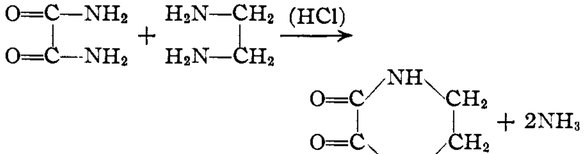
undertaken which, using anhydrous reagents and vigorous stirring, has afforded yields of approximately 50%. The reaction is presumably



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).

carbonates directly with zinc,[4] and without intermediate conversion to carbon dioxide. The phosgene was then prepared photochemically by the reaction of this carbon monoxide with chlorine. Our preparations were made in the apparatus diagramed in Fig. 1.

Experimental Part

Preparation of Carbon Monoxide.—About 50 g. of reagent zinc was cleaned with dilute acetic acid, washed, dried and placed in tube E. This cleaning was necessary since otherwise the hot zinc would evolve slowly a small quantity of permanent gas (presumably carbon monoxide from decomposition, with reduction, of zinc carbonate). Radioactive barium carbonate ($\sim$20 mg. was convenient for our apparatus) was placed in I, and the entire system evacuated. Tube E was surrounded by a small electric furnace and baked out overnight at about 370° (necessary for each fresh batch of zinc only). Temperature was adjusted manually by means of a Variac and read with a thermocouple connected to a millivoltmeter.

With the system open to the high vacuum, radioactive carbon dioxide was next generated by dropping 85% phosphoric acid into I and, after passing through phosphorus pentoxide in H, was trapped in F with liquid air. Stopcock G was now closed and the small quantity of air introduced by the phosphoric acid was pumped off. The temperature of E was raised to 385° and thereafter held within 5° of this temperature: the reaction is too slow at 370° and above 400° there is considerable tendency for the tube E to become plugged, due probably to sublimation and recrystallization of the zinc.

The stopcocks leading to the pumping system were closed; next the liquid air was removed from F and the pressure of carbon dioxide in the system (F and the capillary line extending to, and including, the capillary monometer C) was measured. Carbon monoxide subsequently was stored in the same portion of the apparatus, as it was generated, its pressure thus serving as a measure of the yield.

The two-liter Töpler pump D was now used to pump the carbon dioxide several times, alternately clockwise and counterclockwise, through the hot zinc in E. After each traverse through the zinc, unreacted carbon dioxide was trapped with liquid air in the appropriate spiral S_1 or S_2 while carbon monoxide was pumped into F and its pressure measured with manometer C. The first traverse through the zinc would produce about a 50% yield of carbon monoxide and 5 or 6 more passes made the conversion quantitative within the limit of error in reading the manometer (0.4%). The process, from generation of carbon dioxide to complete conversion to monoxide, required three to four hours.

Preparation of Phosgene.—Bulb B ($\sim$500 cc.) contained chlorine (introduced on another gas-handling system) equal in amount to about 2.5 times the stoichiometric quantity required for union with the carbon monoxide. This chlorine was frozen down into the bottom of the bulb with liquid air and the carbon monoxide in F was introduced with the Töpler pump, a small fraction ($<2\%$) remaining in the capillary line. B was then isolated from the line and after removal of the liquid air the gas mixture was irradiated with an ultraviolet mercury vapor lamp. Spiral S_4 was then cooled with liquid air and B was opened to high vacuum *via* this spiral S_4, a small amount of residual carbon monoxide thus being removed from the condensable gases (phosgene and chlorine) which were trapped in the spiral.

The system was again isolated and the mixture of phosgene and chlorine distilled with liquid air to A which contained antimony. Bulb A and spiral S_3 were then closed off from the rest of the system, removed from the line as a unit, warmed to room temperature, and shaken to remove excess chlorine. The antimony appears to react with phosgene to a slight extent to produce a little carbon monoxide; after A and spiral S_3 were re-attached to the line permanent gas was pumped off while the phosgene was trapped with liquid air in spiral S_3. After distillation to F the pressure of phosgene was read and the yield thus measured. In five runs the yields ranged from 80.0% to 84.5%, based on the original barium carbonate.

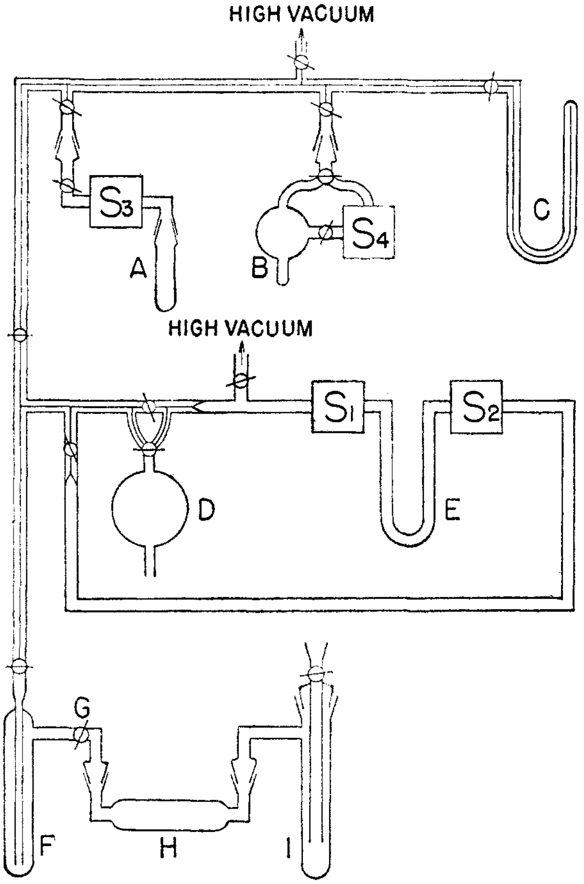

Fig. 1.

It should be noted that since the equilibrium $2CO = C + CO_2$ lies well to the right at these temperatures, reduction to carbon is thermodynamically possible. That our yields of carbon monoxide were quantitative, within the limits of error of our measurements, is in accord with an observation made by Maier and Ralston[5] in their quantitative measurements on the equilibrium $ZnO(s) + CO(g) = Zn(g)$ in the temperature range 500 to 850°. They observed a slight deposition of carbon on molten zinc but estimated that carbon monoxide was thus consumed at about $^1/_{100}$ its rate of formation from carbon dioxide. It should be noted that our procedure was designed to minimize the contact time of carbon monoxide and zinc.

The time required for our procedure could be shortened by substitution of a Dry Ice trap for the drying tube H and the use of molten zinc instead of the solid granular material. Alternatively, if granular zinc is used an automatic Töpler pump could be used to decrease the time required to pump the gases through the zinc. Some of the phosgene was probably absorbed by stopcock grease and its yield could be improved by irradiation in an all-glass container. However, it is doubtful that the labor involved in using this procedure would sufficiently improve the yield to be worth while.

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[4] Kenicutt, *Am. Chem. J.*, **5**, 43 (1883); Schwartz, *Ber.*, **19**, 1141 (1886).

[5] Maier and Ralston, THIS JOURNAL, **48**, 364 (1926).