

stirrer. The temperatures and the durations of the reaction for three experiments will be found in Table III. The distillation process was the same as that described for Procedure 2. For the first two runs, in which chloronitrile was recovered, corrected yields have been given. In this procedure, however, more polymerization occurred than in Procedure 2, but less than in Procedure 1.

TABLE III
DATA FOR EXPERIMENTS

Run	Approx. temp., °C.	Reaction time, hrs.	Yield, %	Yield (corr.), %
1	30	7-8	41	64.7
2	Refluxing	16	69.4	80.2
3	Refluxing	25	74.7	..

Summary

1. Cyclopropyl cyanide may be obtained in 75-90% yields by the action of sodamide on γ -chlorobutyronitrile in a liquid ammonia-ether solution. The reaction in ether solution appears to be less efficient.

2. Trimethylene chlorobromide may be prepared in 90-94% yields by the action of phosphorus tribromide on trimethylene chlorohydrin.

TROY, NEW YORK

NOTES

The Cholesterol Content of Shrimp Waste.—The ethyl ether extraction of the dried shrimp and shrimp waste prepared by Vilbrandt and Abernethy¹ produced a viscous oil, dark red by transmitted light and soluble in the common organic solvents. According to elemental analysis the oil contains no sulfur, halogens, nitrogen or heavy metals.

Treatment of the oil with alcohol at 60° precipitated an insoluble brown resinous material and subsequent cooling of the alcoholic solution to 0° effected a fairly rapid separation of monoclinic crystals from the viscous, red oily residue.

Purification of Crystals.—Decolorization of the hot alcoholic solution of the crystals thus obtained with animal charcoal and subsequent crystallizations from hot alcohol produced a material which melted at 146.5°. Measurements under the microscope showed monoclinic plates with angles of 79.5 and 100.5°. The average yield of these crystals from three separate crystallizations and purifications is 19.08% on the basis of the original oil. The total quantity of sterols in the shrimp waste was not determined.

Identification.—The purified crystals were then treated with digitonin by the method of Windaus² and further identified by the Liebermann³

¹ F. C. Vilbrandt and R. F. Abernethy, "Utilization of Shrimp Waste," United States Fisheries Document No. 1079 (1930).

² A. Windaus, *Chem.-Ztg.*, **37**, 1001 (1913).

³ Oliver Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, 1924, p. 123.

and the Hagersalkowski⁴ tests for cholesterol, obtaining positive tests. Further identification of the crystals as cholesterol was accomplished by the preparation of the benzoate⁵ and acetate⁶ derivatives.

The high cholesterol content of the shrimp oil led to feeding tests for antirachitic potency of the oil by the authors and F. P. Brooks,⁷ giving encouraging results. Since the extract of shrimp waste amounts to 2.25% of the waste, a production of 80,000 pounds of cholesterol could have been accomplished by the extraction of the waste of the 1927 crop of shrimp.

ROY F. ABERNETHY⁸
FRANK C. VILBRANDT⁹

RECEIVED AUGUST 4, 1930
PUBLISHED JULY 8, 1931

A Simple Method for the Preparation of Glycine.—The preparation of glycine by the classical method,¹ employing the reaction between monochloroacetic acid and ammonia, has proved generally unsatisfactory because of the lengthy procedures involved in the isolation of a product free from ammonia and chloride and because of the low yield of pure glycine resulting. Robertson² found after a careful study of the course of the reaction between monochloroacetic acid and ammonia, that the yield of glycine could be greatly increased by the use of a large excess of ammonia and that there occurred a corresponding decrease in the amount of imino-diacetic acid and trimethylene-amine-tricarboxylic acid, the principal impurities resulting from side reactions. Based upon this observation, he proposed a method in which a 60 to 1 molecular ratio of ammonia to monochloroacetic acid was employed. This increased the actual concentration of glycine formed in solution to 86% of the theoretical. While a 50% final yield of pure glycine was obtained, the isolation of the product was accomplished after the laborious and expensive procedure of removing the ammonium chloride by the use of silver oxide.

