ence encountered in the rates make exact comparison unnecessary.

Discussion.—The results recorded in Fig. 10 bear a marked similarity to certain observations of Almquist and Black.[19] Following Almquist,[20] we can calculate an excess free energy for the surface iron atoms inactivated toward the isotope exchange by oxygen poisoning. Using 0.3% for the concentration of the water in the hydrogen, we obtain a value of 8 kcal. for this quantity. This value must lie at the lower end of an energy spectrum of surface sites for stepwise removal of the oxygen from the hydrogen produces a stepwise increase in the rate of isotope exchange.

Thus, it seems certain that the surface concerned with nitrogen isotope exchange is heterogeneous. Since it has a free energy some 8 or more kcal. in excess of bulk iron, it would seem reasonable to assume that it is a small portion of the total surface.

It is to be noted that, depending upon the purity of the gas used for reduction, one may reproduce on the same catalyst and in the same system, both the rapid exchange observed by Emmett,[16] or the slow exchange observed by Joris and Taylor.[17]

The results obtained with rhenium show great variation. Rapid reaction at 500° is observed if proper reduction techniques are employed. If, on the other hand, tank hydrogen is used for reduction, rates of the order of magnitude observed in the horizontal chamber are obtained. Since Joris and Taylor used a horizontal reactor in which hydrogen was passed over the catalyst during reduction, while Emmett used vertically disposed beds of material, the conclusion is reasonable that when one reduces a catalyst by passing hydrogen *over* it, the surface is left in a partially oxidized condition. It may very well be that unless reduction is carried out by passing the hydrogen with turbulence *through* the well-packed catalyst bed, the process controlling the escape of oxygen from the surface may be too slow to allow reduction of the highly active sections of the catalyst necessary for nitrogen exchange in any reasonable period of time.

General Discussion

The results described in the previous four sections warrant the conclusion that rhenium catalysts have many properties in common with those of iron. There is a similarity in the kinetics of ammonia decomposition. Both show three distinct, if overlapping, types of interaction with hydrogen and, in both, the addition of hydrogen to the reaction mixture accelerates the nitrogen isotope exchange. Although rhenium is active at a somewhat higher temperature, suitable promotion might reduce this difference.

The non-uniformity of the surface of the metallic rhenium employed has been demonstrated. Both the results with hydrogen adsorption, and those with oxygen poisoning of the surface for nitrogen isotope exchange place such a conclusion beyond reasonable doubt. The negligible effect of nitrogen adsorbed from the gas phase on both macro- and micro-decomposition of ammonia is an indication of the same fact.

It would seem evident that studies of reactions at surfaces by indirect techniques, *i.e.*, adsorption and isotope exchange should be conducted with extreme caution. Unless experimental conditions in the two cases are identical, such subsidiary reactions may occur on parts of the surface which are not operative in the catalysis.

PRINCETON, N. J. RECEIVED JULY 26, 1950

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[19] J. A. Almquist and H. L. Black, THIS JOURNAL, **48**, 2814 (1926).

[20] J. A. Almquist, *ibid.*, **48**, 2820 (1926).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Studies Relating to Boron. III. Some Reactions of the Aliphatic Boranes with Alkali Metals in Liquid Ammonia and Ethylamine[1]

BY J. EDWARD SMITH[2] AND CHARLES A. KRAUS

In this paper are presented the results of a study of reactions of the alkali metals with trimethyl- and tributylboron in liquid ammonia and ethylamine. In ammonia, the metals react quantitatively with both of the boranes according to the equation $Alk_3B \cdot NH_3 + M = MNH_2BAlk_3 + {}^1/_2H_2$. In ethylamine the reactions are more complex; the amount of hydrogen evolved is less than equivalent to the metal required to complete reaction. The solutions of the reaction product of lithium with trimethylborane in ethylamine evolves two moles of methane per mole of borane. In the case of tributylborane, butane is evolved but the reaction is slower and the maximum amount of butane that may be obtained has not been determined. The reaction products of potassium with the boranes are also unstable in ethylamine solution but their rates of decomposition are much slower than those of the corresponding lithium compounds.

