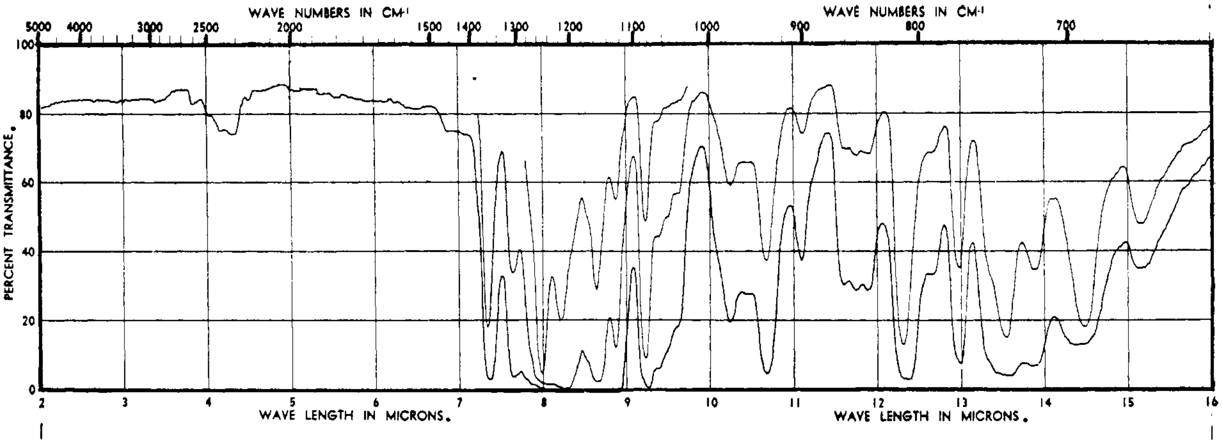

Fig. 3.—Infrared spectrum of 1-bromoundecafluoropentane: lower curve was taken in a 5-cm. gas cell; upper curves are for vapor diluted with dry nitrogen gas taken in same cell.

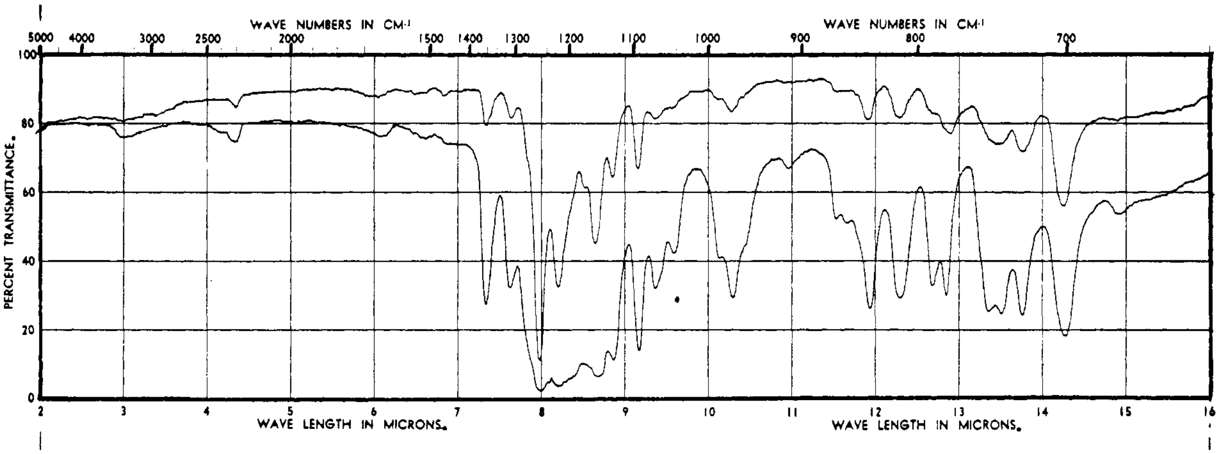

Fig. 4.—Infrared spectrum of 1-chloroundecafluoropentane: lower curve was taken in a 5-cm. gas cell; upper curve is for vapor diluted with dry nitrogen gas taken in same cell.

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

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 α-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).

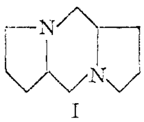
[2] H. Adkins and H. R. Billica, *ibid.*, **70**, 3121 (1948).

[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°.

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RECEIVED JULY 27, 1951

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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).

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