Since, when a large excess of ammonia was used, the concentration of glycine formed was large in comparison with the amount of side reaction products, the possibility of *direct* precipitation of glycine seemed worthy of investigation. As was suggested by Robertson, 60 moles of

⁴ D. Holde and E. Mueller, "Saponifiable Hydrocarbons, Fats and Waxes," 1922, p. 519.

⁵ S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 172.

⁶ R. J. Anderson, *J. Biol. Chem.*, 71, 707 (1926).

⁷ F. C. Vilbrandt, R. F. Abernethy and F. P. Brooks, "Preliminary Report on the Antirachitic Properties of Shrimp Oil," *THIS JOURNAL*, 52, 4940 (1930).

⁸ Department of Chemistry, University of North Carolina, Chapel Hill, N. C.

⁹ Department of Chemical Engineering, Iowa State College, Ames, Iowa.

¹ Kraut, *Ann.*, 266, 295 (1891).

² G. R. Robertson, *THIS JOURNAL*, 49, 2889 (1927).

ammonia and 1 mole of monochloroacetic acid were allowed to react. The excess ammonia was distilled off and the resulting aqueous solution was concentrated to a small volume. When 95% methyl alcohol was added to this solution, glycine promptly crystallized out and a 72–74% yield of an impure product resulted. By careful recrystallization a 60–64% yield of ammonia and chloride-free glycine was obtained. Our work does not indicate that the use of pyridine with methyl alcohol in the precipitation of glycine is necessary as was reported by Boutwell and Kuick.³ As a result of our experiments, a simple, rapid and inexpensive method for the preparation of pure glycine is offered.

Experimental

Method of Preparation.—One mole (94.5 g.) of monochloroacetic acid is added gradually with shaking to 4 liters of ammonium hydroxide (sp. gr. 0.90) in a 5-liter round-bottomed flask. When all of the monochloroacetic acid is dissolved and the solution is thoroughly mixed, the flask is stoppered and set aside undisturbed for forty-eight hours at room temperature. The solution, which is colorless or faintly yellow, is then concentrated on a water-bath under reduced pressure to a volume of about 200 cc. The concentrated aqueous solution is then made up to 250 cc. with water and transferred to a 2-liter beaker, and the glycine is crystallized out by gradually adding, with stirring, 1500 cc. (six volumes) of 95% methyl alcohol (the use of absolute methyl alcohol offers no advantage). The mixture is placed in an ice box for four to six hours to allow complete crystallization. The supernatant liquid is then decanted from the crystals onto a Büchner funnel, the remaining crystals are suspended in approximately 500 cc. of 95% methyl alcohol, and are transferred to the filter. The beaker is rinsed twice with 100–120 cc. portions of 95% methyl alcohol, and the rinsings are poured over the crystals in the funnel. Finally, as much of the liquid as possible is pressed out, the crystals are washed with a small amount of ethyl ether, and dried in air. A yield of 54–55 g. of glycine, 72–74% of the theoretical, is obtained.

Since the product contains a trace of ammonia (by Nessler's reagent) and chloride (by silver nitrate), a second crystallization is carefully made by dissolving the crystals in 210–215 cc. of water, with warming, and precipitating with 5 volumes (1250 cc.) of 95% methyl alcohol. After crystallization in an ice box, the glycine is filtered, washed and dried, as previously outlined. A yield of 48–49 g., 64–65% of the theoretical, results. If the product still shows a faint trace of ammonia, a second recrystallization may be made, which will yield 45–48 g. The final product is white and finely crystalline. The recovery of further amounts of glycine from filtrates is not practicable because only a small amount

³ P. W. Boutwell and L. F. Kuick, *THIS JOURNAL*, **52**, 4166 (1930).

of the product, heavily contaminated with ammonium chloride, is obtained. The recovery of the excess ammonia and of the methyl alcohol greatly reduces the cost of preparation by this method. The use of permutit in removing the last traces of ammonia was not found to be superior to precipitation with methyl alcohol alone.