I. Introduction

Although the chemistry of boron has received increasing attention in recent years, few investigations have been reported concerning the properties of the alkali metal salts of the alkyl boranes or salts derived from their addition compounds with ammonia and the amines.

Krause and Polack[3] have shown that aromatic boranes in ether solution add an atomic equivalent of alkali metal to form highly colored salts, which correspond to the formula Ph_3BM, where M is an alkali metal[4]; Robinson has shown that a similar reaction occurs in ethylamine. The salt obtained here is associated with one molecule of solvent.

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[1] This paper is based on a portion of a thesis submitted by J. Edward Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1930.

[2] University Fellow, Brown University, 1928–1929; du Pont Fellow in Chemistry, 1929–1930.

[3] E. Krause and H. Polack, *Ber.*, **59**, 777 (1926).

[4] A somewhat similar affinity for electrons is exhibited by tri-β-naphthylborane, which forms the compound Na_2BAr_3. H. E. Bent and M. Dorfman, THIS JOURNAL, **57**, 1259 (1935). B_2H_6 also adds alkali metal forming $K_2B_2H_6$. A. Stock, W. Sutterlin and F. Kuozen, *Z. anorg. allgem. Chem.*, **225**, 225 (1935).

However, when triphenylborane is treated with an alkali metal in liquid ammonia, a mixed reaction was found to occur.[5] Judging by the amount of hydrogen evolved, the main reaction is one involving solvent in which sodium ammidotriphenylboride is formed according to the equation

$$Ph_3B + Na + NH_3 = Ph_3BNH_2Na + {}^1/_2H_2$$

This reaction illustrates the propensity of boron to form coördinate linkages with electron donor groups. In general, the triphenylboron group is found to form complexes with small negative ions, some of which possess a high degree of stability.[6] The alkyl boranes do not appear to react with alkali metals to form compounds of the type Alk_3BM as do the aryl boranes.[7]

It seemed of interest to study the reactions of the alkali metals with aliphatic boranes in liquid ammonia and ethylamine. Trimethyl- and tributylborane were selected for this purpose. Since these substances form quite stable addition compounds with the ammono bases, it is probable that we are here dealing with the chemistry of these addition compounds.

Sodium and potassium react quantitatively with trimethylborane in liquid ammonia, producing the corresponding salt in the sense of Equation (1). Thus, sodium forms sodium ammidotrimethylboride; the same compound may be prepared by treating trimethylborane with sodium amide in liquid ammonia. Likewise, lithium reacts quantitatively with trimethylborane in ethylamine to form lithium ethylammidotrimethylboride. Concentrated solutions of this salt are not stable; decomposition takes place fairly promptly with the production of two moles of methane per mole of product. In ethylamine, the reduction with potassium does not proceed in as straightforward a fashion as in ammonia. The amount of hydrogen evolved was found to be as low as 0.56 atom per mole of borane. Contrary to expectation, there was no direct evidence to indicate that metal had, in part, added to the borane as is the case with the triphenyl compound. Treating the product with ammonium bromide regenerated approximately 90% of the borane, but hydrogen was not formed.

Reaction of the alkali metals with tri-*n*-butylborane proceeds in much the same manner as with the methyl compound. In liquid ammonia, potassium reacts quantitatively with the borane forming potassium ammidotri-*n*-butylboride. But, as with the methyl compound, the yield of hydrogen in ethylamine is less than the calculated value. Even lithium does not appear to react quantitatively in the sense of Equation (1) since only approximately 93% of the calculated amount of hydrogen was recovered. Concentrated solutions of the lithium salt decompose slowly to evolve butane. Whereas the lithium salts were found to be uniformly unstable when in solution in ethylamine, for all practical purposes, the potassium salts are stable. This may be related in some manner to the relative basic strengths of the amides. Potassium amide is a much stronger base than lithium amide.

II. Apparatus and Materials

The apparatus employed in this study was similar to that described in earlier papers from this Laboratory which deal with reactions in ammona and the amines.[8] Reactants were sealed in weighed, fragile bulbs which were broken in the reaction tube in the absence of air. Usually, the borane was first converted to its ammono derivative in the reaction vessel by treating it with solvent vapor. If the alkali metal was also contained in a fragile bulb, it was then broken and solvent was condensed on the reactants. Lithium was introduced from an addition tube after the borane had been put into solution. Gases evolved during reaction in liquid ammonia were collected over water, purified by treating with moist phosphorus pentoxide, and stored over mercury. Gases contaminated with ethylamine were first passed through a cold trap to remove most of the solvent; they were then treated as outlined above. Volumes and gas densities were determined by standard methods.

