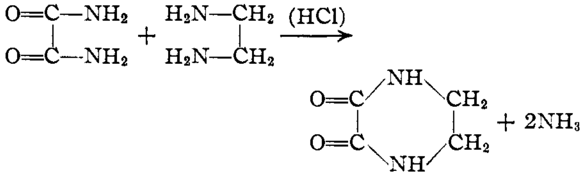
undertaken which, using anhydrous reagents and vigorous stirring, has afforded yields of approximately 50%. The reaction is presumably



Procedure.—To 63 g. of finely powdered oxamide in a three-necked flask, 60 g. of anhydrous 1,2-ethanediamine in 250 ml. of anhydrous 1,4-dioxane, and thereafter as a catalyst, 2 ml. of concentrated hydrochloric acid was added. The mixture was heated to reflux and stirred with a collapsible, stainless steel stirrer which swept the sides of the flask for twenty-four hours until ammonia was no longer evolved.

The 1,4-dioxane was removed by evaporation *in vacuo*, the solid material macerated in 3 liters of boiling water and filtered. The filtrate was evaporated on a steam-bath to 300 ml. and the solid 2,3-diketopiperazine removed by filtration. The yield was 41.1 g. (or 50.3%) melting with decomposition at 285°. The product was identified by means of the 1,4-dinitrate-2,3-diketo derivative, m. p. 150°, which, mixed with an authentic sample of the 1,4-dinitrate derivative, melted at 149–150°.

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Trifluoroethanol

BY ALBERT L. HENNE, ROBERT M. ALM AND MALCOLM SMOOK

CF_3CH_2OH has been prepared by Swarts[1] by reduction of trifluoroacetic anhydride under pressure, on a platinum catalyst. Although no one has ever voiced any doubt, this reduction has never been successfully repeated, due apparently to Swarts' failure appropriately to describe his catalyst. The reduction of CF_3CONH_2 is also mentioned by Swarts, and has been successfully developed by Gilman[2]; we duplicated Gilman's 77% yield, but had to consume 5 g. of platinum per mole of amide. Scherer[3] has made trifluoroalcohol by treating CF_3CH_2Cl with fused potassium acetate at 225°, and saponifying the resulting acetate. We have repeated this work and found the yields exceedingly sensitive to the reaction temperature, an experience duplicated by other laboratories.

We are now recommending the reduction of a derivative of trifluoroacetic acid (the ester or the acyl halide) with lithium aluminum hydride as the most convenient and efficient way to make the alcohol. Our preferred procedure is given.

Preparation of CF_3COCl.—A two-liter, three-necked flask was fitted with a dropping funnel, a mercury-sealed stirrer and a coiled reflux condenser with outlet leading to a 500-cc. receiver cooled in Dry Ice. The apparatus was thoroughly dried by flaming while sweeping with dry nitrogen; the inlet and outlet were protected by drying tubes. Benzoyl chloride (679 g. or 4.83 moles) was delivered into the flask; then over a one-hour period, trifluoroacetic acid (417 g. or 3.66 moles) was dropped in, with constant stirring. After completing the addition, the dropping funnel was replaced by a thermometer and the mixture heated overnight, up to 150°. The crude trifluoroacetyl chloride distilled through the reflux condenser; its rectification gave 380 g. (2.87 moles = 79%) of pure product, b.p. −27°, and 47 g. (0.41 mole = 11%) of unreacted acid.

Preparation of CF_3CH_2OH.—A five-liter, three-necked flask was fitted with a Dry Ice reflux condenser, a sealed stirrer and a gas inlet tube. The equipment was dried by flaming and sweeping with dry nitrogen. Solid lithium aluminum hydride (54 g. or 1.42 moles) was placed in the flask and covered with three liters of rigorously dried ether; while continuously stirring, CF_3COCl was led into the liquid as fast as the return from the reflux condenser would permit; the addition of 350 g. (2.64 moles) took about three and one-half hours. After this the mixture was refluxed for one more hour on an electric heating mantle. The inlet tube was replaced by a dropping funnel, then 200 cc. of water was slowly added to hydrolyze the excess of hydride. This made a clear solution and a precipitate of white curds. The solution was decanted into 1500 cc. of 6 *N* sulfuric acid containing ice. The ether layer was separated, then used in three portions for extractions of the aqueous layer; the latter was poured back onto the solid residue in the flask, then ether extracted. From the ether extracts, distillation isolated 285 g. of material boiling at 74–75°, which is a mixture of the trifluoroalcohol with 5–10% of water. Distilling from concentrated sulfuric acid gives the desired anhydrous alcohol, CF_3CH_2OH, b. p. 74°. The net yield is 85%.

In later experiments an excess of trifluoroacetyl chloride was used instead of an excess of hydride, because the latter was not readily available; a utilization of about 95% of the hydride was thus obtained, but this procedure is not recommended.

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[1] Swarts, *Bull. soc. chim. Belg.*, **43**, 471 (1934).

[2] Gilman, THIS JOURNAL **70**, 1281 (1948).

[3] Scherer, Scientific Zetko Exchange, P. B. Report No. 765.

Production of Radioactive Carbon Monoxide and Phosgene from Barium Carbonate

BY J. L. HUSTON[1] AND T. H. NORRIS[1]

Recently Kummer[2] has recommended the preparation of radioactive carbon monoxide by exchanging over a hot tungsten filament the C^{14} in a small amount of carbon dioxide with the inactive carbon in a large quantity of ordinary carbon monoxide. Some time ago we had occasion to prepare radioactive carbon monoxide ($C^{14}O$) as the first step in the preparation of radioactive phosgene which was to be used in biological experiments. Since our procedure involves no dilution of the radioactive carbon, and can be accomplished in less time than Kummer's procedure, we are presenting it at this time.

Our method involved the reduction of carbon dioxide to carbon monoxide by hot zinc, which was discovered by Noack.[3] Although this method was considered the most suitable for our purposes it should be pointed out that carbon monoxide can be prepared in good yield by heating alkaline earth

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[2] Kummer, THIS JOURNAL, **69**, 2239 (1947).

[3] E. Noack, *Ber.*, **16**, 75 (1883).