Analysis of Product.—Molar solutions of five samples of glycine prepared by the above method showed no trace of ammonia with Nessler's reagent, nor of chloride with silver nitrate. Melting points and mixed melting points (with Eastman's ammonia-free glycine, No. 445) were determined by the capillary tube method. Both gave values of 236–239° (uncorrected), with decomposition and effervescence, after browning at 228°. Analyses for the nitrogen content, determined by the Kjeldahl method, gave values ranging from 18.44 to 18.76% (theoretical 18.67%).

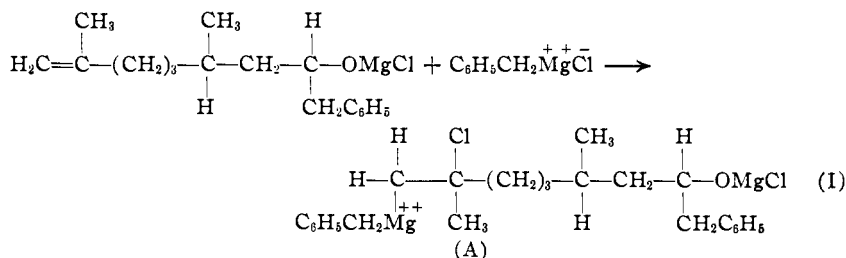
Summary.—1. A simple, inexpensive method for the preparation of glycine from monochloroacetic acid and ammonia is outlined.

2. A 60–64% yield of glycine free from ammonia and chloride is obtained.

CONTRIBUTION FROM THE
DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF COLORADO SCHOOL OF MEDICINE
DENVER, COLORADO
RECEIVED APRIL 21, 1931
PUBLISHED JULY 8, 1931

JAMES M. ORTEN
ROBERT M. HILL

The Purported Addition of Benzylmagnesium Chloride to the Ethylenic Linkage in Citronellal.—It has been suggested¹ that the recent² indirect proof offered for the non-addition of benzylmagnesium chloride to the ethylenic linkage in citronellal is not decisive, and that a new possible mechanism is



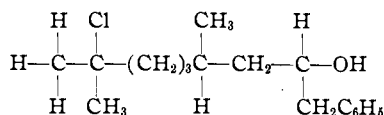
In this manner, "a complex molecule is obtained which is similar to that suggested by Rupe,³ except that the second molecule of the Grignard reagent is attached in a slightly different manner."

¹ Kharasch, "Annual Survey of American Chemistry," 1930, Vol. V, p. 193.

² Gilman and Schulz, *THIS JOURNAL*, **52**, 3588 (1930).

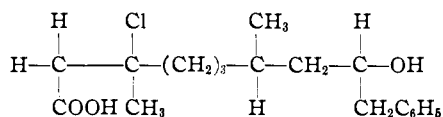
³ Rupe, *Ann.*, **402**, 161 (1914).

Actually, this mode of addition is quite unlike that proposed by Rupe. On hydrolysis, one would expect Compound (A) to give



and toluene. However, Rupe's analysis shows his product to contain no chlorine, and to have in place of the chlorine the equivalent of a benzyl group. Furthermore, the same product is obtained with benzylmagnesium bromide. Accordingly, Compound (A) is without any experimental support.

