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.

(8) A. L. Henne and F. W. Haeckel, This Journal, **63**, 2692 (1941); Halogen Chemicals, Inc., Columbia, S. C.

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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.

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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

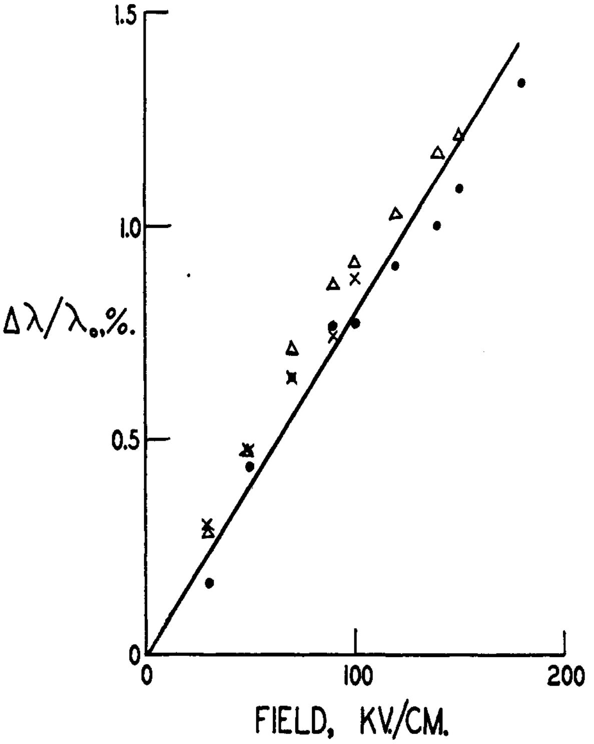

Fig. 1.—The high field conductance of ϵ-amino-*n*-caproic acid. The triangles are experimental points for a 0.1407 molal solution of purified ϵ-amino-*n*-caproic acid. The black dots are experimental points for a 0.06663 *m* solution and the crosses for a 0.06418 *m* solution. All solutions were measured 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).

high field conductance quotient has the value approximately 1.5% at 200 kv./cm., compared to a value of 4% for glycine.[3] Although the capacitance required for balance was appreciably higher than with the usual electrolytes, there was no evidence of change of capacitance with increasing field, or of time-dependent effects during the 4-microsecond pulses employed. The use of hydrochloric acid as a reference electrolyte minimized apparent bridge unbalance due to polarization occurring in different degree in the measurement and reference cells. Hydrochloric acid is a troublesome electrolyte on which to perform conductance measurements at 10^{-4} M concentration, however. The slight curvature observable in the results of Fig. 1 is attributed to variability of the hydrochloric acid reference solution, not to the amino acid.

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Preparation and Properties of Some Octyl Ethers[1]

BY LAWRENCE W. DEVANEY[2] AND GEORGE W. PANIAN

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A few octyl ethers are mentioned in the literature but few physical constants are given and considerable discrepancy exists for those reported. In this investigation, seventeen octyl ethers were prepared by the Williamson reaction and their boiling points, melting points, densities and refractive indices determined.

The physical constants for the octyl ethers prepared are shown in Table I. Within the range of this investigation, the boiling points are linear functions of the molecular weight. The molecular refractions are also linear functions of the molecular weight, and agree closely with the calculated values. The odors of the octyl ethers ranged from pleasant and rather sweet in the lower molecular weight range studied to disagreeable in the mid-molecular weight range. Those of higher molecular weight had faint distinctive but pleasant odors.

Experimental

Most of the materials used were the best grade obtainable from Eastman Kodak Company. If the pure grade was not available, the material was purified by fractional distillation before using.

The general procedure consisted of allowing 11.4 g. (0.5 mole) of sodium to react with 78 g. (0.6 mole) of 1-octanol in a one-liter three neck flask fitted with a dropping funnel, mechanical stirrer and condenser. Gentle heat was applied until the reaction was complete. One-half mole of the alkyl halide (the bromides were used in every case except in the preparation of allyl octyl ether) was then added slowly with stirring and the mixture refluxed for 2 to 4 hours. In some cases it was necessary to cool the flask during the initial addition of the alkyl halide. Moisture was excluded from the reaction flask by the use of drying tubes. The resulting ethers were washed with water, dried, fractionated through a Vigreux column, allowed to stand over sodium for several days to remove any water and alcohol, and then distilled from sodium through a Lecky–Ewell column having an efficiency of approximately 15 theoretical plates. The fractionations were carried out at atmospheric pressure and the only ones which showed any tendency to decompose were those of high molecular weight such as dodecyl octyl and tetradecyl octyl ethers. The yields of the ethers were usually about 50% of the theoretical.

