ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Analogs of Hexaphenylethane. IV. Hexaphenyldigermane[1]

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Hexaphenyldigermane, a compound showing no tendency to dissociate into free radicals, has been found to be inert to oxygen and to iodine in chloroform solution, but it is cleaved appreciably by iodine in refluxing xylene. Hexaphenyldigermane is not cleaved by sodium–potassium alloy in diethyl ether, in benzene, in refluxing xylene, in refluxing di-*n*-butyl ether, or in ethylene glycol dimethyl ether to form triphenylgermylpotassium, but treatment with sodium–potassium alloy in diethyl ether accompanied by tetrahydrofuran, bromobenzene or tetraphenylgermane gives triphenylgermylpotassium. Triphenylgermyllithium may be prepared by the action of lithium on hexaphenyldigermane in ethylene glycol dimethyl ether.

Previous reports from this Laboratory have dealt with the preparation of a number of Group IV-B analogs of hexaphenylethane and their possible tendency to dissociate into free radicals. The purpose of this paper is to report the extension of these studies to hexaphenyldigermane.

Because of the great similarity between germanium and silicon in organic compounds it is not surprising to find that hexaphenyldigermane, like hexaphenyldisilane,[2] shows no tendency to dissociate into free radicals. Morgan and Drew[3] found no dissociation of hexaphenyldigermane in their ebullioscopic molecular weight determinations in benzene, and Selwood,[4] by magnetic susceptibility measurements, placed the upper limits of dissociation at 1% in the solid and 20% in a nearly saturated benzene solution at 25°, but he considered it improbable that any dissociation took place under these conditions.

Hexaphenyldigermane may be prepared by a Wurtz reaction using triphenylbromogermane and sodium in refluxing xylene,[3] by the reaction of a dilute ether solution of triphenylgermane with a refluxing, concentrated ether solution of phenyllithium,[5] or by the action of a large excess of phenylmagnesium bromide on germanium tetrachloride in a refluxing mixture of five volumes of ether and two volumes of toluene.[6] The latter reaction is the method of choice starting from germanium tetrachloride, but yields obtained in this Laboratory were low, and the separation of the hexaphenyldigermane from the tetraphenylgermane that is formed causes considerable difficulty.

Hexaphenyldigermane is a white solid which melts at 340–341° and volatilizes[7] at 476–479° with some brown coloration appearing at 450°. It is soluble in chloroform but insoluble in all other common organic solvents; however, it can be recrystallized from benzene and from toluene. Hexaphenyldigermane has been cleaved by bromine in refluxing carbon tetrachloride[3] to form triphenylbromogermane, and by sodium in liquid ammonia[8] to form triphenylgermylsodium. It has been found in this Laboratory that, like hexaphenyldisilane,[9] hexaphenyldigermane is inert to oxygen in refluxing benzene, but unlike hexaphenyldisilane it is inert to sodium–potassium alloy in diethyl ether.

The difference in ease of cleavage of hexaphenyldisilane and hexaphenyldigermane by sodium–potassium alloy in diethyl ether is interesting inasmuch as it demonstrates one of the not too few cases where there is a difference in reactivity between analogous compounds of silicon and germanium. When hexaphenyldisilane, in a small amount of ether, is treated with sodium–potassium alloy,[10] cleavage begins after only a few minutes and is probably complete after only a few hours, but under identical conditions hexaphenyldigermane is unaffected. This difference prompted the investigation of various cleavage agents and solvents in an attempt to prepare a triphenylgermylmetallic compound which would be very useful in the synthesis of organogermanium compounds. Triphenylgermylsodium[8] has been prepared by the action of sodium on either hexaphenyldigermane or tetraphenylgermane in liquid ammonia, and triphenylgermyllithium[11] has been made by treating triethylsilyltriphenylgermane with lithium in ethylamine. However, an attempt was made in these studies to find a solvent and a cleavage agent which would be more versatile and free from side reactions.

The majority of the cleavage reactions which were carried out proved to be of little or no value for the preparation of the desired triphenylgermylmetallic compound. Some of these reactions gave results which indicated reasonably complete cleavage of the hexaphenyldigermane, but which did not yield any identifiable product. These reactions might bear further investigation of their possibilities as preparative methods.

