Two recrystallizations of fractions 19–23 from ether–ethanol–water afforded the bromohydrin (810 mg.) as colorless needles, m.p. 111–112°. This material (150 mg.) was subjected to chromatography and the heart fraction (88 mg.) recrystallized for analysis, m.p. 111.5–112.5°, $[\alpha]^{25}\mathrm{D}$ 14.0 ± 1.5° (c 1.78, chf).

Anal. Calcd. for $C_{27}H_{47}OBr$: C, 69.35; H, 10.13; Br, 17.09. Found: C, 69.35; H, 10.11; Br, 17.17.

A sample of 200 mg. of bromohydrin, m.p. 111–112°, in 6 ml. of acetone was treated with a solution of 130 mg. of digitonin in 11 ml. of 95% ethanol, and the resulting mixture was filtered. The filtrate was evaporated under reduced pressure and the residual solid was extracted well with pentane. Removal of the pentane and recrystallization of the residue from ether–ethanol–water yielded 125 mg. of bromohydrin, m.p. and mixture m.p. with starting material 111–112°. The digitonide was dissolved in 3.5 ml. of dry pyridine and the solution was diluted with pentane (40 ml.). The mixture was filtered, the filtrate was washed with water, dilute hydrochloric acid and again with water and evaporated. Recrystallization of the residue gave 30 mg. of bromohydrin, m.p. and mixture m.p. 111–112°.

Two recrystallizations of fractions 24–29 yielded 160 mg. of a mixture of epimeric bromohydrins, m.p. 103–106° not changed appreciably by two further recrystallizations.

Anal. Found: C, 69.39; H, 10.16.

The same bromohydrin, m.p. and mixture m.p. 111–112°, could be obtained by chromatography when the sodium borohydride reduction is carried out in ether–ethanol or in absolute ethanol alone. When the reaction mixture was worked up by fractional crystallization, the various crops obtained showed melting points ranging from 95–97° to 103–106°. The infrared spectra of the mixtures were very much like that of the pure bromohydrin, m.p. 111–112° (see Discussion), the important difference being a small shoulder at 9.60 μ (1042 cm.$^{-1}$) in the spectra of the mixtures. Absorption at this position might be due to the C–O stretching vibrations of a 3α-hydroxyl group.

Recrystallization of fractions 6–10 from ether–methanol afforded 153 mg. of cholestane-3-one, m.p. 127–128.5°, undepressed upon admixture with a pure sample, m.p. 129.3–130.3°. In addition the infrared spectrum of this substance was identical with that of cholestane-3-one.

2β,3β-Oxidocholestane.—A solution of 370 mg. of the bromohydrin, m.p. 111–112°, and 3.0 g. of potassium hydroxide in 50 ml. of isopropyl alcohol was heated in an atmosphere of purified nitrogen at 55° for 1.5 hours. A precipitate of potassium bromide appeared after *ca.* 5 minutes of heating. The product crystallized from the reaction mixture after addition of water and cooling. Recrystallization from ether–ethanol–water yielded 232 mg. (75.5%) of the β-oxide, m.p. 89–90°. Two evaporative distillations (160° at 0.05 mm.) yielded pure β-oxide, m.p. 90.8–91.4°, $[\alpha]^{25}\mathrm{D}$ +57.4 ± 1.0° (c 1.53, chf) (reported for 2β,3β-oxidocholestane,[8] m.p. 87.5–88.5, $[\alpha]\mathrm{D}$ +50.5°; reported for 2α,3α-oxidocholestane[8], m.p. 105°, $[\alpha]\mathrm{D}$ +36°).

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.60; H, 12.02.

The infrared spectrum of the oxide showed no hydroxyl or carbonyl absorption.

