ably to the 28% yield of $CF_2BrCH_2CF_2Br$ obtained by adding CF_2Br_2 to 1,1-difluoroethylene.[7]

The Attempted Addition of Bromochlorodifluoromethane to 1-Chloropropene.—The autoclave, charged with the methane derivative (920 g., 5.6 moles), 1-chloropropene (152 g., 20 moles) and benzoyl peroxide (20 g., 0.08 mole), was rocked and heated four hours at 100°. No material boiling higher than the chloropropene was obtained and 918 g. of bromochlorodifluoromethane was recovered.

1-Chloro-1,1-difluorobutane.—A mixture of 3-bromo-1-chloro-1,1-difluorobutane (115 g.), zinc dust (113 g.) and hydrochloric acid (600 ml. of 1.5 molar) was refluxed for several hours. Distillation of the organic product gave two fractions. The first (11 g.) consisted of 1-chloro-1,1-difluorobutane, b.p. 55.5°, $n^{25}\mathrm{D}$ 1.3476. The higher boiling material (18 g.), b.p. 81.2°, $n^{25}\mathrm{D}$ 1.3660, $d^{25}{}_4$ 1.0647, is believed to be the coupled product $CF_2ClCH_2CH(CH_3)CH(CH_3)CH_2CF_2Cl$.

Anal. Calcd. for $C_8H_{12}Cl_2F_4$: Cl, 27.8. Found: Cl, 27.9.

1-Chloro-1,1-difluoro-3-methylbutane.—A mixture of 3-bromo-1-chloro-1,1-difluoro-3-methylbutane (93 g.), zinc dust (30 g.) and hydrochloric acid (170 ml. of 1.5 molar) was refluxed for six hours. The organic layer was separated and distilled. The reduced compound (34 g.), b.p. 74.5–75.5°, $n^{25}\mathrm{D}$ 1.3665, $d^{25}{}_4$ 1.064, was obtained in a 65% yield and 10 g. of unreacted starting material was recovered.

1-Chloro-1,1-difluoro-2-methylbutane.—Refluxing the 2-butene adduct (100 g.) with zinc dust (130 g.) and hydrochloric acid (200 ml. of 1.5 molar) gave a 30% yield of $CF_2ClCH(CH_3)CH_2CH_3$. A center fraction of the distilled material had the following properties: b.p. 74.5–75°, $n^{25}\mathrm{D}$ 1.3636, $d^{25}{}_4$ 1.0487.

Anal. Calcd. for $C_5H_9ClF_2$: Cl, 24.9. Found: Cl, 24.6.

1-Chloro-1,1-difluoro-2-butene.—1,1-Difluoro-1-chloro-3-bromobutane (165 g.) was added dropwise to potassium hydroxide (84 g.) dissolved in isopropyl alcohol (250 cc.) in a liter flask equipped with stirrer, addition funnel and six-inch column with variable take-off head. Reflux was maintained at 75°. The material was removed, washed, dried and fractionated. One fraction of 47 g. was obtained with the following constants: b.p. 59.5–60°, $n^{25}\mathrm{D}$ 1.3656, $d^{25}{}_4$ 1.1100; MR_{D} calcd. for $C_4H_5F_2Cl$: 25.07, found 25.17; chlorine analysis calcd. for $C_4H_5F_2Cl$: 28.1, found 26.42. The yield was 46% of the theoretical.

1-Chloro-1,1-difluoro-3-methyl-2-butene.—In the apparatus described above was placed 200 cc. of methanol and potassium hydroxide (28 g.). To this refluxing mixture was added 1,1-difluoro-1-chloro-3-bromo-3-methylbutane (80 g.) dropwise. The olefin resulting was removed, dried and fractionated. The yield of $CF_2ClCH{=}C(CH_3)_2$, b.p. 10–11° (28 mm.) was 78% (39 g.).