The first attempt at cleavage of hexaphenyldigermane involved the use of sodium–potassium alloy in various solvents. We were unable to effect cleavage in diethyl ether or benzene, although in the latter case only 76% of the starting material was recovered, along with 13% of tetraphenylgermane which may have been formed by disproportionation. Yields of recovered starting material in diethyl ether were 96 and 80%, respectively. Complete cleavage apparently did take place when hexaphenyldigermane was treated with sodium–

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[1] For paper III of this series see A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 77 (1954).

[2] H. Gilman and T. C. Wu, *ibid.*, **75**, 3762 (1953).

[3] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, **127**, 1760 (1925).

[4] P. W. Selwood, THIS JOURNAL, **61**, 3168 (1939).

[5] O. H. Johnson and D. M. Harris, *ibid.*, **72**, 5566 (1950).

[6] O. H. Johnson and D. M. Harris, *ibid.*, **72**, 5564 (1950).

[7] The authors are indebted to Dr. R. K. Ingham for this information.

[8] C. A. Kraus and L. S. Foster, THIS JOURNAL, **49**, 457 (1927).

[9] W. Schlenk, J. Renning and G. Rackey, *Ber.*, **44**, 1178 (1911).

[10] H. Gilman, T. C. Wu, H. A. Hartzfeld, G. A. Guter, A. G. Smith, J. J. Goodman and S. H. Eidt, THIS JOURNAL, **74**, 561 (1952).

[11] C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934).

potassium alloy in both refluxing di-*n*-butyl ether and refluxing xylene, but only oils were isolated in both cases when the mixtures were hydrolyzed. In an attempt to use tetrahydrofuran as a solvent it was found that the sodium–potassium alloy reacted with the solvent; however, no hexaphenyldigermane was recovered from the reaction. It seemed worthwhile to investigate the use of this solvent as a possible initiator in the cleavage of hexaphenyldigermane in diethyl ether. When hexaphenyldigermane was treated with sodium–potassium alloy in a small amount of diethyl ether, and a few drops of tetrahydrofuran were added to the mixture, cleavage began within a few minutes and was complete some time before 27 hours had elapsed. At this time a 64% yield of triethylsilyltriphenylgermane was obtained upon the addition of triethylchlorosilane to the reaction mixture according to the equations

$$(C_6H_5)_3GeGe(C_6H_5)_3 + Na/K \xrightarrow{C_4H_8O} 2(C_6H_5)_3GeK \quad (1)$$

$$(C_6H_5)_3GeK + (C_2H_5)_3SiCl \longrightarrow (C_6H_5)_3GeSi(C_2H_5)_3 \quad (2)$$

Reaction (1) above has been substantiated in this Laboratory[12] by the carbonation of the reaction mixture to obtain an 83% yield of triphenylgermanecarboxylic acid. The role of tetrahydrofuran in this reaction is not clear, but it has been found that bromobenzene and tetraphenylgermane also will initiate the cleavage of hexaphenyldigermane. With bromobenzene the reaction may be formulated as

$$C_6H_5Br + 2Na/K \longrightarrow C_6H_5K + KBr \quad (3)$$

$$C_6H_5K + (C_6H_5)_3GeGe(C_6H_5)_3 \longrightarrow (C_6H_5)_4Ge + (C_6H_5)_3GeK \quad (4)$$

$$(C_6H_5)_3Ge + Na/K \longrightarrow (C_6H_5)_3GeK + C_6H_5K \quad (5)$$

We have found that reaction (5) above does indeed take place by allowing tetraphenylgermane to react with sodium–potassium alloy in diethyl ether.[13]

When a mixture containing 83.3% of hexaphenyldigermane and 16.7% of tetraphenylgermane was treated with sodium–potassium alloy in a small amount of diethyl ether, only 40% of the hexaphenyldigermane was recovered as such and 158% (based on tetraphenylgermane alone) of the derivative, triethylsilyltriphenylgermane, was isolated. The amount of derivative formed is in excess of the theoretical amount which could be formed from the tetraphenylgermane alone. This reaction may then be formulated as

$$(C_6H_5)_4Ge + Na/K \longrightarrow (C_6H_5)_3GeK + C_6H_5K \quad (6)$$

$$C_6H_5K + (C_6H_5)_3GeGe(C_6H_5)_3 \longrightarrow (C_6H_5)_3GeK + (C_6H_5)_4Ge \quad (7)$$

Because an excess of sodium–potassium alloy is always used, the tetraphenylgermane formed in reaction (7) above undergoes reaction (6) again.

