added slowly. The solution was allowed to warm up slowly to room temperature and was then boiled until the hydrogen peroxide had completely decomposed. The flask was then cooled in ice, and 1.5 ml. of concentrated sulfuric acid was added. The uracil-6-C^{14}-4-aldehyde acetal, which precipitated, was hydrolyzed and the sulfur dioxide expelled by boiling the mixture for 2 minutes. The flask was again cooled in ice, 1.20 g. (12 mM.) of chromic acid was added, followed by 1.5 ml. of concentrated sulfuric acid. The solution was allowed to stand at room temperature for two hours, was heated to 85° for 15 minutes, and cooled in ice. The precipitate of orotic acid was filtered, washed with cold water, and was recrystallized from dilute hydrochloric acid (Norit), and then from hot water. The yield of orotic acid-6-$C^{14}\cdot H_2O$ was 475 mg. (2.7 mM.), and represented a 65% yield from the thiouracil acetal or 38% over-all from barium carbonate.

The identity of the compound was established by means of a sharp decomposition point of 345°, a neutral equivalent of the anhydrous compound of 158 (calcd. 156), and an ultraviolet absorption identical to that reported in the literature.[14] That the compound was more than 99% homogeneous was demonstrated by filter paper chromatography in two sets of solvents (phenol, water; and butanol, propionic acid, water). Specific activity, 1.9×10^6 c./m./mg., 1.7 μc/mg.

Summary

1. Oxalacetic acid-1-C^{14} (3-ketosuccinic acid-1-C^{14}) has been synthesized in good yield by pyrolysis of di-*t*-butyloxalacetate.

2. Orotic acid-6-C^{14} (4-carboxyuracil-6-CH) has been synthesized by extensive experimental modifications of a known synthesis.

[14] H. K. Mitchell and J. F. Nyc, THIS JOURNAL, **69**, 674 (1947).

RECEIVED APRIL 3, 1950

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Compounds of Germanium and Hydrogen. III. Monoalkylgermanes. IV. Potassium Germanyl. V. Electrolysis of Sodium Germanyl[1]

BY GORDON K. TEAL[2] AND CHARLES A. KRAUS

In an earlier paper, Carney[3] has described a convenient method for the preparation of monogermane and has shown that it reacts quantitatively with sodium in liquid ammonia to form sodium germanyl, a salt which is readily soluble in liquid ammonia.

It is well known that salts of the type MAR_3, where M is an alkali metal, A is a fourth group element and R is an organic radical, react readily with alkyl halides according to the equation[4]

$$MAR_3 + R'X = R'AR_3 + MX \qquad (1)$$

It seemed of interest, therefore, to interact sodium germanyl with alkyl halides in expectation of producing the corresponding alkyl germanes. Methyl-, ethyl- and propylgermanes were prepared in this way.

Since sodium germanyl is an electrolyte, it was of interest to study the products of its electrolysis in liquid ammonia. Using a mercury cathode, we might expect to obtain the digermane, Ge_2H_6, at the anode. Actually, the anode reaction was found to proceed as

$$6GeH_3^- + 2NH_3 = 6GeH_4 + N_2 + 6e^- \qquad (2)$$

Finally, potassium germanyl was prepared by the method used earlier by Carney in preparing sodium germanyl. Excess metal was found to have no action on the germanyl ion, but potassium amide enters into reaction with it.

III. Monoalkylgermanes

1. **Apparatus and Procedure.**—Sodium germanyl was prepared according to the method of Carney and the apparatus employed was much the same as that of Carney.[3] Methyl iodide and methyl and propyl bromides were introduced into the reaction mixture with a stream of ammonia vapor. Methyl- and ethylgermane are evolved as gases as reaction proceeds. They were collected over water and later purified by scrubbing out ammonia with moist phosphorus pentoxide and water with dry pentoxide. The resulting gases were cooled to liquid nitrogen temperature and permanent gases were eliminated with a pump. The residual material was fractionated at a series of temperatures. The final products were stored in weighed glass containers.

