

rods, many with six-sided outline, and fibrous fragments. In parallel polarized light (crossed nicols), the extinction is inclined and the sign of elongation negative; the rods do not extinguish sharply with crossed nicols, many of them remaining essentially bright when the stage is rotated. In convergent polarized light (crossed nicols), biaxial interference figures are common, these showing one optic axis up or slightly inclined. The refractive indices are: n_{α} , 1.506; n_{β} , 1.655; n_{γ} , 1.685; all ± 0.003 .

Summary

Rissic acid which is obtained by oxidation of derric acid is converted into decarboxyrissic acid with elimination of one carboxyl group. Nitro-decarboxyrissic acid is formed by the action of dilute nitric acid on rissic acid. Chlorodecarboxyrissic acid results from the action of phosphorus pentachloride on decarboxyrissic acid. Decarboxyrissic acid is shown by synthesis to be 3,4-dimethoxyphenoxyacetic acid. The 2,5-dimethoxy-mandelic acid which was claimed to be identical with decarboxyrissic acid was also prepared synthetically. The formulas for derric and rissic acid are established by analogy.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

ALKYL OXALATES AND OXAMATES

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Among the known di-alkyl oxalates¹ described in the literature, the methyl and ethyl esters have been thoroughly studied. Regarding the higher homologs, however, very few data can be found even for their simple physical constants. With the calculated amount of ammonia, these esters were reported to give crystalline partial amides, alkyl esters of oxamic acid.² Here, again, only the ethyl derivative was studied in full detail. For the rest, their melting points were not given.

By direct esterification of anhydrous oxalic acid in the presence of hydrogen chloride, we have successfully prepared six alkyl oxalates in a very pure condition and carefully determined their simple constants. By allowing these esters to react with the calculated amount of ammonium hydroxide in alcoholic solution, beautiful crystals of alkyl oxamates were isolated and further purified by recrystallization. Their melting points were carefully

¹ (a) Beilstein, "Handbuch der organischen Chemie," Band II, pp. 534-540 (1920); (b) *ibid.*, Band II (suppl.), pp. 231-234 (1929).

² (a) Dumas and Boullay, *Ann. chim. phys.*, [2] 37, 38 (1828); (b) Dumas, *ibid.*, [2] 54, 241 (1833); *Ann.*, 10, 292 (1834); (c) Liebig, *ibid.*, 9, 131 (1834); (d) Dumas and Peligot, *Ann. chim.*, [2] 58, 60 (1835); *Ann.*, 15, 46 (1835); (e) Balard, *ibid.*, 52, 314 (1844); (f) Cahours, *Comptes rendus de l'Académie des Science*, 77, 746, 1408 (1873); *Bull. soc. chim.*, [2] 21, 77, 358 (1874); (g) Weddige, *J. prakt. Chem.*, [2] 10, 196 (1874); *ibid.*, 12, 435 (1875); (h) Wallach and Liebermann, *Ber.*, 13, 507 (1880).

determined and their nitrogen content analyzed for by the Kjeldahl method.

Experimental

Preparation of Dialkyl Oxalates.³—One hundred grams of anhydrous oxalic acid and 500 cc. of absolute alcohol (methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl and *i*-butyl) containing 30 g. of dry hydrogen chloride were refluxed for two hours. The solution was distilled until the thermometer registered 20° above the boiling point of the alcohol. The residue was further mixed with 500 cc. of absolute alcohol containing 30 g. of hydrogen chloride and the process of reflux and distillation repeated. The residue was then fractionated under reduced pressure. The constant boiling fraction was collected and refractionated three times at atmospheric pressure. Upon chilling, dimethyl oxalate solidified into a mass of white crystals, m. p. 53–55°, b. p. 166–167°. The other higher homologs remained as colorless liquids with a faint odor, insoluble in water but soluble in ether, petroleum ether, ethyl alcohol, ethyl acetate, benzene, acetone, chloroform, carbon tetrachloride, carbon bisulfide and glacial acetic acid. Their physical constants are tabulated.

TABLE I
SIMPLE CONSTANTS OF DIALKYL OXALATES

Dialkyl	B. p., °C.	d_4^{20}	d_4^{25}	n_D^{20}	n_D^{25}
Ethyl	184–186	1.07823	1.07336	1.4105	1.4074
<i>n</i> -Propyl	214–215	1.01693	1.01203	1.4168	1.4142
<i>i</i> -Propyl	193–194	1.00097	0.99635	1.4100	1.4072
<i>n</i> -Butyl	247–249	0.98732	.98157	1.4240	1.4221
<i>i</i> -Butyl	229–231	.97373	.97545	1.4180	1.4160

Conversion to Alkyl Oxamates.—One mole of dialkyl oxalate was dissolved in absolute alcohol and cooled in ice water. To this solution, while stirring, was added one mole of ammonia in the form of NH₄OH (sp. gr. 0.9). The reactants were allowed to stand in the ice box overnight. The solution was then heated on the water-bath to boiling and filtered while hot. The clear filtrate was allowed to crystallize. The crystals were filtered off and recrystallized twice from alcohol (methyl or ethyl). Their melting points and chemical analyses are tabulated.