The use of ethylene glycol dimethyl ether as a possible solvent for these reactions was suggested by the fact that hexaphenyldisilane is cleaved easily by sodium–potassium alloy in this solvent to form triphenylsilylpotassium.[14] Results, however, with hexaphenyldigermane were disappointing with as much as 64% of the starting material being recovered from the reaction mixture and no derivative of triphenylgermylpotassium being isolated. It is believed that cleavage does occur in the beginning of the reaction, but that because of the insolubility of hexaphenyldigermane in this solvent, the triphenylgermylpotassium present is attacked preferentially by the alloy because of the solubility of the triphenylgermylpotassium in the solvent. This is corroborated partially by the fact that when two equivalents of potassium metal were allowed to react with one equivalent of hexaphenyldigermane in ethylene glycol dimethyl ether, all of the potassium was used up and yet 38% of the hexaphenyldigermane was recovered. It must be mentioned, however, that it is possible that the triphenylgermylpotassium formed reacts with the solvent thus accounting for the failure to isolate a derivative of this compound, and that the potassium may be used up in reacting with the products of this reaction.

Although sodium–potassium alloy and potassium metal appear to be too reactive in ethylene glycol dimethyl ether to effect cleavage of the hexaphenyldigermane alone, it appears that lithium will give the desired results. When lithium is allowed to react with hexaphenyldigermane in a small amount of ethylene glycol dimethyl ether, reaction proceeds smoothly to completion in about 4–5 hours. Although only a 40% yield of triethylsilyltriphenylgermane was obtained as a derivative, it is believed the mixture consists essentially of triphenylgermyllithium. Other confirmatory experiments for the existence of triphenylgermyllithium are in progress.

The above-mentioned results and results of other studies are listed in Table I.

Experimental[15]

Dissociation Experiments with Hexaphenyldigermane.—When a stream of dry air was bubbled through a mixture of 1.0 g. (0.00165 mole) of hexaphenyldigermane[3,5,6] in 50 ml. of sodium-dried xylene for 48 hours, no change was noted. When the solution was cooled, 0.8 g. of material crystallized out which melted at 344–345°. Removal of the xylene under reduced pressure yielded a residue which, when washed with ether, weighed 0.1 g. and melted at 344–345°. A mixed melting point with the starting material showed no depression.

When 0.5 g. (0.000823 mole) of hexaphenyldigermane and 4 drops of an approximately 1% solution of iodine in chloroform were refluxed with 25 ml. of chloroform for 24 hours, no consumption of iodine was noted. When the chloroform was distilled, the residue remaining weighed 0.5 g. and melted at 340–342°. A mixed melting point with the starting material showed no depression. When 1.0 g. (0.00165 mole) of hexaphenyldigermane, 0.5 g. of iodine and 3 drops of quinoline were refluxed in 50 ml. of sodium-dried xylene for 24 hours and the mixture was allowed to cool, there separated 0.5 g. (50% recovery) of material melting at 335–340°. The iodine was removed with aqueous sodium sulfite and the xylene layer was separated and the xylene distilled, yielding a residue which, when washed with petroleum ether (b.p. 60–70°), weighed 0.3 g. and melted at 175–300°. Recrystallization of this material from petroleum ether (b.p. 60–70°) yielded 0.1 g. (10%) of hexaphenyldi-

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[12] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 77 (1954).

[13] Unpublished studies.

[14] A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 278 (1954).

[15] All melting points are uncorrected. Reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen.