Propylgermane separates out as a liquid in the bottom of the reaction tube. This material was vapor distilled with ammonia into a special receiver which carried a tube of small diameter at the bottom. The propylgermane collected in this tube, and the layer of ammonia above it was withdrawn therefrom through a capillary. The germane was then slowly distilled through a tube of calcium chloride to remove ammonia. The germane was condensed at liquid air temperature and thereafter distilled through a tube of moist phosphorus pentoxide and condensed in weighed fragile bulbs.

2. **Analytical Procedure.**—Germanium was determined by oxidation with fuming sulfuric and nitric acids as described in earlier papers.[5]

However, because of the volatility of the germanes, the procedure was modified slightly. The known sample of germane was condensed on 3 cc. of fuming sulfuric acid in a glass tube at liquid air temperatures, all gases having been removed previously with a pump. After condensation, the tube was sealed and warmed to room temperature. The tube, on removing from the liquid air bath, should be warmed rapidly with the hand, or otherwise, so as to melt the acid next the walls; on slow warming, the expansion of the acid may crack the containing tube. The lower end of the tube and its contents are now heated to 250° in a bath for several hours. It is then carefully opened and 1 cc. of fuming nitric acid is added. After standing at room temperature for several hours, the contents are washed into a weighed Pyrex test-tube and 5 cc. of fuming nitric acid is added. The tube is heated to

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[1] This paper is based on a portion of a thesis submitted by Gordon K. Teal in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1931.

[2] Edgar L. Marston Scholar, Brown University, 1927–1928; University Fellow, 1928–1929; Metcalf Fellow, 1929–1930. Bell Telephone Laboratories, Murray Hill Laboratory, Murray Hill, N. J.

[3] Kraus and Carney, THIS JOURNAL, **56**, 765 (1934).

[4] Kraus, *Chem. Revs.*, **8**, 251 (1931).

[5] Kraus and Brown, THIS JOURNAL, **52**, 3693 (1930).

just below the boiling point of the mixture with an air stream carrying off the vapors. When the water has been carried off, the acids are fumed off and the tube is weighed back to determine the weight of GeO_2.

3. **Molecular Weights.**—The molecular weight of the germanes was determined by filling the vapors into a weighed flask of approximately 125-cc. volume, the pressure and temperature of the vapors being determined. The flask was weighed against a counterpoise of nearly the same volume and surface area.

4. **Methylgermane.**—Methylgermane, prepared as described above, was condensed from the weighed storage cylinder onto the fuming sulfuric acid as already described. The results of two analyses follow: g. sample, 0.1125, 0.1306; g. GeO_2, 0.1296, 0.1503; % Ge found: 80.00, 79.86; calcd. for CH_3GeH_2: Ge, 80.09.

Vapor density determinations yielded the following results: volume of gas, cc. (S. T. P.), 27.03, 30.61; wt., g., 0.1095, 0.1242; mol. wt. found: 90.75, 90.89; calcd. for CH_3GeH_3: mol. wt., 90.65.

Methylgermane freezes at approximately −158° and boils at approximately −23°. The gas has a pungent odor characteristic of volatile germanium compounds.

5. **Ethylgermane.**—Ethyl bromide was treated with sodium germanyl as outlined above and samples were analyzed as already described: g. sample, 0.1524, 0.1383; g. GeO_2, 0.1525, 0.1385; % Ge found: 69.42, 69.49; calcd. for $C_2H_5GeH_3$, Ge, 69.37.

Vapor density determinations yielded molecular weights as follows: cc. gas (S. T. P.), 23.66, 26.41; wt., g., 0.1078, 0.1229; mol. wt. found: 104.26, 104.24; calcd. for $C_2H_5GeH_3$: mol. wt. 104.66. Ethylgermane boils at approximately 9.2°; it solidifies at liquid nitrogen temperature but not at the temperature of liquid oxygen. The odor of this compound resembles that of the methyl derivative.

6. **Propylgermane.**—Samples of propylgermane were prepared and analyzed as described above: g. sample, 0.1533, 0.2752; g. GeO_2, 0.1361, 0.2440; % Ge found: 61.56, 61.55; calcd. for $C_3H_7GeH_3$: Ge, 61.17.

Vapor density determinations yielded molecular weights as follows: cc. gas (S. T. P.), 15.40, 41.83, 40.84; wt., g., 0.0821, 0.2252, 0.2118; mol. wt. found: 119.42, 120.59, 116.17; calcd. for $C_3H_7GeH_3$: mol. wt., 118.68.