Reduction of the β-oxide (52 mg.) with lithium aluminum hydride (40 mg.) in ether (15 ml.) at room temperature yielded cholestane-2β-ol (31.5 mg.) as glistening plates, m.p. 153–154°, $[\alpha]^{25}\mathrm{D}$ +35.6° (c 1.03, chf) (reported[8] m.p. 154°, $[\alpha]\mathrm{D}$ +34.2°). The infrared spectrum of this material was identical with that published for cholestane-2β-ol.[7c]

Reaction of the pure bromohydrin with potassium hydroxide in methanol–ether at room temperature for 48 hours afforded after recrystallization a 66.5% yield of β-oxide, m.p. 89–90.5°.

Reaction of the impure bromohydrin, m.p. 97–100°, with isopropanolic potassium hydroxide under the conditions described above gave a brown mixture which upon dilution deposits only a rather small amount of oily solid. The pure β-oxide was obtained by evaporation of alcohol under reduced pressure, addition of water, extraction with pentane, evaporation of the pentane under reduced pressure and chromatography of the residue on basic alumina. The oxide was eluted with 1:1 benzene–cyclohexane and had m.p. 90.5–91.0°.

Hydrogenolysis of 2α-Bromocholestane-3β-ol.—A solution of 50.6 mg. of the pure bromohydrin and 50 mg. of potassium hydroxide in 7 ml. of absolute ethanol was stirred with 15 mg. of 11% palladium-on-Darco catalyst for two hours. The catalyst was removed by filtration and water was added to the filtrate to precipitate the sterol. Recrystallization from ethanol–water gave 33 mg. of cholestane-3β-ol as glistening plates, m.p. 140.6–141.5°, undepressed upon admixture with an authentic sample, m.p. 141.8–142.0°.

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2-Fluoropropene

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The synthesis of 2-fluoropropene was undertaken in order to investigate the polymerizability of this new fluoroölefin. Although its isomer, 3-fluoropropene, had been known for many years,[1] 2-fluoropropene had been unreported. Two procedures for preparing the olefin are described here. The compound has been synthesized[2] (1) by the thermal dehydrofluorination of 2,2-difluoropropane at 731°, which is comparable to the conversion of 1,1-difluoroethane to vinyl fluoride under similar conditions,[3] and (2) by the dechlorination of 1,2-dichloro-2-fluoropropane (a commercial research chemical) with magnesium, a reagent that has also been used to obtain vinyl fluoride from 1,1-difluoro-2-iodoethane[4] and vinylidene fluoride from 1,1,1-trifluoro-2-iodoethane.[5] The intermediate 2,2-difluoropropane was prepared by the addition of hydrogen fluoride to propyne[6] or to allene.

A comparison of the boiling point of 2-fluoropropene with those of related compounds shows it to fall in the expected position:

	B.p., °C.		"I.C.T." b.p., °C.
2-Fluoropropene	−24.0	2-Chloropropene	22.7
3-Fluoropropene	−3[1]	3-Chloropropene	44.6
2-Fluoropropane	−9.5[7]	2-Chloropropane	36.5

The infrared spectrum of 2-fluoropropene exhibits the absorption bands of the carbon–fluorine bond and the double bond at 7.9 and 5.8 μ, respectively. The compound forms copolymers and low molecular weight homopolymers.[2]

Acknowledgment.—The authors are indebted to Miss Doris Huck for determination of the infrared spectra.

Experimental

Hydrofluorination of Allene.—Anhydrous hydrogen fluoride (100 g., 5 moles) was charged into a silver reactor cooled in Dry Ice–acetone and fitted with oil-sealed nickel stirrer, thermocouple, inlet line and off-gas line protected with a calcium chloride tube. Ten grams (0.25 mole) of allene

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[1] M. Meslans, *Ann. chim. phys.*, [7] **1**, 374 (1894).

[2] P. R. Austin, U. S. Patent 2,585,529 (Feb. 12, 1952).