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Kolbe Electrolysis of *dl*-α-Bromopropionate in Water

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The electrolysis of potassium *dl*-α-bromopropionate in concentrated aqueous solution yields ethylidene bromide, plus some unidentified material. This is a surprising result. If the general acid R·COOH be converted to a salt and electrolyzed with a smooth platinum anode, the typical products are R·R· (R minus H), R·COO·R, and R·So, So being a radical derived from the solvent anion.[2] Ethylidene bromide is none of these; nor is it the (R minus Br) which might be expected by analogy to (R minus H). Instead it is (R plus Br).

The extra Br gained by R must have come from another R, directly or indirectly. Although the solvent after electrolysis shows much bromide ion, the direct transfer seems likelier, for these reasons: (a) there is practically no H transfer between solvent and R in the electrolysis of acetate to methane[3]; (b) in the electrolysis of acetate to methane at low current densities, the H gained by R comes from another methyl, not the solvent[4]; and (c) in the electrolysis of propionate to ethylene, which is (R minus H), the hydrogen is lost from the β-carbon.[5] Hydrogen (electropositive) lost thus would correspond to bromine (electronegative) lost from the α-carbon.

In presence of excess bromide ions, the efficiency of the electrolysis becomes low, apparently due to the preferential discharge of bromide. This was discovered in an attempt to conserve the potassium ion by replenishing free acid as the electrolysis proceeded; the process was impracticable. This is held as an additional argument against the extra acquired bromine atom being derived from an ion in the solvent. As a further argument in the same direction, the oily yield appears in the first few minutes of electrolysis, before hydrolytic or reductive development of bromide ion in the solvent could have proceeded far.

Experimental

Thirty ml. (51 g., 0.33 g.-mole) of Eastman Kodak Co. *dl*-α-bromopionic acid was mixed, with cooling, with 42 ml. of distilled water and 21 ml. of aqueous saturated (room temperature) potassium hydroxide solution. The anode used was Pt wire approx. 0.17 cm.^{2} surface and the cathode Pt foil, about 1.4 cm.^{2} surface. The temperature in the cell was held to 40° or less by external cooling, the mean current density about 1.2 amp./cm.^{2} at anode and the total throughput, about 0.4 faraday. No diaphragm was used. Excessive temperature or throughput yields free bromine; excess free acid hinders separation of the yield.

The electrolyte soon becomes cloudy and deposits about 3 g. of heavy amber oil. Gases evolve simultaneously, being mostly hydrogen and carbon dioxide in about equal amounts; a few per cent. of oxygen may appear, with traces at most of carbon monoxide and unsaturates. The yield from several electrolyses is united to form a working crude sample. Washing with cold concd. sulfuric acid yields a portion more dense than the acid, which boils in the neighborhood of 105° with some decomposition to produce HBr. Its density is 2.03, $n^{25}\mathrm{D}$ 1.515, 84.9% Br; for ethylidene bromide, the b.p. is 108–110°, density 2.05, $n^{25}\mathrm{D}$ 1.513, 85.1% Br. No satisfactory derivative for ethylidene bromide was found recorded.

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(1) Assistance from the Research Corporation is gratefully acknowledged.

(2) G. Thiessen, *Trans. Ill. Acad. Sci.*, **43**, 77 (1950).

(3) H. Erlenmeyer and W. Schoenauer, *Helv. Chim. Acta*, **20**, 222 (1937).

(4) K. Clusius and W. Schanzer, *Z. physik. Chem.*, **A192**, 273 (1943).

(5) W. Schanzer and P. Kruis, *ibid.*, **A191**, 301 (1942).

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Phenylsilanetriol

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Previous investigators[1,2] have made use of the hydrolysis of alkoxysilanes with distilled water to prepare the corresponding hydroxy compounds. These mild conditions allow the isolation of un-

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(1) J. F. Hyde, THIS JOURNAL, **75**, 2166 (1953).

(2) S. W. Kantor, *ibid.*, **75**, 2712 (1953).