The compound is a liquid boiling slightly above room temperature. It has a pungent odor resembling that of the other germanes.

7. **Reaction with Methylene Bromide.**—Sodium triphenylgermanyl reacts with methylene bromide according to the equation

$$2NaGePh_3 + CH_2Br_2 + NH_3 = Ph_3GeNH_2 + CH_3GePh_3 + 2NaBr^{6} \quad (3)$$

It was thought that with the smaller GeH_3 group, two germanium atoms might be coupled to the same carbon atom. It appears, however, that reaction proceeds according to the equation

$$2NaGeH_3 + CH_2Br_2 + NH_3 = H_3GeNH_2 + CH_3GeH_3 + 2NaBr \quad (4)$$

6.51 mmoles of sodium germanyl reacted with 3.03 mmoles of methylene bromide. The evolved gases were collected over water and purified as described above. They were then condensed at liquid air temperature and fractionated. 1.20 mmoles of gas was pumped over between −133 and −113° at a pressure of 1 cm. This gas had a molecular weight of 77.4; it evidently consisted of germane with a slight admixture (5%) of methylgermane. The total amount of germane obtained was 1.14 mmoles.

The fraction of gas taken over between −108 and −60°, 1.83 mmoles, had a molecular weight of 92.3. This was evidently, for the most part, methylgermane, whose molecular weight is 90.65. The melting point and boiling point of this product checked with those of methylgermane. Less than 1 cc. of gas was obtained that liquefied under 12 cm. pressure at 25°. It had an extremely nauseating odor. Conceivably, this may have been digermanylmethane.

Thus 6.51 mmoles of sodium germanyl reacted with 3.03 mmoles of methylene bromide and there were obtained 1.14 mmoles of germane and 1.89 mmoles of methylgermane. Approximately one-half of the germanium was unaccounted for. In all likelihood, this was the germanylamine, H_3GeNH_2, which may have reacted with water in the collecting tower or with the moist phosphorus pentoxide. The monogermane probably resulted from the reaction of sodium germanyl with ammonium bromide formed by the ammonolysis of methylene bromide.

It seems that the main product of reaction of sodium germanyl with methylene bromide is methylgermane according to equation (4). However, side reactions evidently occur. In the case of tin, the existence of the volatile compound, $(CH_3)_3SnNH_2$, has been established.[6a]

IV. Potassium Germanyl

1. **Preparation and Properties.**—A weighed sample of potassium was treated with germane in a weighed reaction tube according to the procedure of Carney.[3] Reaction proceeded readily with the evolution of hydrogen. On completion of the reaction the gases were swept out, the ammonia was evaporated at −33° and the reaction tube was exhausted and weighed: 0.09013 g. K (2.481 m. at.) yielded 0.2856 g. $KGeH_3$ (2.489 mmoles); calcd. for $KGeH_3$, 0.2846 g. (2.481 mmoles).

Potassium germanyl is very soluble in liquid ammonia, its saturated solution containing 4.604 moles of ammonia per mole of salt. The vapor pressure of the saturated solution at −33.3° is 20.4 cm. It crystallizes from ammonia as a white crystalline solid. From the pressure–concentration diagram of the system it was shown that the solid is ammonia-free. It decomposes slowly at liquid ammonia temperature and more rapidly at room and higher temperatures. It appears to be somewhat more stable than the corresponding sodium compound.

2. **Stability of the GeH_3^- Ion toward Metals and Amides.**—The purity of the product obtained on treating the alkali metals with germane indicated that the GeH_3^- ion is stable in the presence of alkali metal. To establish this more definitely, 2.056 mmoles of $KGeH_3$ was treated with 1.847 m. atoms of potassium in a weighed reaction tube. On standing 24 hours, only 2 or 3 cc. of hydrogen was evolved although the solution was concentrated to the point where metallic reflection began to appear.

A weighed, rusty iron nail was then introduced. Hydrogen was evolved and the solution was decolorized at the end of half an hour. The evolved gas was then collected and its volume and density were determined. There were found 5.832 mmoles of hydrogen in excess of that due to the formation of KNH_2, and 0.15 mmole of germane. The presence of germane was confirmed by the germanium mirror formed on passing the gases through a hot tube.

