Velick[4] having prepared undecyne-10-al-1 ethyl acetal by reduction of 10,11-dibromoundecanoyl chloride and elimination of hydrogen bromide in 25% over-all yield.

Kharasch[5] has reported that sulfuryl chloride chlorination of butyric acid gives approximately 45% of γ-chlorobutyryl chloride and 45% of the β-chloro isomer. Using essentially his conditions, we obtained the desired γ-chloro compound in 31% yield (based on sulfuryl chloride), but the β-isomer was found only to the extent of 3%. Instead we isolated as much as 21% of α-chlorobutyryl chloride.

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Experimental

A mixture of 600 cc. of carbon tetrachloride, 665 cc. (7.28 moles) of technical butyric acid, 486 cc. (6 moles) of sulfuryl chloride and 10 g. of benzoyl peroxide was refluxed in the dark two hours. The mixture was cooled and 600 cc. (8.3 moles) of thionyl chloride was cautiously added. After eight more hours of refluxing, everything boiling below 100° (40 mm.) was removed by distillation. Redistillation through an 18-plate column gave the following fractions: 174 g. of **butyryl chloride**, b.p. 46–47.5° (100 mm.); 170 g. of α-**chlorobutyryl chloride**, b.p. 44–49° (40 mm.); 28 g. of β-**chlorobutyryl chloride**, b.p. 64–68° (40 mm.); and 263 g. of γ-**chlorobutyryl chloride**, b.p. 83–90° (40 mm.).

γ-**Chlorobutyraldehyde.**—A mixture of 168 g. (1.19 moles) of γ-chlorobutyryl chloride, 900 cc. of toluene, 16 g. of palladium–barium sulfate catalyst[2] and 1.66 cc. of poison[2] was refluxed and vigorously stirred in a two-liter, 3-neck flask. Hydrogen was passed through and the effluent gas bubbled through water. After nine hours the evolution of hydrogen chloride ceased at 94% of the theoretical. The toluene was washed with water, twice with sodium bicarbonate solution and twice more with water. Distillation through a Vigreux column at 35 mm. gave 58 g. (46%) of γ-**chlorobutyraldehyde**, b.p. 69–70° (35 mm.), $n^{20}\text{D}$ 1.4480. The dinitrophenylhydrazone recrystallized from alcohol had m.p. 130–131°.[6]

Anal. Calcd. for $C_{10}H_{11}O_4N_4Cl$: C, 41.89; H, 3.87. Found: C, 42.20; H, 3.65.

γ-**Chlorobutyraldehyde Diethyl Acetal.**—The aldehyde could be converted to the diethyl acetal in 63% yield by reaction with five parts of ethanol and calcium chloride. Better over-all yields were obtained if the aldehyde was not isolated. Thus, 250 cc. of absolute ethanol and 50 g. of calcium chloride were added to the cold Rosenmund reduction mixture and stirring was continued 16 hours. The mixture was filtered, the phases separated and the upper layer washed twice with sodium bicarbonate solution and once with water. Water was removed by brief boiling. Distillation yielded 118 g. (55% based on the acid chloride) of γ-chlorobutyraldehyde diethylacetal, b.p. 89–92° (14 mm.).

Anal. Calcd. for $C_8H_{17}O_2Cl$: C, 53.19; H, 9.49. Found: C, 53.76; H, 9.49.

(4) J. English and S. F. Velick, THIS JOURNAL, **67**, 1413 (1945).

(5) M. Kharasch and H. Brown, *ibid.*, **62**, 925 (1940).

(6) R. Paul and S. Tchelitcheff (*Bull. soc. chim.*, [5] **15**, 197 (1948)) report a melting point of 135° for this dinitrophenyl hydrazone.

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Pentafluorobenzoic Acid

BY E. T. MCBEE AND EDWARD RAPKIN

Pentafluorobenzoic acid has been synthesized in low yield by sulfuric acid hydrolysis of perfluorotoluene according to the method of LeFave.[1] The slow rate of hydrolysis and the low yield obtained may be attributed to the relatively low boiling point (103°) of the fluorocarbon as well as to its lack of solubility in sulfuric acid. Even with rapid stirring two layers were still apparent and neither the reaction rate nor the yield were appreciably increased.

Reduction of pentafluorobenzoic acid with lithium aluminum hydride gave pentafluorobenzyl alcohol in good yield. The alcohol was not isolated but was converted to the corresponding *p*-nitrobenzoate and isolated as such.

Experimental[2]

Pentafluorobenzoic Acid.—A mixture of 10 g. (0.042 mole) of perfluorotoluene[3] and 30 g. of concd. sulfuric acid was stirred vigorously at reflux temperature for one week. During this period the lower acid layer became black while the unreacted fluorocarbon layer remained colorless. Hydrogen fluoride evolution was extremely slow.

When the fluorocarbon layer had completely disappeared the black acid solution was poured on ice, diluted with water to a volume of 250 ml., and boiled with Norite for several minutes. After filtration, the resulting colorless solution was ether extracted and the extract dried with Drierite. Evaporation of the ether gave white crystals of pentafluorobenzoic acid. While the material can be recrystallized from water, a mixture of petroleum ether (90–100°) diluted with some toluene proved more satisfactory. From this solvent pair 2.2 g. (25% yield) of large square plates of pentafluorobenzoic acid, m.p. 106–107°, was obtained.

Anal. Calcd. for $C_7HF_5O_2$: C, 39.6; H, 0.47. Found: C, 39.4; H, 0.47.

Pentafluorobenzyl *p*-Nitrobenzoate.—Pentafluorobenzoic acid (0.5 g.) was added to a refluxing mixture of lithium aluminum hydride (0.5 g.) and 10 ml. of ether. The mixture was hydrolyzed with excess dilute hydrochloric acid and the ether layer removed and dried. Evaporation of the ether left a colorless, pleasant-smelling oil. This oil was converted to the *p*-nitrobenzoate (0.63 g.) which was alternately recrystallized four times from alcohol and petroleum ether (90–100°). The colorless crystals sintered at 108° and melted at 110–112°.

Anal. Calcd. for $C_{14}H_6F_5NO_4$: C, 48.4; H, 1.73; N, 4.03. Found: C, 48.6; H, 1.85; N, 4.11.

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(1) G. M. LeFave, THIS JOURNAL, **71**, 4148 (1949).

(2) Microanalyses by Dr. H. Galbraith.

(3) E. T. McBee, V. V. Lindgren and W. B. Ligett, *Ind. Eng. Chem.* **39**, 378 (1947).

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Some Azoproteins and Their Isoelectric Points[1]

BY R. L. MCGEACHIN AND B. D. ASHLEY

Haurowitz[2] found that the introduction into proteins of azophenyl radicals containing acidic groups gave azoproteins whose isoelectric points were lower than those of the original proteins. We have coupled casein, ovalbumin, pumpkin seed globulin and beef serum protein with excess diazotized *p*-arsanilic acid and determined the isoelectric points of these azoproteins. In all cases, the isoelectric point of the azoprotein was lower than that of the original protein, confirming Haurowitz's findings on

(1) Taken from the M. S. thesis of B. D. Ashley.

(2) F. Haurowitz, *Kolloid Z.*, **74**, 208 (1936).