[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Reaction of Germanes. I. With Alkali Metals and Amides. II. Polyalkylgermanes. III. Phenyl Bromide and Sodium Germanyl[1]

BY SIVERT N. GLARUM[2] AND CHARLES A. KRAUS

Teal and Kraus[3] have described the preparation of monoalkylgermanes. In preliminary experiments, Teal[4] has shown that they react with alkali metals in liquid ammonia to form germanyl salts and hydrogen. This suggested that polyalkylgermanes might be prepared by treating such salts with appropriate alkyl halides. However, it was found that usually the reactions of alkali metals with alkylgermanes in liquid ammonia or ethylamine are not quantitative. More than one equivalent of germane is required to complete reaction with one equivalent of metal and the hydrogen evolved is greatly in excess of one atom per atom of metal. Before proceeding to the preparation of polyalkylgermanes, the reaction of alkylgermanes with metals was studied in liquid ammonia and in ethylamine. With the latter solvent, measurable amounts of ethane were evolved in the case of ethylgermane.

The chief product of reaction of alkylgermanes with alkali metals is the germanyl salt of the metal. Accordingly, such salts were employed in the preparation of polyalkylgermanes.

While alkyl groups are readily coupled with the germanium atom by interaction of their halides with germanyl ions, a similar coupling often fails to take place in the case of aryl halides. Sodium germanyl reacts with phenyl bromide according to the equation

$$\mathrm{NaGeH_3 + C_6H_5Br = NaBr + C_6H_6 + GeH_2} \quad (1)$$

The dihydride decomposes according to the equation

$$\mathrm{3GeH_2 = GeH_4 + 2GeH} \quad (2)$$

The monohydride, as Carney has shown,[5] decomposes according to the equation

$$\mathrm{GeH = Ge + {}^1/_2H_2} \quad (3)$$

I. Reaction of Germanes with Alkali Metals and Amides

1. **Apparatus and Procedure.**—Reactions of the alkali metals with alkylgermanes were carried out in closed systems in the absence of air. The apparatus employed was similar to that described in earlier papers.[5] All reactions were carried out at −33°.

Volatile alkylgermanes were carried into the reaction tube containing the alkali metal by means of a stream of ammonia vapor. Additions were continued until completion of reaction as was indicated by the disappearance of the blue color due to the metal. Less volatile germanes were condensed in the reaction tube or introduced in sealed fragile bulbs and metal was added until a faint, permanent blue color resulted.

When germanes are formed in the reaction tube, the lower alkylgermanes, being volatile at −33°, are carried over with ammonia vapor and collected over water. Less volatile germanes separate out in the reaction tube from which they may be distilled in a stream of ammonia vapor, condensed and separated from the supernatant ammonia.

All products of reaction were freed from ammonia by means of suitable absorbents. Gaseous products were cooled to liquid air temperature and the permanent gases were separated from the condensable gases. The condensable gases were evaporated at a series of temperatures to separate various constituents. The molecular weights of all volatile products were determined by means of their vapor densities.

2. **Ethylgermane and Sodium in Ammonia.**—In Table I are presented the results for the reaction of ethylgermane with sodium in liquid ammonia.

TABLE I

REACTION OF SODIUM AND ETHYLGERMANE IN LIQUID AMMONIA

Reaction	1	2	3
M.atoms Na	2.965	3.117	2.304
Mmoles $\mathrm{EtGeH_3}$	3.619	4.016	3.127
Mmoles $\mathrm{H_2}$	2.790	4.527	2.960
Moles $\mathrm{EtGeH_3}$/at. Na	1.23	1.29	1.36
Atoms H/at. Na	1.88	2.91	2.57

It will be noted that from 1.23 to 1.36 moles of germane was required to complete the reaction with one atom of metal. In place of one atom of hydrogen per atom of metal, from 1.88 to 2.57 atoms of hydrogen was produced.

On evaporating the ammonia, a glassy material was deposited which crystallized on warming to room temperature. The crystals were of a deep yellow color. On standing, hydrogen was slowly evolved; reaction (1) 2.785, (2) 1.619 mmoles of hydrogen. It is of interest to note that the total amount of hydrogen evolved, the sum of the initial and the decomposition reactions, is in the ratio of 3.1 atoms of hydrogen per atom of germanium. This result may be purely adventitious.