Boron Trichloride.—Boron trichloride (b.p. 12.5°) was employed as source material for preparing the boranes. It was prepared by reaction of chlorine with calcium boride under rigid exclusion of air and moisture at a temperature of 550°. The product was purified by fractional distillation. The chief impurity, aside from chlorine, traces of which were removed by means of mercury, proved to be silicon tetrachloride, b.p. 58–62°.

Boron tribromide was prepared in the same way as the chloride. The yield was lower, b.p. 91°.

Amminotrimethylborane.—Trimethylborane was prepared by the action of methylmagnesium iodide on boron trichloride in ether solution. The ether and borane were distilled under nitrogen into a second vessel where the crude product was converted to its ammonia derivative by passing ammonia vapor into the solution. The bulk of the ether was distilled away and residual solvent was removed by heating to 95° *in vacuo*. The product was recrystallized from petroleum ether (45–55° fraction) and, finally, from liquid ammonia. After sublimation, the product melted at 73–74°. This value checks well with the value of 73.2–73.7° reported recently by Brown, *et al.*[9]

Ethylamminotrimethylborane.—The ethylamine derivative was prepared from the ammonia derivative by dissolving the latter in ethylamine and distilling off excess solvent. The process was repeated several times to ensure complete replacement of ammonia by ethylamine. After removing solvent, the addition compound was sublimed under a pressure of 0.10 mm. into a trap cooled with liquid ammonia and was purified by recrystallizing from petroleum ether (45–55°) in a closed system, m.p. 24–24.5°. The same melting point has been reported by Brown.[10]

Tri-*n*-butylborane.—This compound was prepared by reaction of boron trichloride with *n*-butylmagnesium bromide in ether solution. The product was purified by fractional distillation, b.p. 77–82° at 8 mm. Johnson, Snyder and Van Campen[11] report 90–91° at 9 mm.

Anal. Boron, g., 0.2992, 0.3006; % B found: 5.95, 5.92. Calcd. for $C_{12}H_{27}B$, B, 5.94.

III. Reaction of Trimethylborane with Alkali Metals

1. **Sodium in Ammonia at −33°.**—Sodium reacts quantitatively with trimethylborane in liquid ammonia according to the equation

$$(CH_3)_3B + NH_3 + Na = (CH_3)_3BNH_2Na + {}^1/_2H_2 \quad (2)$$

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(5) W. B. Robinson, Thesis, Brown University, 1928.

(6) C. A. Kraus and W. W. Hawes, THIS JOURNAL, **55**, 2776 (1933); D. L. Fowler and C. A. Kraus, *ibid.*, **62**, 1143 (1940).

(7) However, Booth has obtained evidence that tri-*n*-butylborane reacts with sodium–potassium alloy in ether solution. Colored solutions were formed on standing several weeks at room temperature. Manipulation or heating caused the color to disappear; attempts to isolate a compound were unsuccessful. R. B. Booth, Thesis, Brown University, 1934.

(8) C. A. Kraus and F. E. Toonder, THIS JOURNAL, **55**, 3547 (1933); C. A. Kraus and E. S. Carney, *ibid.*, **56**, 765 (1934).

(9) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *ibid.*, **66**, 435 (1944).

(10) H. C. Brown, *ibid.*, **67**, 1452 (1945).

(11) J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., *ibid.*, **60**, 115 (1938).

