

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 organo-metallic 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.

Experimental⁹

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 Ice⁷ 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_D^{20} 1.4533,¹⁴ and a small amount of pleasant-smelling lower-boiling material, presumably dicyclopentyl ketone.

(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).

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Refractive Indices for the Methyl Esters of the C₁₂–C₂₈ Saturated *n*-Aliphatic Acids

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In connection with a recent investigation on the composition of buckwheat leaf meal fat,¹ refractive

(1) Manuscript in preparation.

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 C₁₈ were available in the literature. To obtain comparative data, methyl esters of C₁₅–C₂₈² 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 confirmed³ 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.)		—Index of refraction—	
	Found	Lit. ⁴	50° Found	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

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(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 C₁₂ and C₁₄ *n*-acids; K. S. Markley of the Southern Regional Research Laboratory for samples of *n*-acids, C₂₀–C₂₈; 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 LOFTFIELD¹

We find that γ -chlorobutyryl chloride is reduced to the aldehyde in very satisfactory yield under usual Rosenmund conditions² 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

(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).