When the product of reaction (3) was treated with an excess of ammonium bromide, 1.926 mmoles of ethylgermane was recovered. Reaction occurred according to the equation

$$\mathrm{NaEtGeH_2 + NH_4Br = EtGeH_3 + NaBr + NH_3} \quad (4)$$

The recovered germane was approximately 62% of the total germane originally treated and 83% of that equivalent to the sodium used. The indications are that some of the germane may have reacted with ammonia to produce hydrogen and an amino derivative of germanium. In this connection, it may be noted that in reaction (2), when one mole of germane had been added per atom of sodium, the solution was allowed to stand one hour before completing the reaction. This reaction showed the greatest evolution of hydrogen per atom of sodium.

In the light of the above results we may tentatively draw the following conclusions: (1) The main portion of the germane reacts with metal according to the equation

$$\mathrm{EtGeH_3 + Na = NaEtGeH_2 + {}^1/_2H_2} \quad (5)$$

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(1) This paper is based on a portion of a thesis presented by Sivert N. Glarum in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1933.

(2) University Scholar, Brown University, 1929–1930; Metcalf Fellow, 1931–1932. Research Laboratory, Ciba Company, Wyncote, Pennsylvania.

(3) Teal and Kraus, THIS JOURNAL, **72**, 4706 (1950).

(4) Teal, Thesis, Brown University, 1931.

(5) Kraus and Carney, THIS JOURNAL, **56**, 765 (1934).

(2) There is a side reaction, probably catalyzed by metal, in which germanium is directly coupled to nitrogen somewhat as follows

$$EtGeH_3 + NH_3 \xrightarrow{Na} EtGeH_2(NH_2) + H_2 \quad (6)$$

This reaction may proceed all the way to $EtGe(NH_2)_3$ or one of its deammoniation products.

The large quantities of hydrogen evolved in these reactions can only be accounted for in some such way as indicated above. In this connection, it will be recalled that triethylsilane, in the presence of lithium, reacts with ethylamine according to the equation[6]

$$Et_3SiH + EtNH_2 \xrightarrow{Li} Et_3SiNH{\cdot}Et + H_2 \quad (7)$$

The large amounts of hydrogen evolved are in reasonably good accord with the above interpretation.

3. **Methylgermane and Sodium.**—Methylgermane reacted with sodium in liquid ammonia. The results were substantially the same as those obtained with the ethyl compound: m.atoms Na, 2.857; mmoles CH_3GeH_3, 4.279; mmoles H_2, 4.124. The hydrogen evolved corresponds to 2.89 at./at. Na and approximately a 50% excess of methylgermane was needed to complete the reaction.

A viscous, yellow liquid remained at room temperature when the ammonia was evaporated. No gas came off until the tube was surrounded by a water-bath at 35°. Decomposition was rapid at this temperature and a reddish-brown residue remained in the tube. The gas was collected and its volume and mol. wt. (2.56) were determined which identified it as hydrogen (4.279 mmoles). This corresponds to 3.0 at. H/at. Na or 2 at. H/mole CH_3GeH_3 reacted. The residue dissolved in liquid ammonia to form a red solution. Treating with ammonium bromide (6.392 mmoles) dispelled the red color without evolution of gas. As with the ethyl compound, the weight of the products exceeded that of materials used.

4. **Methylgermane and Lithium in Ethylamine.**—The reaction of monoalkylgermanes with lithium in ethylamine was investigated in the hope that reactions in the amine might prove to be more efficient than in ammonia. Such was found to be the case, although the efficiency for different germanes differed.

Reaction with 3.66 m.atoms of lithium was completed on addition of 3.81 mmoles of methylgermane with the evolution of 3.56 mmoles of hydrogen. The ratio H/Li is 1.95 which is markedly lower than for similar reactions in ammonia. The germane was very nearly equivalent to the lithium used. On adding excess ammonium bromide to the product of reaction, methylgermane was regenerated; 2.20 mmoles was recovered and some was left in the ethylamine.

