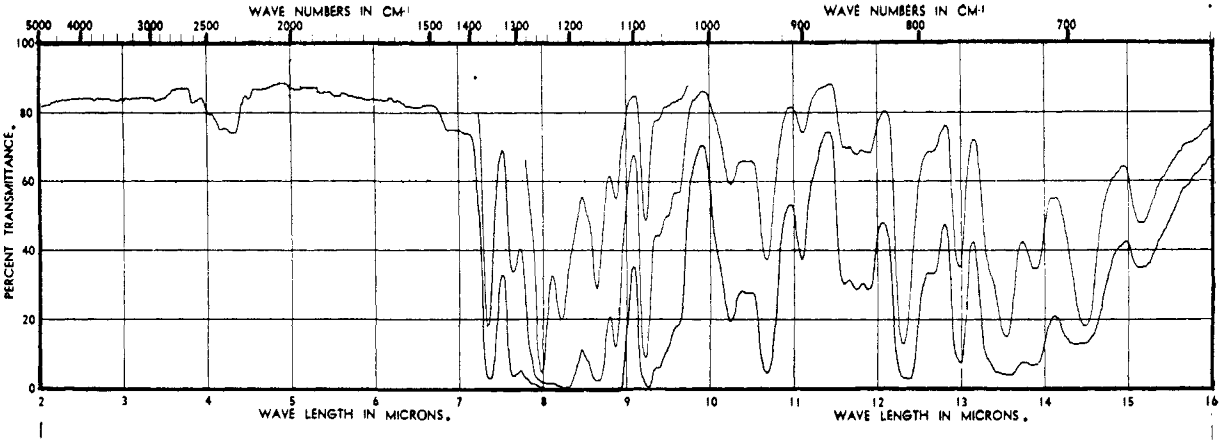

Fig. 3.—Infrared spectrum of 1-bromoundecafluoropentane: lower curve was taken in a 5-cm. gas cell; upper curves are for vapor diluted with dry nitrogen gas taken in same cell.

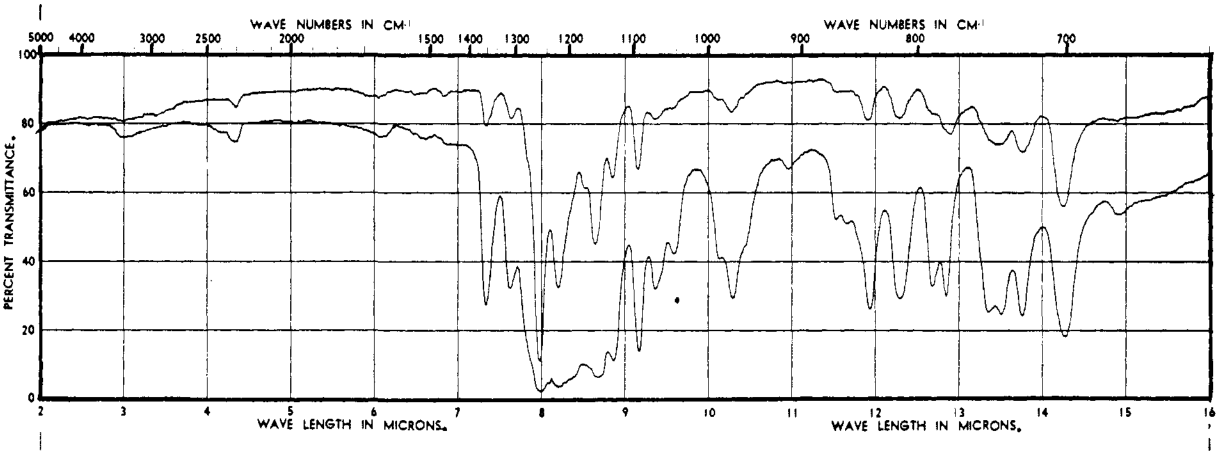

Fig. 4.—Infrared spectrum of 1-chloroundecafluoropentane: lower curve was taken in a 5-cm. gas cell; upper curve is for vapor diluted with dry nitrogen gas taken in same cell.

**Preparation of 1-Chloroundecafluoropentane.**—An excess of chlorine was passed through a long Pyrex tube, equipped with a Dry Ice refluxer and refrigerated collecting traps. The tube was partially filled with 23 g. (0.0546 mole) of powdered silver *n*-undecafluorocaproate, which was heated intermittently with a bunsen flame at approximately 100° for eight hours. The yield of AgCl was 93% of theory. After washing and drying there was isolated 11.84 g. (71.2% yield) of the water-white liquid, $n$-$C_5F_{11}Cl$., b.p. 59.0–59.5° (almost entirely 59.5° at 760 mm.).