After removing the ammonia, the reaction tube was exhausted and weighed. The product weighed 0.3870 g.; the sum of the weights of potassium germanyl and potassium was 0.3377 g. The residue had a brownish-red color. The gain in weight was 50 mg., not counting 11.5 mg. of germane that was collected with the gases. The large volume of hydrogen evolved is quite extraordinary, indicating extensive reaction.

The reaction of the germanyl ion with sodium amide appears to be similar to that with potassium amide but it is much slower.

The action of the amides of the germanyls is, perhaps, not surprising. The fourth group elements have a marked affinity for nitrogen at the expense of hydrogen. Thus, with triethylsilane, we have the reaction

$$2Et_3SiH + KNH_2 = KN(SiEt_3)_2 + 2H_2{}^{7} \quad (5)$$

In the case of sodium and potassium germanyls, the problem is complicated because several reactions appear to be involved.

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[6] Kraus and Nutting, THIS JOURNAL, **54**, 1622 (1932).

[6a] Kraus and Neal, *ibid.*, **52**, 695 (1930).

[7] Kraus and Nelson, *ibid.*, **56**, 195 (1934).

V. Electrolysis of Sodium Germanyl

On electrolysis of sodium germanyl between a platinum anode and a mercury cathode, germane and nitrogen are produced at the anode according to equation (2). Electrolyses were also carried out between two platinum electrodes.

1. **Apparatus and Procedure.**—Sodium germanyl was prepared in a cylindrical cell provided with two movable platinum electrodes. After preparation of the solution, mercury was introduced under air-free conditions and one electrode was immersed under the mercury while the other, a platinum disk, was lowered to within about 1 cm. of the mercury surface. The platinum disk served as anode and mercury as cathode; the sodium dissolved in the mercury as rapidly as formed on electrolysis. When electrolyzing between platinum electrodes, the mercury was left out of the apparatus.

The current passing through the cell was measured with a milliameter, the voltage across the cell with a voltmeter. By means of a resistance in the line, the voltage was varied so as to keep the current substantially constant at about 50 milliamperes. Initially, a current of 50 milliamperes was obtained with a potential of 7.9 volts; when electrolysis was nearly complete, the potential was 113 volts.

When electrolysis of the salt was nearly complete, the gases were collected and purified, and their volume and density determined. A portion of this gas was passed through a liquid air trap to separate the permanent from the condensable gases. The volume and density of both fractions were determined. The percentage of nitrogen and hydrogen in the permanent fraction was then computed on the assumption that only these gases were present.

2. **Electrolysis of $NaGeH_3$ with Mercury Cathode.**—The results of a typical experiment are given in Table I.

TABLE I

Initial Products of Electrolysis of $NaGeH_3$

Mmoles $NaGeH_3$	4.043
Meq. electricity	4.01
Non-condensable gas, mmoles	0.624
Nitrogen	0.551
% theory	82.4
Hydrogen	0.073
Condensable gas, mmoles	3.43
% theory as GeH_4	85.6
Mol. wt. found	78.4
Mol. wt. GeH_4, theory	76.63
Moles GeH_4/mole N_2	6.25

The molar ratio of germane to nitrogen approximates the theoretical ratio of 6 as closely as might be expected. The yield of gases is somewhat low. Some losses, perhaps the major, were due to solubility of gases in the water of the collecting tube. There seems little doubt that the anode reaction occurs according to equation (2).

So long as sodium germanyl was present in significant amount, the mercury surface remained bright and there was little or no evolution of gas at the cathode. In a number of experiments, the cathode mercury was withdrawn on completion of electrolysis of the salt. The amalgam was decomposed with water, the aqueous solution of sodium hydroxide was separated and neutralized with sulfuric acid and the sodium determined as sodium sulfate. The results of three such determinations are shown in Table II.

TABLE II

SODIUM FOUND IN AMALGAM

Wt. Na_2SO_4 obtd.	0.2088	0.1931	0.8971
M. atoms Na obtd.	2.938	2.719	5.591
Mmoles $NaGeH_3$ used	2.922	2.978	5.791

The above results show that the sodium amalgamated with the mercury of the cathode substantially in quantitative amount.