It seems probable that the metal replaces a hydrogen in the coördination compound, $(CH_3)_3B\cdot NH_3$. In a typical reaction, 2.587 m.at. (0.0595 g.) of sodium was treated with 2.586 mmoles (0.1886 g.) of amminotrimethylborane in a weighed reaction tube. When reaction was completed (24 hours) as evidenced by the disappearance of the blue color, the hydrogen was collected and measured and identified by its mol. wt.; yield 2.581 m.at. or 0.998 atom H/mole of $(CH_3)_3B$. Solvent was evaporated and the reaction tube was exhausted and weighed. Found: 0.2468 g.; calcd. for $(CH_3)_3BNH_2Na$, 0.2454 g. The salt was redissolved and an equivalent quantity of ammonium bromide was added from an addition tube attached to the reaction tube. On evaporating the ammonia, the product was extracted with ether and trimethylborane was recovered. Evidently, reaction with sodium occurred in the sense of Equation (2); treating the product with ammonium bromide regenerated the borane according to the equation

$$(CH_3)_3BNH_2Na + NH_4Br = (CH_3)_3B\cdot NH_3 + NaBr + NH_3 \qquad (3)$$

Reaction at −78° proceeded somewhat slower than at −33°. Approximately 36 hours were required for the reaction: m.at. Na, 7.379; mmoles $(CH_3)_3B$, 7.345; m.at. H, 7.095; at.H/mole $(CH_3)_3B$, 0.966.

Sodium Ammidotrimethylboride.—The sodium salt obtained in the above reaction proved to be identical in every respect with the product obtained directly by treating trimethylborane with sodium amide. As with the aromatic boranes,[6] trimethylborane adds sodium amide in liquid ammonia according to the equation

$$(CH_3)_3B\cdot NH_3 + NaNH_2 = (CH_3)_3BNH_2Na + NH_3 \qquad (4)$$

The reaction was carried out in a weighed tube; sodium amide was prepared *in situ* from sodium in liquid ammonia by catalyzing the conversion to amide with a rusty iron wire. Sodium amide is virtually insoluble and deposits as a white powder. On adding the borane (as the ammonia complex), reaction commenced immediately as evidenced by the solution of the sodium amide. After standing 24 hours, the ammonia was evaporated, leaving a viscous solution. Residual solvent was removed with a pump and the tube was exhausted to constant weight. Data on two reactions follow: wt. Na g., 0.0633, 0.0464; $(CH_3)_3B\cdot NH_3$, 0.1939, 0.1475; wt. product, 0.2495, 0.1889; calcd. for $(CH_3)_3BNH_2Na$, 0.2524, 0.1914.

Anal. To determine ammonia, the compound was hydrolyzed in a closed system in the absence of air; evolved ammonia was collected in standard acid. The trimethylborane was removed by absorption in a column packed with moist sodium hydroxide pellets. Nitrogen: wt. subst. g., 0.1914, 0.3396; cc., 0.1137 *N* HCl, 17.60, 30.19; %N found, 14.64, 14.16. Calcd. for $(CH_3)_3BNH_2Na$: N, 14.76. Sodium: sodium was determined by titrating the hydroxide solution remaining after hydrolysis. Wt. subst. g., 0.1914, 0.3396; cc., 0.1137 *N* HCl, 17.70, 31.20; %Na found, 24.18, 24.02; calcd. for $(CH_3)_3BNH_2Na$: Na, 24.22.

Sodium ammidotrimethylboride is a white, crystalline solid, very soluble in ether and ammonia, slightly soluble in benzene and insoluble in petroleum ether. It oxidizes readily in air and inflames if the oxygen content is raised sufficiently. It may be purified readily by recrystallizing from ether.

2. **Lithium in Ethylamine.**—Substances which ammonolyze in liquid ammonia may often be prepared and handled readily in ethylamine. Hence, it was thought that under suitable conditions, it might be possible to obtain direct addition of metal to an aliphatic borane in this solvent. However, reaction with lithium proceeds quantitatively according to the equation

$$(CH_3)_3B\cdot C_2H_5NH_2 + Li = (CH_3)_3BNHC_2H_5Li + {}^1/_2H_2 \qquad (5)$$

On standing, the resulting solution of lithium salt decomposed; methane was liberated, but the nature of the nonvolatile decomposition product was not determined.