5. **Ethylgermane and Lithium in Ethylamines.**—Four reactions were carried out between ethylgermane and lithium. The results are presented in Table II.

TABLE II

REACTION OF LITHIUM AND $EtGeH_3$ IN ETHYLAMINE

Reaction	1	2	3	4
M.atoms Li	3.42	8.14	8.59	7.59
Mmoles $EtGeH_3$	3.44	8.16	8.74	7.78
Mmoles H_2	1.319	5.07	3.44	2.76
Mmoles C_2H_6	0.729	1.67	1.83	1.66
Moles C_2H_6/atom Li	0.213	0.205	0.213	0.219
Atoms H/atom Li	0.767	1.248	0.801	0.728

The germane and the metal reacted in very nearly equivalent amounts. With the exception of experiment no. 2, the hydrogen evolved was low. Remarkable is the evolution of ethane amounting to 0.2 mole per atom of lithium. In three experiments, the ethane and hydrogen, together, are nearly equivalent to the lithium used. The molecular weight found for the ethane samples (No. 2, 3 and 4, Table II) were: 30.53, 31.88, 31.48; calculated for C_2H_6, 30.07.

The solution from reaction (1) was evaporated at −33°; a white solid was obtained. On warming to room temperature, the product turned yellow in color and hydrogen was evolved; a total of 3.36 mmoles of hydrogen was obtained, which corresponds to 1.96 atoms of hydrogen per atom of lithium. This is what would be expected if $C_2H_5GeH_2Li$ decomposed to yield C_2H_5GeLi and hydrogen.

The products of reactions (2), (3) and (4) were employed in the preparation of polyalkylgermanes as will be described below.

6. **Isoamylgermane**, prepared by the action of isoamyl bromide on sodium germanyl in ammonia, reacted with lithium in ethylamine. The results were: m.atoms Li, 2.32, mmoles $C_5H_{11}GeH_3$, 2.42; m.atoms H, 0.82. The lithium salt was not isolated but it yielded ethylisoamylgermane on treatment with ammonium bromide. The molecular weight found was 175; calculated 174.7. Other properties corresponded to those of known ethylisoamylgermane.

7. **Monogermane and Potassium Amide.**—The results for four reactions between germane and potassium amide are presented in Table III.

TABLE III

REACTION OF MONOGERMANE AND POTASSIUM AMIDE IN LIQUID AMMONIA

Reaction	1	2	3	4
Mmoles KNH_2	2.795	2.415	2.629	2.100
Mmoles GeH_4 reacted	2.862	2.614	2.772	2.278
Mmoles H_2	1.311	1.267	1.240	1.039
Atoms H/mole KNH_2	0.938	1.049	0.943	0.990

It will be noted that somewhat more than one equivalent of germane was required to complete reaction with one mole of potassium amide. Hydrogen was evolved, approximately in the ratio of one atom of hydrogen per mole of potassium amide.

Although a side reaction obviously occurred, the chief product of reaction was potassium germanyl, formed according to the reaction equation

$$GeH_4 + KNH_2 \longrightarrow KGeH_3 + NH_3 \quad (7a)$$

The presence of potassium germanyl was shown by the vapor pressure of the saturated solution after reaction. This was found to be 21 cm. at −33°. Teal[3] reports 20.4 cm. for the saturation pressure of this compound at −33.3°. The weights of the products from reactions (1) and (2) were found to be: 0.3646, 0.3112; calculated for $KGeH_3$, 0.3206, 0.2770, respectively.

On heating the products of reactions (1) and (2), gas was slowly evolved at 75° and rapidly at 100°. There were obtained, respectively, from reactions (1) and (2): 4.10, 3.58 mmoles of hydrogen, corresponding to 2.98, 2.97 atoms H/mole KNH_2. This ratio approximates what we should expect from the decomposition of $KGeH_3$.

The products of reactions (3) and (4) were treated with ammonium bromide in liquid ammonia. There were recovered: (3) 2.49, (4) 2.00 mmoles of germane of molecular weight 75.5, 76.3; calculated 76.6. Based on the potassium amide used, the recovery was approximately 95%. The weight of the residual products after withdrawal of all ammonia was approximately 10% greater than that calculated for potassium bromide. The presence of nitrogen in the residues was established. Evidently, there is a side reaction accompanying the reaction of germane and amide in which ammonia is involved.

