_3 Fluoride

BY WALTER F. EDGELL AND L. PARTS

RECEIVED DECEMBER 10, 1954

Tribromomethyl fluoride, carbon dioxide, phosgene and 1,2-propylene carbonate have been reduced with lithium aluminum hydride. The reduction of tribromomethyl fluoride yielded methane and methyl fluoride. From carbon dioxide and phosgene low yields of methanol, based on lithium aluminum hydride, were obtained. The reduction of 1,2-propylene carbonate gave a satisfactory yield of methanol and the method was adopted for the synthesis of methyl-d_3 alcohol, using lithium aluminum deuteride as the source of deuterium. Methyl-d_3 *p*-toluenesulfonate, prepared from methyl-d_3 alcohol led to methyl-d_3 fluoride on reaction with potassium fluoride.

Introduction

Continued progress in this Laboratory on the theoretical aspects of the rotation-vibration spectra of fluorinated hydrocarbons suggested a study of the infrared and Raman spectra of methyl-d_3 fluoride.[1] The results of microwave studies on methyl-d_3 fluoride have been reported[2] without a reference to its preparation.

In the course of the study of reactions which would lead to methyl-d_3 fluoride a new synthesis of methyl-d_3 alcohol was discovered. It was found that methyl-d_3 alcohol can be prepared in a high yield on reduction of 1,2-propylene carbonate with lithium aluminum deuteride. No special apparatus is required for this reaction.

Since methyl-d_3 alcohol is a convenient starting material for compounds containing the CD_3 group we are reporting its preparation prior to the publi-

(1) Walter F. Edgell and L. Parts, to be published.

(2) C. M. Johnson, R. Trambarulo and W. Gordy, *Phys. Rev.*, **84**, 1178 (1951); W. Gordy, *Ann. N. Y. Acad. Sci.*, **55**, 774 (1952).