3. **Electrolysis of Ammonia.**—After substantially complete electrolysis of the $NaGeH_3$, gas was evolved from both electrodes. The cathode crusted over and at times it was necessary to break the crust by a stream of ammonia vapor passed through the mercury. The evolved gases were collected, purified and their composition determined as before. The results of one such experiment are presented in Table III. The solution was that remaining after obtaining the results of Table I.

TABLE III

Products of Electrolysis after Removal of $NaGeH_3$

Mmoles N_2	0.343
Mmoles H_2	1.144
Mmoles GeH_4	0.067
Total meq. electricity	2.378
Meq. elect. cor. for GeH_4	2.311
Meq. H/F	0.99
Meq. N/F	0.297
Moles H_2/mole N_2	2.92

It is evident that little germanium remained after completion of the initial electrolysis as reported in Table I. On further electrolysis, hydrogen and nitrogen were obtained in a molar ratio of 3/1 and in amount equivalent to charge passed through the solution.

The products indicate the electrolysis of ammonia. Just what the electrode reactions were remains uncertain. The production of nitrogen at the anode indicates the discharge of an amide ion. The hydrogen corresponds to the discharge of an ammonium ion at the cathode. The source of the ammonium ion remains obscure. Ammonia itself is not ionized to an appreciable extent. Thus, Hnizda[8] has obtained ammonia having a specific conductance of 1×10^{-11} mho, and the true value for pure ammonia is probably much lower. The amount of sodium present in the above experiment was very small and scarcely capable of carrying the current actually obtained.

4. **Electrolysis of $NaGeH_3$ between Platinum Electrodes.**—Electrolyses were also carried out between platinum electrodes of 1 sq. cm. area. From 10 to 50 ma. of current was passed through the solution. Initially, a blue color, due to sodium, appeared at the cathode and spread through the solution. The metal, however, reacted with ammonia to form amide and little current appeared to have been carried by the metal.

Four successive samples of gas (the first three small and the fourth large) were taken and analyzed. The first sample contained a small amount of germane, later samples very little. The analysis of the residue on completion of electrolysis after passage of 2.3 equivalents of electricity/mmole of $NaGeH_3$ showed a loss of 0.100 mmoles of $NaGeH_3$ out of a total of 2.929 mmoles, or, approximately, 3%.

The bulk of the evolved gas consisted essentially of hydrogen and nitrogen in the molar ratio of 3/1 as indicated by its density.

The absence of any considerable amount of germane, even in the early stages of electrolysis, is surprising. Evidently, the bulk of the current is carried by a compound which is formed rapidly as electrolysis proceeds. There is little doubt that $NaNH_2$ is formed by the sodium that appears at the cathode but sodium amide, as was pointed out above, reacts with the germanyl ion and this reaction may be quite rapid as indicated by the results with potassium amide. The evolution of nitrogen at the anode accords with the discharge of an amide ion and its conversion to nitrogen and ammonia.

An electrolysis was carried out with a solution of sodium amide, using a mercury cathode. The solubility of sodium amide is low and it is a poor electrolyte. It was diffi-

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[8] Hnizda and Kraus, THIS JOURNAL, **71**, 1565 (1949).

cult to maintain an adequate current through the solution. After electrolyzing for several hours with the current ranging from 50 to 1 ma. 7.9 cc. of gas was collected having a molecular weight of 22.14, which corresponds to 77.46% of nitrogen, assuming the remaining gas to be hydrogen. It does not seem possible to ascribe the results with sodium germanyl with platinum electrodes to the electrolysis of sodium amide. It seems more likely that substances are formed by interaction of the germanyl ion with sodium amide that lead to the observed results.

Summary

1. Methyl-, ethyl- and propylgermanes have been prepared by the reaction of sodium germanyl with the appropriate alkyl halides in liquid ammonia solution.

2. The reaction of methylene bromide with sodium germanyl is complex; the chief product is methylgermane.

3. Potassium germanyl has been prepared by reaction of monogermane with the metal in liquid ammonia solution. One mole of potassium germanyl is soluble in 4.604 moles of ammonia; the vapor pressure of the saturated solution is 20.4 cm. at −33.3°.