II. Polyalkylgermanes

1. **Ethylisoamylgermane.**—Isoamyl bromide reacted with the product of reaction (3) (Table II). The product, after separating from the ammonia, was sealed into fragile

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[6] Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934).

bulbs. The total yield was 0.903 g. or 64% based on the weight of isoamyl bromide used. Vapor densities yielded molecular weights of 165.3, 186.3, 179.7; cryoscopic determinations in benzene yielded a molecular weight of 166; calculated for $(C_2H_5)(C_5H_{11})GeH_2$, 174.7.

Samples were analyzed for germanium by the method described by Teal: wt. subst. g., 0.2159, 0.1738; wt. GeO_2, 0.1291, 0.1042; % Ge found, 41.50, 41.61; calcd. for $(C_2H_5)(C_5H_{11})GeH_2$, 41.56.

Ethylisoamylgermane is a colorless liquid having a vapor pressure of approximately 1 cm. at room temperature. It is soluble in petroleum ether and benzene and insoluble in and unaffected by water; its vapor causes severe headache.

2. **Diethylisoamylgermane.**—The product of reaction (4) (Table II) which resulted from the reaction of 7.59 m.atoms of lithium and 7.78 mmoles of ethylgermane, reacted with 7.45 mmoles of isoamyl bromide in ethylamine. The product of this reaction, in turn, reacted with 7.27 m.atoms of lithium. The color due to the metal was dispelled at the end of about two hours. There was evolved 3.62 mmoles of hydrogen which was equivalent to the lithium used; the reaction was, therefore, not accompanied by side reactions.

The lithium salt of ethylisoamylgermanyl in the reaction tube now reacted with 7.66 mmoles of ethyl iodide. After allowing the reaction mixture to stand about one-half hour to ensure completion of the reaction, the ethylamine was distilled off under reduced pressure keeping the reaction tube at −33°. The residue consisted of a pasty white mass. The reaction tube was now removed from the ammonia-bath and connected to a weighed trap cooled with liquid ammonia. The product was distilled into the trap under a pressure as low as 0.1 mm. There were collected 1.376 g. of material. About two-thirds of the material was distilled from the trap and the remainder was filled into weighed, fragile bulbs.

Samples of the product were analyzed for germanium as in the case of ethylisoamylgermane; wt. g., 0.3228, 0.3491; wt. GeO_2, 0.1666, 0.1800; % Ge found, 35.82, 35.79; calcd. for $(C_2H_5)_2(C_5H_{11})GeH$, 35.80.

Diethylisoamylgermane is a colorless liquid with a vapor pressure of approximately 2 mm. at room temperature.

The amount of diethylisoamylgermane actually recovered corresponds to a yield of 87.2%, based on the amount of ethylgermane used in the initial preparation of the lithium salt. If the ethane produced in the initial reaction (4) (Table II) had been derived from the ethylgermanyl ion, the maximum yield would have been only 1.247 g. or 78.5%. Furthermore, if lithium reacted with ethylgermane to yield ethane, reaction would be expected to occur according to the equation

$$C_6H_5GeH_3 + 2Li + C_2H_5NH_2 = C_2H_6 + LiGeH_3 + LiC_2H_5NH \quad (8)$$

The actual yield of final product would have been cut down below 78.5% and intermediate products due to reaction with lithium ethylamide would have appeared in the final product. A somewhat analogous reaction takes place between sodium and tetramethyltin.[7]

III. Phenyl Bromide and Sodium Germanyl

1. **Experimental.**—Sodium germanyl and an equimolar quantity of phenyl bromide reacted under air-free conditions in liquid ammonia. There was no evidence of immediate reaction, since the solution remained perfectly clear and colorless. After standing 12 hours, to ensure complete reaction, the main portion of ammonia was evaporated at −33° by absorption in sodium iodide which was contained in an evacuated flask cooled with an ice-bath.