TABLE I

CLEAVAGES OF HEXAPHENYLDIGERMANE

Cleavage agent	Solvent	Initiator	Recov. hexaphenyldigermane, %	Deriv. (% yield)
Na/K	Diethyl ether	....	96, 80	None
Na/K	Di-*n*-butyl ether	....	None	Oil
Na/K	Xylene	....	None	Oil
Na/K	T.H.F.[a]	....	None	None
Na/K	Diethyl ether	T.H.F.	None	Triethylsilyltriphenylgermane (64.1)
Na/K	Diethyl ether	$(C_6H_5)_4Ge$	40.0	Triethylsilyltriphenylgermane (55)
Na/K	Diethyl ether	C_6H_5Br	None	Triethylsilyltriphenylgermane (55)
Na/K	Benzene	T.H.F.	76.7[b]	None
Na/K	G.D.M.E.[c]	....	64.0	None
Na/K	G.D.M.E.	....	28.0	Hexaphenyldigermoxane (24.7)
Cs	Diethyl ether	....	50.0	None
Phenyllithium	Diethyl ether	....	81.0	None
Na	Xylene	....	94.0	None
K	Xylene	....	40.0	Oil
K	G.D.M.E.	....	38.0	None
Li	G.D.M.E.	....	None	Triethylsilyltriphenylgermane (39.8)
O_2	Benzene	....	90.0	None
I_2	Chloroform	....	Quant.	None
I_2	Xylene	....	40.0	Hexaphenyldigermoxane (9.7)

[a] Tetrahydrofuran. [b] 13% of tetraphenylgermane also was recovered. [c] Ethylene glycol dimethyl ether.

germoxane (mixed melting point) melting at 183–185° and 0.1 g. (10%) of hexaphenyldigermane melting at 342–344°.

Attempted Cleavage of Hexaphenyldigermane with Sodium–Potassium Alloy in Diethyl Ether.—When 4.7 g. (0.00772 mole) of hexaphenyldigermane was treated with 1 ml. of 1:5 sodium–potassium alloy in 10 ml. of sodium-dried diethyl ether for a period of 24 hours, there was little evidence of reaction. After addition of 2.64 g. (0.015 mole) of *p*-bromotoluene in 100 ml. of dry ether, the mixture was stirred 6 hours and then hydrolyzed by the dropwise addition of water. Filtration of the reaction mixture yielded 4.4 g. (96% recovery) of hexaphenyldigermane melting at 341.5–343°. Another attempt under the same conditions yielded 3.7 g. (80% recovery) of starting material melting at 342–343.5°.

Attempted Cleavage of Hexaphenyldigermane with Sodium in Refluxing Xylene.—When 5.0 g. (0.00823 mole) of hexaphenyldigermane was refluxed with 0.4 g. (0.0165 g. atom) of sodium in 50 ml. of sodium-dried xylene for 28 hours and the mixture was cooled and the excess sodium destroyed by addition of the residue to absolute ethanol, there was recovered 4.7 g. (94%) of hexaphenyldigermane melting at 336.5–342°.

Attempted Cleavage of Hexaphenyldigermane with Cesium in Diethyl Ether.—To 2.4 g. (0.0078 g. atom) of cesium was added 4.7 g. (0.00772 mole) of hexaphenyldigermane and 15 ml. of sodium-dried ether and the mixture was stirred 48 hours. Then about 50 ml. of toluene was added and the excess cesium was destroyed by the dropwise addition of absolute ethanol. The ether and ethanol were distilled and the solution remaining was cooled and shaken with water in a separatory funnel. The mixture was filtered yielding 1.8 g. (38.3%) of hexaphenyldigermane melting at 338–342°. Concentration of the toluene filtrate yielded an additional 0.6 g. (12.7%) of starting material melting at 340–341°.

Cleavage of Hexaphenyldigermane with Sodium–Potassium Alloy in Refluxing Di-*n*-butyl Ether.—To 5.0 g. (0.00823 mole) of hexaphenyldigermane was added 1 ml. of 1:5 sodium–potassium alloy and 30 ml. of di-*n*-butyl ether. This mixture was refluxed 6 hours and then allowed to stir 20 hours without refluxing. Water then was added to the stirring mixture and after 15 minutes it was filtered yielding 0.5 g. of brown infusible material which was insoluble in all solvents tried. The organic layer was separated and concentrated by distillation, leaving a yellow oil. This oil was distilled at 150° (0.1 mm.), yielding a colorless oil which has not been identified.