TABLE II
MELTING POINTS AND NITROGEN CONTENT OF ALKYL OXAMATES

Alkyl	Formula	M. p., °C.	Subs., g.	N/10 H ₂ SO ₄ used, cc.	N, % Found	N, % Calcd.
Methyl	C ₃ H ₅ O ₂ N	122–123	0.1722	16.36	13.31	13.59
Ethyl	C ₄ H ₇ O ₂ N	114–115	.5060	43.30	11.99	11.97
<i>n</i> -Propyl	C ₅ H ₉ O ₂ N	90–92	.1876	14.34	10.71	10.69
<i>i</i> -Propyl	C ₅ H ₉ O ₂ N	86–87	.2742	20.80	10.63	10.69
<i>n</i> -Butyl	C ₆ H ₁₁ O ₂ N	82–84	.1070	7.40	9.69	9.65
<i>i</i> -Butyl	C ₆ H ₁₁ O ₂ N	75–76	.2352	15.54	9.26	9.65

Summary

1. A simple, general procedure for the esterification of a di-basic acid is described.

³ (a) Rising and Stieglitz, *THIS JOURNAL*, **40**, 726 (1918); (b) Clarke, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1922**, Vol. II, pp. 22–26; (c) Kenyon, *ibid.*, **1925**, Vol. V, pp. 59–61; (d) Bowden, *ibid.*, **1930**, Vol. X, pp. 70–72.

2. The simple physical constants of five dialkyl oxalates are reported.

3. By the action of the calculated amount of ammonia on the dialkyl oxalates, six alkyl oxamates were isolated. Among these, the isopropyl and *n*-butyl esters are new compounds. The methyl, *n*-propyl, and isobutyl derivatives have been mentioned previously, but their melting points are for the first time accurately given.

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NOTE

A Note on a Modification of Pregl's Micro-methoxyl Apparatus.— Considerable experience in this Laboratory with Pregl's¹ micro apparatus for the estimation of methoxyl has shown certain difficulties. The operation requires very close attention on account of the marked bumping of the contents of the decomposition flask and the consequent danger of the sucking back of the washing solution from the washer and that of the silver nitrate solution from the receiver. To avoid these difficulties the following modifications of Pregl's apparatus have been designed and placed in use.

1. This modification (Fig. 1) is a two-piece apparatus in which the two parts are connected by means of a ground-glass joint at G. The upright outlet tube is provided with two bulbs *c, c'* to condense any hydriodic acid carried along by the carbon dioxide stream. The carbon dioxide is led into flask A through the tube B which is sealed on the side of the flask and drawn into a capillary reaching almost to the bottom of the latter. In the procedure the apparatus is charged

through the opening G. The ground joint is then moistened with a drop of hydriodic acid and replaced. Two rubber bands are attached to the

¹ F. Pregl, "Quantitative Organic Microanalysis," second English edition translated from the third German edition by E. Fyleman, P. Blakiston's Son & Co., Inc., Philadelphia, Pa., 1930, p. 181.

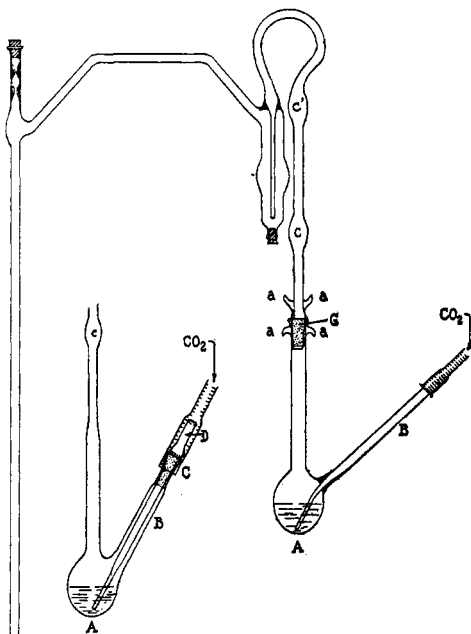


Fig. 2.

Fig. 1.

One-third actual size.