The products of reaction were recovered in four stages: **Stage 1.**—When as much ammonia as possible had been removed as described above, the reaction flask was shut off by a stopcock, and communication was made at intervals for brief periods between the flask containing sodium iodide and an evacuated tube containing moist phosphorus pentoxide. This operation served to carry over benzene which might have collected in the sodium iodide tube. Any ammonia transferred in this operation was completely absorbed by the phosphorus pentoxide. Next, the reaction flask, still at −33°, was opened to the phosphorus pentoxide tube; after practically all of the ammonia had been absorbed, connection was made to a weighed trap cooled with liquid air. A white solid collected in the trap. After 45 minutes, the solid in the reaction tube suddenly turned from a very light yellow to a dark yellow; thereupon, the stopcock connecting this tube to the rest of the system was closed. The material which had collected in the trap was identified as benzene through its vapor pressure, freezing point and vapor density. It was free of germane and other more volatile constituents. The amount of benzene collected was determined by weighing the trap.

Stage 2.—The reaction tube, still at −33°, was opened for three additional hours to the liquid air trap through the phosphorus pentoxide tube. Both germane and benzene were collected and the amount of each was determined.

Stage 3.—The reaction tube was slowly brought to room temperature and left for one hour. A trace of germane was obtained together with a small quantity of benzene.

Stage 4.—Finally, the tube was heated to 180°. Gases were removed as rapidly as formed and fractionated to separate the constituents. At the end, a small amount of gas was recovered at 300°.

2. **Results.**—The results of these several determinations are presented in Table IV, for a reaction in which 3.981 mmoles each of sodium germanyl and phenyl bromide were employed.

TABLE IV

PRODUCTS OF REACTION OF SODIUM GERMANYL AND PHENYL BROMIDE IN LIQUID AMMONIA

Stage	Benzene	Millimoles Germane	Hydrogen
1	1.471	None	None
2	1.823	1.125	None
3	0.229	Trace	Trace
4	0.379	0.208	1.26
Total	3.902	1.333	1.26
Calcd. (reactn. eq. (1), (2) and (3))	3.981	1.327	1.327
Mol. wt. found	79.4	76.3	2.16
Mol. wt. calcd.	78.1	76.6	2.02

From Table IV it will be noted that only benzene was recovered in stage 1 while the solution was being evaporated. This would seem to indicate that benzene was a primary product of reaction. The dry germanium dihydride, however, is quite unstable at −33°. During a period of three hours (stage 2), it decomposed, giving off approximately 85% of the germane required according to equation (2); the remainder was recovered when the material was warmed to room and higher temperature (stages 3 and 4). Little hydrogen was given off until the residue was heated to higher temperatures; this is the behavior expected of germanium monohydride.

The residue after thermal decomposition, which should consist of only germanium metal and sodium bromide, was weighed: wt. g. found, 0.6030; calcd., 0.6033. Sodium bromide was removed by washing with water and the germanium was put into solution with nitric acid. It was finally precipitated with hydrogen sulfide from a 6 *N* solution of sulfuric acid and converted to oxide by ignition: wt. GeO_2 found, 0.2789; calcd., 0.2795.

According to these data, the initial reaction takes place according to equation (1) and the decomposition of the products proceeds according to equations (2) and (3).

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[7] Kraus and Sessions, THIS JOURNAL, **47**, 236 (1925).

3. **Properties of GeH_2.**—Germanium dihydride is readily soluble in liquid ammonia, yielding a colorless solution. It appears to be stable in solution, since it does not become colored on standing for 24 hours. On removal of the ammonia at −33°, it is obtained as a white solid which can be pumped until it appears dry without immediate decomposition. On continued pumping at −33°, or on warming to room temperature, it decomposes to germane and the monohydride, GeH.

Royan and Schwarz[8] have described the preparation of a yellow, amorphous solid hydride of germanium to which they assign the formula, GeH_2. However, this hydride, which was prepared by the hydrolysis of CaGe in aqueous sulfuric acid solution, appears quite different from the dihydride herein described. It was stable when dry; when heated it decomposed producing only germanium and hydrogen.

4. **Action of Sodium on GeH_2.**—One gram atom of sodium reacts with one mole of germanium dihydride without evolution of gas to form a deep red solution. On adding ammonium bromide, monogermane is obtained.

