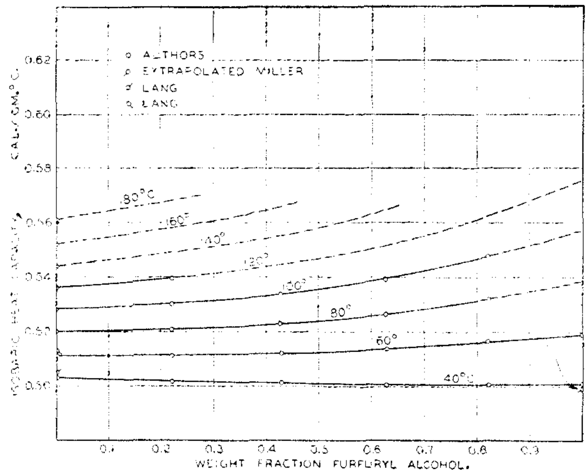

Fig. 1.—Isobaric heat capacity of the furfuryl alcohol–aniline system.

values for pure furfuryl alcohol[7] and aniline[8] are included. The maximum error of these data is estimated to be 1.0%. Density measurements were made with a pycnometer for a number of mixtures at compositions between 0.0 and 1.0 weight fraction furfuryl alcohol at temperatures between 5 and 90°, and the smoothed data are presented in Table II. In Table III is presented the refractive index for several mixtures at compositions between 0.0 and 1.0 weight fraction furfuryl alcohol at 25°. For comparison, data reported in the literature for pure furfuryl alcohol[9] and pure aniline[10] are included.

TABLE III

REFRACTIVE INDEX OF FURFURYL ALCOHOL–ANILINE SYSTEM AT 25°

Composition, weight fraction furfuryl alcohol	Refractive index, λ = 5893 Å. Measured	Literature[9,10]
0.0000	1.5832	1.5863(20°)
.2184	1.5631	....
.4247	1.5433	....
.6248	1.5219	....
.8213	1.5023	....
1.0000	1.4835	1.4843–5

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(7) P. Miller, *Iowa State Coll. J. of Sci.*, **10**, 91 (1936).

(8) H. R. Lang, *Proc. Roy. Soc. (London)*, **A118**, 138 (1928).

(9) Dunlop and Peters, *Ind. Eng. Chem.*, **34**, 814 (1942).

(10) Brühl, *Z. physik. Chem.*, **16**, 193 (1895).

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The Chemistry of Scandium. III[1,2]

BY MORTON J. KLEIN AND PETER M. BERNAYS

The exact nature of the precipitate obtained when a scandium-containing solution is treated with oxalic acid has been the subject of much disagreement in the literature.

Based upon the complete analysis of the salt, Nilson[3] assigned to it the formula $Sc_2(C_2O_4)_3 \cdot 6H_2O$. However, Crookes,[4] who did not determine the scandium oxide, refers varyingly to a mono-, di-, tri- and pentahydrate. Meyer and Winter[5] prepared an oxalate salt whose analysis corresponds closely to that of a tetrahydrate. By precipitating scandium out of acid solution, using oxalic acid or ammonium oxalate, Meyer and Wassjuchnow[6] prepared the pentahydrate. These authors reported no analyses. By far the most careful work was done by Sterba-Böhm. He precipitated the salt from a slightly acid solution at 60° and allowed the crystals to dry in air, excluding all ammonia vapors.[7] The analyses he reports strongly indicate the hexahydrate. The method described below produces pure scandium oxalate hexahydrate.

Experimental

A dilute solution of $ScCl_3$ was heated to 60° and treated with an excess of dilute oxalic acid solution. After 20 minutes, shiny white crystals appeared. Two days drying in air, protected from ammonia vapors, did not yield a homogeneous material. A second batch of crystals were prepared as described above, and dried in a desiccator over anhydrous calcium chloride. After 2 days the material fell apart into a fine powder.

In order to determine the composition of the product, weighed samples were heated in a closed system through which dried nitrogen was passed. The moisture evolved was collected in a phosphorus pentoxide drying tower. Oxalate was determined by the permanganate method, and scandium by the basic tartrate procedure.[8] Typical results are

Preparation no.	Sc, %	$C_2O_4^{=}$, %	H_2O, %
1	19.39	57.10	23.25
2	19.93	57.02	23.77
3	19.60	57.23	23.46
Calcd. for $Sc_2(C_2O_4)_3 \cdot 6H_2O$	19.51	57.11	23.38

All analyses are the average of two or more determinations.

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(1) Paper II, submitted to *Analytical Chemistry*.

(2) Aided by a Frederick Gardner Cottrell grant from the Research Corporation.

(3) L. F. Nilson, *Ber.*, **13**, 1448 (1880).

(4) (a) W. Crookes, *Chem. News*, **98**, 295, 307 (1908); (b) W. Crookes, *Z. anorg. Chem.*, **61**, 368 (1909).

(5) R. J. Meyer and H. Winter, *ibid.*, **67**, 409 (1910).

(6) R. J. Meyer and A. Wassjuchnow, *ibid.*, **86**, 9 (1914).

(7) J. S. Sterba-Böhm, *Coll. Czechoslov. Chem. Comm.*, **1**, 1 (1929).

(8) R. Fresenius and G. Janeler, "Handbuch der Analytischen Chemie," Springer, Berlin, 1942, Part III, p. 734.

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The Carbonation of Grignard Reagent Solutions

BY ALLEN S. HUSSEY

A convenient technique for the carbonation of Grignard reagents to give high yields of carboxylic acids involves the addition of the Grignard solution to a well-stirred slurry of powdered Dry Ice and dry ether. This procedure[1] permits rapid carbonation at a low temperature, conditions which minimize the secondary reactions which form ketones and tertiary alcohols,[2–5] but has the advantage over the use of powdered Dry Ice[6] in that the reaction mixture can be easily stirred, thus immediately exposing all of the organometallic compound to the action of carbon dioxide.

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(1) The use of an ether–Dry Ice slush in the carbonation of organolithium compounds has been reported by Gilman and Beel, THIS JOURNAL, **71**, 2328 (1949).

(2) F. Bodroux, *Compt. rend.*, **137**, 710 (1903).

(3) D. Iwanov, *Bull. soc. chim.*, **37**, 287 (1925).

(4) H. Gilman and N. St. John, *Rec. trav. chim.*, **49**, 1172 (1930).

(5) The marked effect of these secondary products on the yield of carboxylic acid has been pointed out by C. R. Kinney and M. L. Mayhue, THIS JOURNAL, **53**, 190 (1931).

(6) J. F. Spencer and E. M. Stokes, *J. Chem. Soc.*, **93**, 68 (1908); L. F. Fieser, H. L. Holmes and M. S. Newman, *ibid.*, **58**, 1055 (1936).

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).

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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

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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).