[3] F. B. Downing, A. F. Benning and R. C. McHarness, U. S. Patent 2,480,560 (Aug. 30, 1949); D. D. Coffman and R. D. Cramer, U. S. Patent 2,461,523 (Feb. 15, 1949); O. W. Cass, U. S. Patent 2,442,993 (June 8, 1948).

[4] A. L. Henne, THIS JOURNAL, **60**, 2275 (1938).

[5] H. Gilman and R. G. Jones, *ibid.*, **65**, 2037 (1943).

[6] A. V. Grosse and C. B. Linn, *ibid.*, **64**, 2289 (1942).

[7] A. V. Grosse, R. C. Wackher and C. B. Linn, *J. Phys. Chem.*, **44**, 275 (1940).

was distilled into the reactor during 25 minutes. The temperature rose from −76 to −69°. The reaction mixture was stirred for 30 minutes and then worked up. The off-gas line was connected to a bubbler containing 100 ml. of 5% aqueous sodium hydroxide, towers packed with soda lime and with calcium chloride, and a trap cooled with Dry Ice–acetone. Water (100 ml.) was added dropwise through the inlet line and the reaction mixture was then allowed to warm to room temperature and the system finally swept with nitrogen. The product which collected in the cold trap was distilled to give 10 g. (50% yield) of 2,2-difluoropropane boiling at −2 to 0° and having a molecular weight of 79. 2,2-Difluoropropane is reported to boil at −0.1°[6] and has a molecular weight of 80.1. The infrared absorption spectrum of 2,2-difluoropropane prepared from allene agreed with that of 2,2-difluoropropane prepared from propyne.

2-Fluoropropene from 2,2-Difluoropropane.—2,2-Difluoropropane was pyrolyzed by passing it through a $^1/_8$-inch Inconel pipe having a heated zone of 8 inches. The outlet of the tube was connected to the following in the order mentioned: a pipe packed with 2000 g. of soda lime, a wet test meter, towers packed with calcium chloride and with phosphorus pentoxide, and a trap cooled with Dry Ice–acetone. Nitrogen was passed through the apparatus as the reactor was brought to a temperature of 731°. The nitrogen cylinder was then replaced with one containing 2,2-difluoropropane. 2,2-Difluoropropane (94 g.) was passed through over a period of 60 minutes. The contact time was 0.5 sec. Fractional distillation of the material collected in the trap gave 33 g. boiling at −24° to −22°, 9 g. boiling at −22° to 0°, and 36 g. boiling at 0°. The material boiling at −24° to −22° was 2-fluoropropene as indicated by its infrared spectrum and molecular weight (59.7, calcd. 60.07). Assuming for calculation that the material boiling from −22° to 0° was 2,2-difluoropropane, the 2-fluoropropene obtained corresponds to 42% conversion and 90% yield. Traces of propyne were removed by passing the material through successive scrubbers filled with ammoniacal cuprous chloride solution, water and 50% aqueous sulfuric acid, and then through calcium chloride and phosphorus pentoxide. The pure material boiled at −24.0°.

2-Fluoropropene from 1,2-Dichloro-2-fluoropropane.—In a 1-l., 3-necked flask fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel were placed 600 ml. of anhydrous ether and 20 g. (0.83 atom) of magnesium powder. Then 18.5 g. (0.07 mole) of iodine was gradually added with stirring until it had reacted with the magnesium. The top of the condenser was connected to an ice trap and this in turn was connected to a trap cooled with Dry Ice–acetone and protected with a calcium chloride tube. 1,2-Dichloro-2-fluoropropane[8] (95 g., 0.73 mole) was added through the dropping funnel over 2 hours while the ethyl was kept refluxing. After 4 hours, gas was still being slower evolved so the mixture was stirred at room temperature for 16 hours longer. A preliminary distillation of the material collected in the cold trap gave 30 g. (68% yield) of 2-fluoropropene. This was redistilled at −24.0° (757 mm.) through a Podbielniak column of *ca.* 60 plates efficiency. The product had a molecular weight of 59.7 as measured in an Edwards gas density balance and agreed in its infrared spectrum with the 2-fluoropropene obtained from 2,2-difluoropropane. The compound adds bromine.