Germanium dihydride was prepared by treating 2.84 mmoles each of sodium germanyl and phenyl bromide. A slight excess over one equivalent of sodium, 2.96 m.atoms, was cut into small pieces and added piecewise to the solution. Just before the last piece was added, the solution assumed a very dark, reddish-brown color. Addition of the last piece gave a blue solution characteristic of free metal. The blue color was discharged with ammonium bromide, the hydrogen was removed and an excess of ammonium bromide was added. This dispelled the red color and gas was evolved. The gas was purified and its molecular weight was determined: vol. of gas (S. T. P.), 25.08; wt. g., 0.0875; mol. wt. found, 78.19; calcd. for GeH_4, 76.63. The reaction was not investigated further.

Summary

1. Ethyl-, methyl- and isoamylgermane react with sodium in liquid ammonia to yield germanyl salts. The reactions are not quantitative; more than one equivalent of germane is required to complete reaction with a given quantity of metal and more than an equivalent amount of hydrogen is evolved.

2. With lithium in ethylamine, the reactions of monoalkylgermanes are more nearly quantitative but even here considerable side reaction occurs. With lithium and ethylgermane in ethylamine, a considerable amount of ethane is evolved; some, if not all, of this appears to come from the amine. Ethylisoamylgermane reacts substantially quantitatively with lithium in ethylamine.

3. Potassium amide reacts with germane in liquid ammonia to form potassium germanyl in considerable amount. The reaction is not quantitative and approximately one atom of hydrogen is evolved per mole of amide.

4. Ethylisoamyl- and diethylisoamylgermane were prepared by reaction of appropriate alkyl halides with lithium germanyls in ethylamine.

5. Phenyl bromide reacts with sodium germanyl according to the equation $C_6H_5Br + NaGeH_3 = C_6H_6 + GeH_2 + NaBr$. The digermane, GeH_2, is soluble in liquid ammonia from which it may be crystallized as a white solid. It decomposes slowly at −33° and rapidly at higher temperatures to form GeH_4 and GeH.

6. One mole of GeH_2 reacts with one atom of sodium to form a soluble salt. On addition of ammonium bromide, GeH_4 is evolved.

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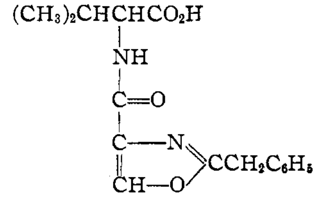
[8] Royan and Schwarz, *Z. anorg. allgem. Chem.*, **211**, 412 (1933).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Synthesis of N-(2-Benzoyl-4-oxazoloyl)-valine[1,4a]

BY HOMER ADKINS,[2] ROBERT M. ROSS[3] AND DOROTHY C. SCHROEDER[4]

Several investigations that have been carried out recently in this Laboratory were motivated by a desire to study the properties and methods for the preparation of certain substituted oxazoles and oxazolines. Reported in the present communication is the synthesis of a valine-substituted oxazole (I).[4a]



I

The crucial intermediate in the preparation of the oxazole I was found to be 2-benzyl-4-carbethoxyoxazole (VI). The English workers, Cornforth and Cornforth,[5] described an elegant synthesis of 2-methyl-4-carbethoxyoxazole, which method we found conveniently adaptable to the preparation of 2-benzyl-4-carbethoxyoxazole (VI). Since the completion of this investigation in 1948, Cornforth, Fawaz, Goldsworthy and Robinson[6]

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[1] Abstracted in part from the theses of Robert M. Ross and Dorothy C. Schroeder, presented to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree.

[2] Deceased August 10, 1949.

[3] Allied Chemical and Dye Corporation Fellow, 1947–1948. Department of Chemistry, University of Illinois.

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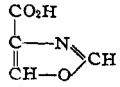
[4a] It was found convenient to name I as a derivative of 4-oxazoloic acid to which we assigned the structure



Thus, I will be referred to in this communication as N-(2-benzyl-4-oxazoloyl)-valine.

[5] Cornforth and Cornforth, *J. Chem. Soc.*, 96 (1947).

[6] Cornforth, Fawaz, Goldsworthy and Robinson, *ibid.*, 1549 (1949).