A weighed, fragile bulb of amminotrimethylborane was broken in the reaction tube and was converted to the ethylamine derivative as described above. Approximately 15 cc. of ethylamine was condensed in the tube and an equivalent amount of lithium was added from the addition tube. The blue color of free metal disappeared in 18 hours leaving a clear, colorless solution; the gas evolved was collected, measured and identified as hydrogen. A viscous solution remained on evaporating the ethylamine. M. at. Li, 3.170, 3.083, 3.429; mmoles $(CH_3)_3B$, 3.097, 3.016, 3.439; m. at. H, 3.090, 3.007, 3.257; at. H/mole $(CH_3)_3B$, 0.998, 0.997, 0.950. Since the amount of hydrogen evolved is consistent with Equation (5), it seems evident that lithium ethylimidotrimethylboride was formed.

Decomposition of the Lithium Salt.—Gas was evolved on allowing a solution of the lithium salt to stand 24 hours at −33°. Heating to 100° after removing solvent failed to produce significant amounts of additional gas. The gas was identified as methane from its molecular weight and by analysis. Mmoles $(CH_3)_3B$, 3.016, 3.442; mmoles gas collected, 6.155, 6.754; mol. wt. (av. several determinations), 16.57, 16.43; calcd. for CH_4, 16.05. Moles CH_4/mole $(CH_3)_3B$, 2.04, 1.96. Evidently, two moles of methane are produced per mole of lithium salt, indicating substantial rupture of carbon–boron bonds. The gas was analyzed for carbon and hydrogen by exploding with oxygen and determining the carbon dioxide and water which were formed. Expressed as the mole ratio of $CH_4{:}H_2O{:}CO_2$, the results were: 1.00:1.98:1.03, 1.00:1.93:0.96.

The residue after decomposition was a white crystalline solid whose properties varied somewhat depending upon prior treatment. If the substance was not heated, it was readily soluble in ether. After heating to 100°, it was insoluble in ether, partially soluble in ethylamine and insoluble in ammonia. A marked loss in weight was realized after ammonia was condensed on the product and was then allowed to evaporate. Analysis for nitrogen indicated the presence of more than one mole of ethylamine per mole of original borane.

3. **Potassium in Ethylamine.**—The reaction with potassium proceeded somewhat differently from that with lithium. The hydrogen produced was usually substantially below that required by Equation (5). M. atoms K, 2.821, 2.512, 3.297, 3.379; mmoles $(CH_3)_3B$, 2.822, 2.523, 3.270, 3.359; m. at. H, 2.254, 2.330, 2.324, 1.875; at. H/mole $(CH_3)_3B$, 0.799, 0.928, 0.711, 0.558.

The addition of ammonium bromide to a solution of the salt in liquid ammonia served to largely regenerate the borane (88% recovery), but no hydrogen or other gas was evolved; potassium was recovered quantitatively as KBr. Hydrogen would be an expected product if a portion of the metal had added directly to the borane; the low yield of hydrogen in the original reaction remains unaccounted for.

Although methane was evolved from a concentrated solution of the salt at room temperature, the decomposition was so slow that a quantitative recovery was not possible.

IV. Reaction of Tri-*n*-butylborane with Alkali Metals

1. **Potassium in Liquid Ammonia.**—Potassium reacts quantitatively with tri-*n*-butylborane in liquid ammonia forming hydrogen and potassium ammidotri-*n*-butylboride. Although reaction was extremely vigorous at first, approximately 4 hours was required to discharge the blue color of the solution. M. at. K, 3.120, mmoles $(C_4H_9)_3B$, 2.978, m.at. H, 2.591; at. H/mole $(C_4H_9)_3B$, 0.881. A viscous liquid remained after exhausting the reaction tube to constant weight with a Hyvac pump. However, the weight of product corresponded closely with that calculated for the potassium salt. Wt. K g., 0.1220, $(C_4H_9)_3B$, 0.5420; wt. product, 0.6999; calcd. for $(C_4H_9)_3BNH_2K$, 0.7062. The compound is exceedingly soluble in liquid ammonia and oxidizes readily in air.

2. **Potassium in Ethylamine.**—Whereas the reaction of potassium with tri-*n*-butylborane in ammonia appeared perfectly normal, in ethylamine it proceeded much like that with the methyl compound. Approximately one week was required for complete reaction and the amount of hydrogen produced was well below one equivalent. M. at. K, 2.718; mmoles $(C_4H_9)_3B$, 2.616; m. at. H, 1.593; at. H/mole $(C_4H_9)_3B$, 0.609. A viscous liquid remained after removing solvent with a pump; the product appeared stable in solution.