4. On electrolyzing sodium germanyl between a platinum anode and a mercury cathode, a reaction occurs at the anode: $6GeH_3^- + 2NH_3 = 6GeH_4 + N_2 + 6e^-$. When electrolysis of the salt is substantially complete, hydrogen and nitrogen are evolved in a molar ratio of 3/1; ammonia is electrolyzed.

On electrolysis of sodium germanyl between two platinum electrodes, hydrogen and nitrogen are evolved in a molar ratio of 3/1. A small amount of germane is evolved initially.

5. On electrolyzing sodium amide between a platinum anode and mercury cathode, little current passes because of the low solubility of the amide. A small quantity of gas was evolved of molecular weight 22, probably nitrogen admixed with hydrogen.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

The Kinetics of the Decomposition of Malonamic Acid in Aqueous Solutions

BY GEORGE A. HALL, JR.[1]

In a recent paper on the decomposition of malonic acid in aqueous solutions[2] it was suggested that the mechanism of the reaction involved the simultaneous first order decomposition of the unionized acid and of the acid malonate ion. It was of interest then to carry out a similar kinetic study on the decomposition of malonamic acid, the half amide of malonic acid. The results obtained might lend further support to the mechanism proposed for the malonic acid and would be of interest in observing the effect of substitution on the reaction rate.

This paper reports a study of the effect of changing *p*H on the rate of decomposition of malonamic acid. The results obtained are in agreement with the mechanism proposed for malonic acid.

Experimental

Materials.—Malonamic acid was prepared from diethyl malonate by the method of Galat.[3] The product obtained had a neutral equivalent of 101.9 (calcd. 103.1). The water used as a solvent was doubly distilled and of conductivity grade. The *p*H of the solution was varied by using either standard hydrochloric acid or sodium hydroxide solutions as solvents.

Procedure.—The rate of reaction was followed by the previously described procedure[1] of titrating the undecomposed acid. For those solutions containing hydrochloric acid or sodium hydroxide suitable corrections had to be made for the amounts of these substances present. The fact that the acidity of the solution decreased in the expected manner during the course of an experiment was taken as evidence that the reaction was indeed the decarboxylation of the acid since the only alternative reaction would have formed acetic acid and formamide with no change in acidity with time. Qualitative tests on the reacting solutions failed to detect the presence of ammonia which would have been formed had the amide hydrolyzed. The *p*H measurements were made at 25° on samples of the solutions used for the rate experiments with a Beckman glass electrode *p*H meter.

Results

The rate of decomposition of malonamic acid was measured at temperatures of 80 and 90° at concentrations of 0.01 and 0.1 *M* together with sufficient hydrochloric acid or sodium hydroxide

TABLE I

THE EFFECT OF CHANGING *p*H ON THE DECOMPOSITION OF MALONAMIC ACID

Initial concn., m./l.	Concn. of added substance, m./l.	*p*H	k_{80} sec.$^{-1}$ $\times 10^6$	k_{90} sec.$^{-1}$ $\times 10^6$	E_{80-90}, kcal.
0.0901	0.2045[a]	0.80	1.78	6.81	34.2
.0923	.1141[a]	0.91	1.78	6.79	34.1
.00902	.0474[a]	1.34	1.79	6.78	33.9
.00846	.0255[a]	1.51	1.79	6.69	33.5
.00885	.00630[a]	2.33	1.53	5.89	34.3
.00898	......	2.88	1.27	5.26	36.2
.00864	.00068[b]	2.98	1.22	4.74	34.5
.00845	.00106[b]	3.11	1.13	4.62	35.8
.00893	.00288[b]	3.41	0.967	3.90	35.5
.00808	.00346[b]	3.59	.838	3.32	35.0
.00834	.00479[b]	3.86	.568	2.11	33.4
.00850	.00528[b]	3.94	.468	1.92	35.9
.00807	.00598[b]	4.12	.343	1.27	33.3
.00847	.00699[b]	4.33	.216	.845	34.7

[a] HCl added. [b] NaOH added.

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[1] West Virginia University, Morgantown, W. Va.

[2] Hall, THIS JOURNAL, **71**, 2691 (1949).

[3] Galat, *ibid.*, **70**, 2596 (1948).