*Anal.*[5] Calcd. for $C_5F_{11}Cl$: mol. wt., 304.5; C, 19.72. Found: mol. wt. (gas density balance), 304; C, 19.70.

**Acknowledgment**.—The authors wish to express their sincere appreciation to the Minnesota Mining & Manufacturing Co., Saint Paul, Minnesota, for supplying the perfluorocaproic acid used in these experiments.

THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY
PHILADELPHIA, PENNSYLVANIA RECEIVED AUGUST 27, 1951

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## Reductive Cyclization of Butyl Pyroglutamate. Synthesis of a New Nitrogen Heterocycle, Decahydrodipyrrolo[a,d]pyrazine

BY EDWARD SEGEL

The only reported product from the hydrogenation of the $\alpha$-amido ester, ethyl pyroglutamate, is 5-hydroxymethyl-2-pyrrolidone[1,2]; the amide group does not enter into the observed reaction. However, by using a somewhat higher reaction temperature (250°) than that used by Sauer and Adkins (210–220°),[1] the amide group can be completely hydrogenated. The amino alcohol, 2-hydroxymethylpyrrolidine, logically expected as the product, is not actually isolated; while it may have a transitory existence during the reaction, it cannot remain under the experimental conditions employed. The alkylating action of alcohols on amines at elevated temperatures in the presence of copper-chromium oxide catalyst and hydrogen is well established[3]; ring closure accompanying such alkylation has also been noted.[4,5] Since hydrogenation of the ester group of butyl pyroglutamate results in the formation of two alcohols, butanol, and 5-hydroxymethyl-2-pyrrolidone, either of which can then react with amino nitrogen when it arises by hydrogenation of the amide group. If the two

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(1) J. C. Sauer and H. Adkins, THIS JOURNAL, **60**, 402 (1938).

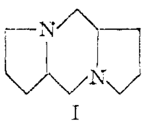
(2) H. Adkins and H. R. Billica, *ibid.*, **70**, 3121 (1948).

(3) H. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 26.

(4) J. P. Bain and C. B. Pollard, THIS JOURNAL, **61**, 532, 2704 (1939).

(5) B. G. Wilkes, U. S. Patent 2,479,657.

alcohols react with the amine at comparable rates, two products are possible, N-butyl-2-hydroxymethylpyrrolidine and decahydrodipyrrolo[a,d]pyrazine (I).



I

Compound I may be thought of as arising from ring closure between two molecules of 2-hydroxymethylpyrrolidine, the amino group of each being alkylated by the hydroxyl group of the other. The over-all reaction is another example of reductive cyclization, a concept employed in syntheses of the octahydropyrrocoline nucleus[6] and 1-azabicyclo compounds.[7]

Two products were actually isolated from the reaction mixture resulting when butyl pyroglutamate was hydrogenated over copper–chromium oxide at 250°. One, a white crystalline solid, exhibited a titration curve corresponding to a diamine of molecular weight 167 (theory for Compound I, 166); its elementary analysis was in good agreement with that calculated for decahydrodipyrrolo[a,d]pyrazine. The other product was a liquid exhibiting the titration curve of a monoamine of molecular weight 152 (theory for N-butyl-2-hydroxymethylpyrrolidine, 157).

If the line of reasoning outlined above is correct, hydrogenation in the absence of butanol should eliminate the formation of N-butyl-2-hydroxymethylpyrrolidine and correspondingly increase the yield of decahydrodipyrrolo[a,d]pyrazine. This conclusion was confirmed by experiment. Since the hydrogenation of butyl pyroglutamate occurs stepwise, it was possible to prevent butylation. Butyl pyroglutamate was hydrogenated in dioxane at 150°, the solvent was completely removed by distillation and hydrogenation was completed at 250° in fresh dioxane. By this procedure the yield of decahydrodipyrrolo[a,d]pyrazine was almost tripled. Furthermore, when a sample of pure 5-hydroxymethyl-2-pyrrolidone was hydrogenated, the yield of decahydrodipyrrolo[a,d]pyrazine was practically quantitative.

### Experimental

Dioxane used as reaction medium was purified according to the method of Fieser.[8] Catalyst was prepared as described by Riener.[9] Hydrogenations were effected in a 480-ml. stainless steel bomb at a hydrogen pressure of 2000–3000 p.s.i.

**Butyl Pyroglutamate.**—Two moles of commercial glutamic acid, 16 moles of butanol and 2.5 moles of sulfuric acid were refluxed for 9 hours. The refluxing liquid was fractionated through an 18″ silvered vacuum-jacketed column, and the water phase was continuously collected and removed. The reaction mixture was brought to *p*H 4.5 with 1 *M* $Na_2CO_3$, stripped of butanol *in vacuo*, and then brought to *p*H 9.5 with 5 *N* NaOH while being stirred with 1000 ml. of benzene. The aqueous phase was extracted with three 500-ml. portions of benzene. The combined benzene solution was washed with saturated NaCl solution and distilled through a 6″ Vigreux column. Crude product was collected between 158–163° (1.0 mm.). Redistillation gave 242 g. (65% yield), b.p. 157–160° (1.3 mm.).