The boiling points were determined from a distillation curve for the purified ethers. A standard taper, three-inch immersion thermometer was used for temperatures below 250°. For higher temperatures a 360° total immersion thermometer was used, and stem corrections applied. The purified ethers were subjected to fractional freezing and refreezing in a Dry Ice–isopropyl alcohol bath. When the cooling curve data indicated high purity of product, a melting point was taken on the solidified material. Densities were obtained with the aid of dilatometers used as pycnometers. These had graduations of 0.02 ml. between 10.00 ml. and 10.50 ml. and were calibrated with water at 20°. The refractive indices were determined at 20 and 25° with a Bausch and Lomb Abbé type refractometer.

TABLE I

PHYSICAL CONSTANTS FOR SOME OCTYL ETHERS

Ether	B.p., °C.[a]	M.p., °C.	d^{20}	n^{20}D	n^{25}D	Carbon, %		Hydrogen, %	
						Calcd.	Found[b]	Calcd.	Found[b]
Methyl octyl	172.0[c]	−52.5	0.7845[c]	1.4104	1.4082				
Ethyl octyl	186.5[d]	−51.0	.7847[d]	1.4127	1.4102				
n-Propyl octyl	204.0[e]	−46.0	.7883[e]	1.4162	1.4142				
Isopropyl octyl	198.5	−60.5	.7821	1.4131	1.4110	76.67	76.63	14.04	13.95
Allyl octyl	206.0[f]	−61.0	.8096	1.4267	1.4247	77.58	77.53	13.02	13.05
n-Butyl octyl	221.5[g]	−44.0	.7925[g]	1.4201	1.4181				
s-Butyl octyl	214.0	−54.0	.7891	1.4179	1.4157	77.35	77.25	14.06	14.29
Isobutyl octyl	217.0	−43.0	.7856	1.4169	1.4150	77.35	77.28	14.06	14.21
n-Amyl octyl	240.0	−28.0	.7965	1.4238	1.4215	77.93	77.99	14.09	13.96
Isoamyl octyl	234.5	−56.5	.7938	1.4221	1.4197	77.93	78.09	14.09	14.22
n-Hexyl octyl	257.5	−27.0	.8030	1.4297	1.4276	78.43	78.67	14.10	14.30
n-Heptyl octyl	272.6[h]	−13.8	.8018[h]	1.4291	1.4270				
Dioctyl	286.5[i]	− 7.6	.8064[i]	1.4324	1.4305				
n-Nonyl octyl	301.0	− 4.4	.8068	1.4341	1.4322	79.61	79.89	14.15	14.40
n-Decyl octyl	315.5	3.5	.8095	1.4361	1.4342	79.92	79.96	14.16	14.19
n-Dodecyl octyl	355.0	5.8	.8112	1.4406	1.4388	80.46	80.23	14.18	14.15
n-Tetradecyl octyl	383.0	15.6	.8186	1.4426	1.4408	80.90	80.84	14.20	14.18

[a] Corrected. [b] Appreciation is hereby acknowledged to J. W. Johnson and T. L. Stegant for conducting these analyses. [c] B.p. 173°, d. 0.8014 (0/0°), *Beil.*, **1**, 419. [d] B.p. 182–184°; 189.2°; d. 0.7941 (17°), 0.8008 (0°), *Beil.*, 1, 419. [e] B.p. 207°, d. 0.8039 (0°), *Beil.*, **1**, 419. [f] B.p. 87–88° (12 mm.), *C. A.*, **40**, 5418 (1946). [g] B.p. 225.7°, d. 0.8069 (0°), *Beil.*, **1**, 419. [h] B.p. 278.8°, d. 0.8182 (0°), *Beil.*, **1**, 419. [i] B.p. 280–282°, d. 0.8050 (17/17°), *Beil.*, **1**, 419.

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(2) Linde Air Products Co., Tonawanda, N. Y.