Granting that Compound (A) is correct, it represents an unsymmetrical organomagnesium compound of the general formula $\text{R}-\text{Mg}-\text{R}'$. Although such compounds have not yet been prepared, it is known that the symmetrical $\text{R}-\text{Mg}-\text{R}$ compounds on carbonation (followed by hydrolysis) yield the corresponding carboxylic acids, RCOOH . We do not know how $\text{R}-\text{Mg}-\text{R}'$ compounds would behave on carbonation, but it appears altogether reasonable to expect them to give the two carboxylic acids, RCOOH and $\text{R}'\text{COOH}$, in varying quantities depending on the nature of the $\text{R}-$ groups. If this be true then Compound (A) on carbonation should give $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ and



Actually, the latter acid is not obtained, because when the reaction mixture of citronellal and an excess of benzylmagnesium chloride is carbonated, only phenylacetic acid is obtained, as evidenced by melting point, mixed melting point and neutralization equivalent.

The possibility that RMgX adds to an ethylenic linkage to give an $\text{R}-\text{Mg}-\text{R}'$ compound which might undergo but partial carbonation to give RCOOH to the exclusion of $\text{R}'\text{COOH}$ is rendered remote by other reported experimental evidence. First, a different RMgX compound (phenylmagnesium bromide) after reaction with citronellal and then carbonation gave presumably pure benzoic acid.² Second, if addition of RMgX to an ethylenic linkage did occur with olefins of a type to give rise to $\text{R}-\text{Mg}-\text{R}'$ compounds in which the $\text{R}-$ and the $\text{R}'-$ groups were closely related but not identical, then carbonation should give a mixture of acids, but no such mixtures have been obtained.⁴

⁴ Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928). Earlier pertinent references are contained in this article.

Our unavoidable conclusion is that benzylmagnesium chloride does not add to the ethylenic linkage in citronellal.⁵

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED JUNE 2, 1931
PUBLISHED JULY 8, 1931

HENRY GILMAN
W. F. SCHULZ

COMMUNICATIONS TO THE EDITOR

THE STABILITY OF NITROGEN PENTOXIDE AT 1000 ATMOSPHERES OF OXYGEN IN THE PRESENCE OF NITROGEN TETROXIDE

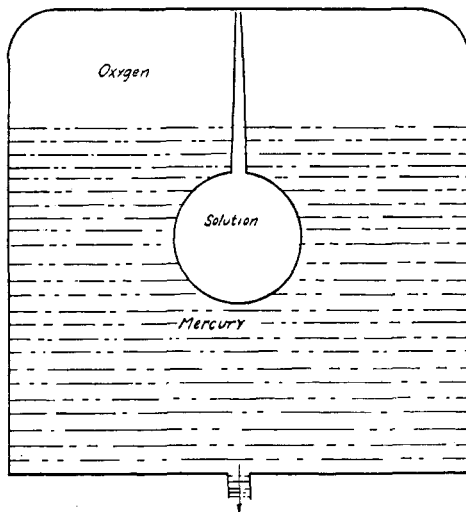
Sir:

The equilibrium



has been investigated at 1000 atmospheres' pressure of oxygen by dissolving nitrogen tetroxide and nitrogen pentoxide in carbon tetrachloride in an apparatus shown schematically in Fig. 1.

It was found that at this pressure of oxygen the reaction goes completely to the right. With the gas evolution apparatus used for analysis it was possible to detect as little as 0.5 cc. of oxygen, which, with the volumes of nitrogen pentoxide solution used, is equivalent to a partial pressure of 0.00155 atmosphere of nitrogen pentoxide at 25°. The partial pressure of nitrogen tetroxide in one of the runs was 0.710 atmosphere, so that the equilibrium constant in atmospheres is greater than 1.48×10^4 . The values given for the partial pressures depend on the assumption of a perfect solution of nitrogen tetroxide, nitrogen pentoxide and carbon tetrachloride and upon a solubility determination of nitrogen pentoxide in a solution of nitrogen tetroxide in carbon tetrachloride. This equilibrium constant gives a free energy change less



To pressure pump
and gage

Fig. 1.

⁵ Professor Rupe is in agreement with this conclusion, and he is now engaged in a further study of the constitution of the product obtained from citronellal and benzylmagnesium chloride.