3. **Lithium in Ethylamine.**—Slightly less than an equivalent amount of hydrogen was recovered in the reaction with lithium in ethylamine. Approximately 40 hours was required for completion of the reaction. M. at. Li, 2.766,

4.409; mmoles $(C_4H_9)_3B$, 2.700, 4.240; m. at. H, 2.513, 3.970; at. H/mole $(C_4H_9)_3B$, 0.932, 0.936.

The concentrated solution of the salt slowly evolved butane, but the rate was too slow for quantitative recovery. At the same time, crystalline material separated. Butane was identified by its mol. wt.: wt. gas g., 0.0302, 0.1010; cc. (S.T.P.), 12.05, 38.57; mol. wt. found, 56.2, 58.7; calcd. for C_4H_{10}, mol. wt., 58.1. The weight of the dry product gave no clue as to its composition; an analysis for ethylamine gave 1.45 moles per mole of original borane.

PROVIDENCE, R. I. RECEIVED OCTOBER 22, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

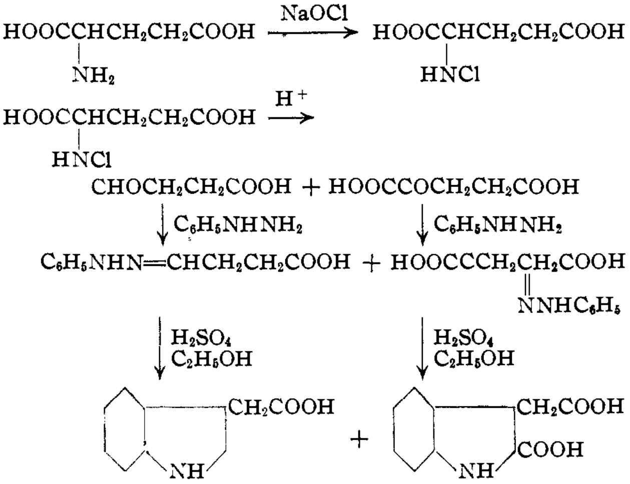
Synthesis of Indoleacetic Acid from Glutamic Acid and a Proposed Mechanism for the Conversion[1]

BY SIDNEY W. FOX AND MILON W. BULLOCK

An economical method for converting glutamic acid to indoleacetic acid, through the intermediate succinaldehydic acid phenylhydrazone, has been developed. α-Ketoglutaric acid has been found as a by-product in the preparation of the succinaldehydic acid. For the decomposition of the intermediate α-N-chloroaminoglutaric acid there is proposed a mechanism which explains the formation of all the products isolated from the reaction mixture.

Indoleacetic acid has been of interest in a large number of phytological applications which depend on its function as a growth hormone,[2-4] *heteroauxin*. Methods of preparation which might increase its general availability have been needed. The various syntheses of indoleacetic acid which may be found in the literature up until 1939 were critically reviewed by Harradence and Lions,[5] who stressed the inaccessibility of the starting materials. Since that time a number of other syntheses have been reported.[6-9] The methods which have been of most preparative value involve the introduction of the acetic acid residue into preformed indole by formaldehyde and hydrocyanic acid,[8] through gramine and cyanide,[9] by reaction of the indolylmagnesium iodide complex with chloroacetonitrile,[10] and by the reaction of indole with ethyl diazoacetate.[11] The principal other route to indoleacetic acid has been through succinaldehydic acid,[7,11,12] but this procedure has suffered from lengthy methods of preparation of the aldehyde. With the availability of glutamic acid[13] from large-scale manufacture however, it is possible to prepare succinaldehydic acid[14] rapidly, in quantity, and to convert it into the phenylhydrazone which serves as a convenient method of isolation. The precipitated oil can then be transformed into indoleacetic acid through the Fischer ring closure.