Cleavage of Hexaphenyldigermane with Sodium–Potassium Alloy in Refluxing Xylene.—A mixture of 5.0 g. (0.00823 mole) of hexaphenyldigermane, 1.1 ml. of 1:5 sodium–potassium alloy and 50 ml. of sodium-dried xylene was refluxed 23 hours giving a brown-colored solution. This solution was hydrolyzed by the dropwise addition of water, and the mixture was filtered, giving 0.5 g. of infusible material. The organic layer was separated and distilled yielding a yellow oil. Upon distillation at 150° (0.1 mm.) a colorless oil was obtained which has not been identified.

Attempted Cleavage of Hexaphenyldigermane with Sodium–Potassium Alloy in Benzene.—To 4.3 g. (0.00708 mole) of hexaphenyldigermane was added 1.5 ml. of 1:5 sodium–potassium alloy and enough sodium-dried benzene to make a slurry. The mixture was stirred 40 minutes while a green color developed; then an additional 45 ml. of benzene was added and the mixture was stirred 6 hours. At the end of this time a large amount of white solid was still visible, so 20 drops of tetrahydrofuran was added and the mixture was stirred 90 hours longer. The excess alloy then was amalgamated[16] and the black suspension was transferred to another flask. Color test I[17] was positive at this point. To this stirring mixture was added 1.5 g. (0.014 mole) of trimethylchlorosilane, and the mixture was stirred 1 hour. Then water was added dropwise and the mixture was stirred 0.5 hour; filtration yielded 3.3 g. (76.7% recovery) of hexaphenyldigermane melting at 332–339°. The benzene layer was separated and dried over anhydrous sodium sulfate, then the benzene was distilled, leaving a solid weighing 1.0 g. and melting at 233–300°. Washing this 3.3 g. of solid with ether yielded 3.2 g. of hexaphenyldigermane melting at 342–343°. Recrystallization from benzene of the 1.0 g. of solid obtained above yielded 0.1 g. of hexaphenyldigermane melting at 344–345° and 0.7 g. (13%) of tetraphenylgermane (mixed melting point) melting at 229–235°.

Triphenylgermylpotassium.—To 5.0 g. (0.00823 mole) of hexaphenyldigermane in 10 ml. of sodium-dried ether was added 2 ml. of 1:5 sodium–potassium alloy. The mixture was stirred 5 minutes and 20 drops of tetrahydrofuran was added. Within 2 minutes after the addition of the tetrahydrofuran a light brown color was evident. After stirring 30 minutes an additional 30 ml. of dry ether was added and the mixture was stirred 27 hours. The excess alloy was then amalgamated and the triphenylgermylpotassium suspension was transferred to another nitrogen-flushed flask by pouring under a stream of nitrogen. To this stirring suspension was added 2.5 g. (0.0165 mole) of triethylchlorosilane in a dropwise fashion. The mixture was stirred 1 hour after the last addition of the halide, and then it was hydrolyzed by the dropwise addition of 50 ml. of water. The ether layer was separated and dried over anhydrous sodium sulfate, and the

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(16) See reference (9) for the use of mercury to remove the excess sodium–potassium alloy in the preparation of triphenylsilylpotassium.

(17) H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

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°.

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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

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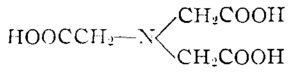
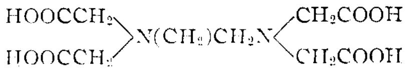
Disodium N,N′-dibutylethylenediamine-N,N′-dimethylenesulfonate, tetrasodium N,N′-ethylenediaminetetramethylenesulfonate, trisodium nitrilomonoacetatedimethylenesulfonate, disodium nitrilohydroxyethyldimethylenesulfonate, trisodium 2-aminobenzoate-N,N-dimethylenesulfonate and trisodium nitrilotrimethylenesulfonate 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.



$$\mathrm{HOOCCH_2{-}N}\begin{array}{l}\diagup\mathrm{CH_2COOH}\\ \diagdown\mathrm{CH_2COOH}\end{array}$$

I



$$\begin{array}{r}\mathrm{HOOCCH_2}\diagdown\\ \mathrm{HOOCCH_2}\diagup\end{array}\mathrm{N(CH_2)CH_2N}\begin{array}{l}\diagup\mathrm{CH_2COOH}\\ \diagdown\mathrm{CH_2COOH}\end{array}$$

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).