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[8] A. L. Henne and F. W. Haeckel, THIS JOURNAL, **63**, 2692 (1941); Halogen Chemicals, Inc., Columbia, S. C.

CONTRIBUTION NO. 326, CHEMICAL DEPARTMENT
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The High Field Conductance of Aqueous Solutions of ε-Amino-*n*-caproic Acid at 25°[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

RECEIVED MAY 15, 1953

The high field conductance of solutions of ε-amino-*n*-caproic acid, approximately 0.06 and 0.14 *m*, has been determined at 25.00 ± 0.015° using the method of Gledhill and Patterson.[2] These measurements were made in order to determine if any interesting or notable dipole orientation, dielectric, or relaxation-time effects were observed as a function of increasing field with this longer carbon chain compound. Similar measurements have been reported for solutions of glycine.[3] In neither case, however, have any such effects been noted for the range of concentrations and fields studied.

The measurements were made with 1 × 10^{-4} *M* hydrochloric acid as reference electrolyte. A sample of Eastman Kodak Co. ε-amino-*n*-caproic acid was used as received for one set of measurements; a once-recrystallized sample of the same material was used for a second set of measurements. The results are shown in Fig. 1. The triangles are experimental points for a 0.1407 *m* solution of once-recrystallized material. The black filled circles are for a 0.06663 *m* solution of the "as received" sample; the crosses are for a 0.06418 *m* solution of the same sample. Although the concentration of the amino acid required to give the same conductance is larger in the case of the recrystallized sample than with the "as received" samples, the high field conductance quotients are, while very slightly higher for the recrystallized materials, still closely the same. The fractional

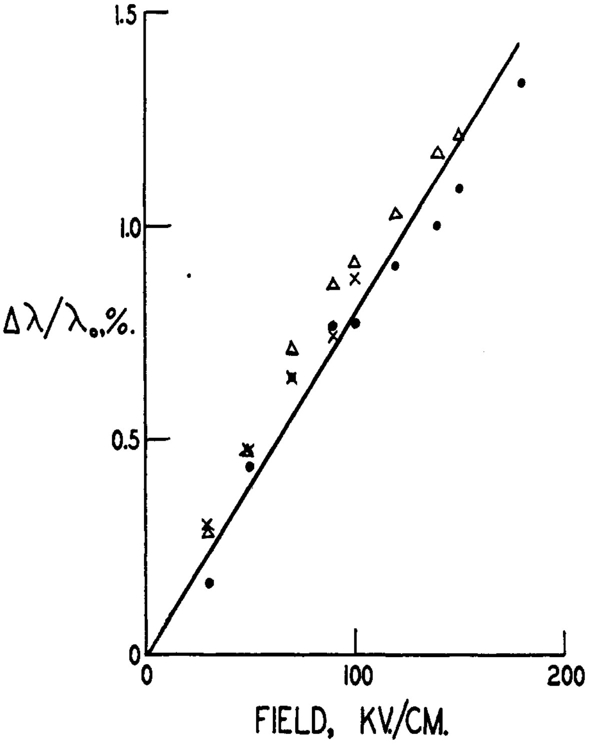

Fig. 1.—The high field conductance of ε-amino-*n*-caproic acid. The triangles are experimental points for a 0.1407 molal solution of purified ε-amino-*n*-caproic acid. The black dots are experimental points for a 0.06663 *m* solution and the crosses for a 0.06418 *m* solution. All solutions were measured relative to a 1 × 10^{-4} *M* hydrochloric acid solution at 25.00 ± 0.02°.

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[1] Contribution No. 1163 from the Department of Chemistry, Yale University.

[2] J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952).

[3] D. Berg and A. Patterson, THIS JOURNAL, **75**, 1482 (1953).