Carbonation by this procedure requires about 1.5 kg. of Dry Ice and 600–700 cc. of dry ether per mole of Grignard reagent.[7] Special precautions to exclude moisture when pulverizing the Dry Ice are not necessary. In one experiment, a 65% yield of benzoic acid was obtained when phenylmagnesium bromide was carbonated using wet ether containing enough water to hydrolyze two-thirds of the organometallic compound. The solution can be added rapidly (about 15 minutes per mole) and the reaction mixture can be conveniently hydrolyzed as soon as the excess Dry Ice has evaporated.

Using this procedure, benzoic acid, *p*-methoxybenzoic acid and α-naphthoic acid were obtained in 88–92% of the theoretical.[8] Most of the remainder of the organic halide used could be accounted for as Wurtz coupling product. Cyclopentanecarboxylic acid was prepared in 86% yield. A very small amount of dicyclopentyl ketone apparently was formed, but no aromatic ketones could be detected in the neutral products.

Experimental[9]

An ether solution of phenylmagnesium bromide was prepared from 157 g. of bromobenzene in 400 cc. of anhydrous ether by reaction with 24.5 g. of magnesium turnings in an atmosphere of dry, oxygen-free nitrogen. The solution was blown through a filter-tube extending to the bottom of the flask into a dropping funnel and the flask was rinsed with a little dry ether. This solution was then added over 15 minutes to a well-stirred slurry of 1.5 kg. of powdered Dry Ice[7] and 600 cc. of dry ether in a 3-l. three-neck flask protected from moisture. After the excess Dry Ice had evaporated (about 1 hour), the reaction mixture was carefully acidified with 400 cc. of cold 6 *M* hydrochloric acid. Isolation of the benzoic acid by extraction with dilute ammonia followed by acidification gave 111 g. (91%) of benzoic acid, m.p. 119.3–120.6°, neut. equiv., 120.8.

From the ether solution there was obtained 5.8 g. of crystalline material from which no benzophenone 2,4-dinitrophenylhydrazone could be prepared. Recrystallization from ethyl alcohol gave 4.5 g. (6%) of biphenyl, m.p. 68.1–69.0°.

By the same procedure, *p*-bromoanisole gave 92% of *p*-methoxybenzoic acid, m.p. 183.2–184.5°,[10] and 5% of 4,4′-dimethoxybiphenyl, m.p. 172.0–173.6°.[11] 1-Bromonaphthalene in ether and benzene gave 89% of 1-naphthoic acid, m.p. 159.5–161.0°,[12] 2% of naphthalene (by sublimation from the neutral product), m.p. 79–80°, and 5% binaphthyl, m.p. 156.5–158.1°[13] (from Skellysolve C). Bromocyclopentane gave 86% of cyclopentanecarboxylic acid, b.p. 101–104° at 9 mm., $n^{20}\text{D}$ 1.4533,[14] and a small amount of pleasant-smelling lower-boiling material, presumably dicyclopentyl ketone.

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[7] Less Dry Ice is required if the carbonation flask is insulated with asbestos floc or similar material.

[8] Compare H. Gilman and H. H. Parker, *Org. Syntheses*, **5**, 75 (1925); H. Gilman, N. St. John and F. Schulze, *ibid.*, **11**, 80 (1931).

[9] All m.p's. corrected.

[10] A. Oppenheim and S. Pfaff, *Ber.*, **8**, 893 (1875).

[11] A. Gillmeister, *ibid.*, **30**, 2849 (1897).

[12] S. F. Acree, *ibid.*, **37**, 627 (1904).

[13] C. Willgerodt and P. Schlosser, *ibid.*, **33**, 698 (1900).

[14] N. Zelinsky, *ibid.*, **41**, 2627 (1908).

CHEMICAL LABORATORIES
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS RECEIVED AUGUST 31, 1950

Refractive Indices for the Methyl Esters of the C_{12}–C_{28} Saturated *n*-Aliphatic Acids

BY CHARLES F. KREWSON

In connection with a recent investigation on the composition of buckwheat leaf meal fat,[1] refractive index values were required for the methyl esters of the even-number saturated fatty acids up to methyl octacosanoate. No data for these compounds above C_{18} were available in the literature. To obtain comparative data, methyl esters of C_{18}-C_{28}[2] acids were prepared by direct esterification of the respective *n*-fatty acids with an excess of absolute methanol, using sulfuric acid as a catalyst. The esters were recrystallized once from ethanol and then from acetone until constant values for refractive indices were obtained. The refractive indices were determined on an Abbe refractometer equipped with a constant-temperature bath and a variable-speed circulating pump. Each recorded value in Table I represents an average of ten readings. The values obtained at 45° for the 12, 14, 16 and 18 carbon atom esters agreed to within 1 or 2 figures in the fourth decimal place of those already reported by Althouse, *et al.*[2] Melting points were taken on a calibrated microscope hot stage.

The identities of these methyl esters were confirmed[3] by comparing the X-ray diffraction patterns with those of Francis and Piper.[4]

TABLE I

MELTING POINTS AND REFRACTIVE INDICES OF METHYL ESTERS OF SATURATED *n*-ALIPHATIC ACIDS

Carbon content of acid	M.p., °C. (cor.) Found	M.p., °C. (cor.) Lit.[4]	Index of refraction 50° Found	Index of refraction 80° Found
12			1.4199	1.4078
14			1.4249	1.4131
16	30.4	30.55	1.4294	1.4173
18	39.0	39.1	1.4328	1.4213
20	46.5	46.6	1.4352	1.4238
22	53.2	53.3		1.4262
24	59.2	58.4		1.4283
26	63.8	63.45		1.4301
28	68.5	67.5		1.4320

EASTERN REGIONAL RESEARCH LABORATORY[5]
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[1] Manuscript in preparation.

[2] P. M. Althouse, G. W. Hunter and H. O. Triebold, *J. Am. Oil Chem. Soc.*, **24**, 257 (1947).

[3] The author wishes to thank E. F. Jordan of this Laboratory for samples of methyl esters of C_{12} and C_{14} *n*-acids; K. S. Markley of the Southern Regional Research Laboratory for samples of *n*-acids, C_{20}–C_{28}; and L. P. Witnauer of this Laboratory for the X-ray examination.

[4] F. Francis and S. H. Piper, THIS JOURNAL, **61**, 577 (1939).

[5] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture. Article not copyrighted.

γ-Chlorobutyraldehyde and its Diethyl Acetal

BY ROBERT BERNER LOFTFIELD[1]

We find that γ-chlorobutyryl chloride is reduced to the aldehyde in very satisfactory yield under usual Rosenmund conditions[2] but not as well by the modified method of Weygand and Meusel.[3] Previously one other haloacid chloride has been reduced by the Rosenmund method, English and

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[1] Chemistry Department, Harvard University, and Medical Laboratories of the Collis P. Huntington Memorial Hospital, Massachusetts General Hospital, Boston, Massachusetts. This is publication No. 728 of the Cancer Commission of Harvard University.

[2] E. B. Hershberg and J. Cason, *Org. Syntheses*, **21**, 84 (1941).

[3] C. Weygand and W. Meusel, *Ber.*, **76**, 502 (1943).

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.

This work was supported by an Institutional Grant from the American Cancer Society, Inc., to the Massachusetts General Hospital.

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}_{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.

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[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).

Purdue Research Foundation and
Department of Chemistry
Purdue University
W. Lafayette, Ind.
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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

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[1] Taken from the M. S. thesis of B. D. Ashley.

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