*Anal.* Calcd. for $C_9H_{15}NO_3$: N, 7.56. Found: N, 7.39.

**5-Hydroxymethyl-2-pyrrolidone.**—Thirty-seven grams (0.2 mole) of butyl pyroglutamate in 125 ml. of dioxane was hydrogenated over 18.5 g. of copper–chromium oxide at 150° for 4 hours. The pressure dropped 820 lb. in the first 3 hours and 10 lb. in the last hour. Catalyst was removed by filtration. Titration of an aliquot of the filtrate demonstrated the absence of amino nitrogen. Solvent was distilled *in vacuo*, leaving a residue which readily crystallized; yield 21.5 g. (96%), m.p. 76–78°; recrystallized from benzene, 16 g., m.p. 84–85°.

**One-step Hydrogenation of Butyl Pyroglutamate.**—Butyl pyroglutamate (37.0 g., 0.2 mole) in 150 ml. of dioxane was hydrogenated over 18.5 g. of copper–chromium oxide at 250° for 5.5 hours. Catalyst and solvent were removed. The residue (20.0 g.) was set in a refrigerator overnight.

Crystals which formed were collected on a buchner funnel; wt. 4.5 g. (27%), m.p. 69–77°. Recrystallization from hexane brought the m.p. to 84.0–84.5°; this solid did not depress the m.p. of an analyzed sample of decahydrodipyrrolo-[a,d]pyrazine.

The filtrate remaining after the solid was filtered from the reaction mixture was distilled through a 3″ Vigreux column; yield 6.0 g. (19%), b.p. 70–73° (1.2 mm.). Its titration curve corresponded closely to that expected for N-butyl-2-hydroxymethylpyrrolidine.

*Anal.* Calcd. for $C_9H_{19}NO$: N, 8.8. Found: N, 8.0.

**Two-step Hydrogenation of Butyl Pyroglutamate.**—Hydrogenation was effected as in the one-step process, but for 4.5 hours at 150°. Catalyst was filtered off and solvent was completely removed from the filtrate by vacuum distillation. The residue (21.1 g.) was hydrogenated for 5.5 hours at 250° in 150 ml. of dioxane over 21.1 g. of copper–chromium oxide. Catalyst and solvent were again removed. The residue was a white crystalline solid; yield 12.8 g. (77%), m.p. 77–80°. Two recrystallizations from hexane raised the m.p. to 84.0–84.5°; the m.p. was unchanged by an additional crystallization.

*Anal.* Calcd. for $C_{10}H_{18}N_2$: C, 72.26; H, 10.90; N, 16.85. Found: C, 72.43; H, 10.45; N, 17.22.

**Hydrogenation of 5-Hydroxymethyl-2-pyrrolidone.**—A mixture of 1.4 g. of 5-hydroxymethyl-2-pyrrolidone, 0.7 g. of copper–chromium oxide and 25 ml. of dioxane was hydrogenated for 5.5 hours at 250°. The product was isolated in the usual way; yield 1.0 g. (100%), m.p. 81–82°, mixed m.p. with an analyzed sample, 82.0–82.5°.

GEORGE M. MOFFETT RESEARCH LABORATORIES
CORN PRODUCTS REFINING COMPANY
ARGO, ILLINOIS

RECEIVED JULY 27, 1951

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## The Preparation of High Purity Silver Chloride

BY WILLIAM ZIMMERMAN, III

Silver chloride containing <0.001% metallic impurities was prepared in large quantities for the growth of single crystals used in plastic flow, solarization and recrystallization studies. Reagent grade AgCl was not sufficiently pure and although a method[1] was available which gave a product containing <0.02% metallic impurities, this method was laborious and time consuming and the product dried to a cake which was difficult to manipulate. The procedure described here gave a granular, easily washed product which dried with the minimum formation of lumps. No single metallic impurity exceeded 0.001%. Reagent grade chemicals were used throughout and were checked spectrographically to determine impurities which might be introduced during preparation. Ammonium hydroxide showed about 0.25% $SiO_2$,

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(6) N. J. Leonard and J. H. Boyer, THIS JOURNAL, **72**, 2980 (1950).

(7) N. J. Leonard and W. E. Goode, *ibid.*, **72**, 5404 (1950).

(8) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 369.

(9) T. W. Riener, THIS JOURNAL, **71**, 1130 (1949).

(1) R. N. Maxson, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 2–4.