The synthesis of indoleacetic acid by this inexpensive conversion of glutamic acid has previously been noted,[15] but the conditions employed at the time did not give satisfactorily reproducible results.[16] This process, illustrated by the reactions below, has been brought under control with details that are presented in the Experimental section.



$$\underset{\text{NH}_2}{\text{HOOCCHCH}_2\text{CH}_2\text{COOH}} \xrightarrow{\text{NaOCl}} \underset{\text{HNCl}}{\text{HOOCCHCH}_2\text{CH}_2\text{COOH}}$$

$$\underset{\text{HNCl}}{\text{HOOCCHCH}_2\text{CH}_2\text{COOH}} \xrightarrow{\text{H}^+}$$

$$\text{CHOCH}_2\text{CH}_2\text{COOH} + \text{HOOCCOCH}_2\text{CH}_2\text{COOH}$$

$$\downarrow \text{C}_6\text{H}_5\text{NHNH}_2 \qquad \downarrow \text{C}_6\text{H}_5\text{NHNH}_2$$

$$\text{C}_6\text{H}_5\text{NHN}{=}\text{CHCH}_2\text{CH}_2\text{COOH} + \underset{\text{NNHC}_6\text{H}_5}{\text{HOOCCCH}_2\text{CH}_2\text{COOH}}$$

$$\downarrow \begin{matrix}\text{H}_2\text{SO}_4\\ \text{C}_2\text{H}_5\text{OH}\end{matrix} \qquad \downarrow \begin{matrix}\text{H}_2\text{SO}_4\\ \text{C}_2\text{H}_5\text{OH}\end{matrix}$$

Although many of the reactions recorded in the above sequence have appeared individually in the literature, it was necessary in this Laboratory to introduce modifications and integration of steps in order to obtain product on a practical scale of operation.

In addition to the succinaldehydic acid formed in the decomposition of the α-N-chloroaminoglutaric acid, a small amount of α-ketoglutaric acid also results, as shown above. The resultant α-ketoglutaric acid phenylhydrazone accompanies the desired product and cyclization of the crude oil gives some of the 2-carboxyindole-3-acetic acid. These two products are easily separated.

Since α-keto acids are not decarboxylated under the conditions employed in the decomposition of the α-N-chloroaminoglutaric acid, the α-keto acid cannot be an intermediate in the formation of the half-aldehyde. To account for the products formed in the reaction mixture the following mechanism

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(1) Journal Paper No. J-1756 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project No. 1110, Chemicals for Agricultural Utility. Also Paper V in a series, Amino Acid Conversion Products. Presented before the Division of Organic Chemistry at the American Chemical Society Meeting, September 8, 1950 at Chicago. From the Ph.D. thesis of Milon W. Bullock, 1950.

(2) F. W. Went and K. V. Thimann, "Phytohormones," The Macmillan Company, Inc., New York, N. Y., 1937.

(3) F. P. Mehrlich, U. S. Patent 2,428,335; *C. A.*, **42**, 717 (1948).

(4) G. S. Avery, E. B. Johnson, R. M. Addoms and B. F. Thompson, "Hormones and Horticulture," McGraw-Hill Book Co., Inc., New York, N. Y., 1947.

(5) R. H. Harradence and F. Lions, *Proc. Roy. Soc. N. S. Wales*, **72**, 221 (1938-1939).

(6) Z. Tanaka, *J. Pharm. Soc. Japan*, **60**, 17 (1940).

(7) Z. Tanaka, *ibid.*, **60**, 75 (1940).

(8) K. Bauer and H. Andersag, U. S. Patent 2,222,344.

(9) H. R. Snyder and F. J. Pilgrim, THIS JOURNAL, **70**, 3770 (1948).

(10) R. Majima and T. Hoshino, *Ber.*, **58**, 2042 (1925).

(11) R. W. Jackson and R. H. F. Manske, *Can. J. Research*, **13B**, 170 (1935).

(12) A. Ellinger, *Ber.*, **37**, 1801 (1904).

(13) S. W. Fox, *Can. Med. Assn. J.*, **56**, 76 (1947).

(14) K. Langheld, *Ber.*, **42**, 2371 (1909).

(15) F. J. Stevens and S. W. Fox, THIS JOURNAL, **70**, 2263 (1948).

(16) F. J. Stevens, Ph.D. thesis, Iowa State College, 1947.