

EXPERIMENTAL⁴

2-Fluoroethylnitroguanidine. To 4.0 g. (0.0296 mole) of 1-nitro-2-methyl-2-thiopseudourea was added 8.7 g. (0.1382 mole) of 2-fluoroethylamine.⁵ An immediate reaction took place which was controlled by cooling with ice. The reaction was maintained at 35–40° for 50 min., cooled to room temperature, 50 ml. of ether added, and the solid was removed by filtration. The precipitate was washed on the filter with three 25-ml. portions of ether. Crystallization from ethanol gave a product which melted at 145–145.5°. The yield based on 1-nitro-2-methyl-2-thiopseudourea was 77.2%.

Anal. Calcd. for C₃H₇FN₂O₂: C, 24.00; H, 4.70; N, 37.32. Found: C, 24.40; H, 4.86; N, 36.94.

2-Fluoroethylguanidine picrate. The picrate was prepared by the hydrogenolysis procedure used for the preparation of 2,2,2-trifluoroethylguanidine picrate¹ and melted at 189–191°.

Anal. Calcd. for C₉H₁₁FN₃O₇: C, 32.34; H, 3.32; N, 25.15. Found: C, 32.46; H, 3.26; N, 24.70.

2-Fluoroethylguanidine nitrate. This salt was prepared by the method used to prepare 2,2,2-trifluoroethylguanidine nitrate¹ and melted at 104–105°.

Anal. Calcd. for C₃H₅FN₃O₃: C, 21.43; H, 5.40; N, 33.33. Found: C, 21.21; H, 5.26; N, 33.13.

2-Imino-1,3-diazacyclopentane tetrahydrofluoride. 2-Fluoroethylnitroguanidine (1.0 g., 0.066 mole) was dissolved in 50 ml. of 1-hexanol and heated at the reflux temperature (157°) for 6 hr. At the end of that time some crystalline material deposited on the side of the flask.

After standing overnight at room temperature, the brown crystalline material was removed, dissolved in hot water, and treated with Norit to remove the color. The Norit was removed, the aqueous solution evaporated to dryness and the residue crystallized from a mixture of ethanol and water. The purified material weighed 0.174 g. An elemental analysis indicated approximately 3.6 molecules of hydrogen fluoride for each molecule of imino compound. After dissolving in 40% aqueous hydrogen fluoride, allowing to stand overnight at room temperature, evaporating to dryness, and crystallizing from an ethanol-water solution, the elemental analysis corresponded to the tetrahydrofluoride salt of 2-imino-1,3-diazacyclopentane and melted at 227–231° dec.

Anal. Calcd. for C₅H₁₁F₄N₃: C, 21.82; H, 6.72; N, 25.45. Found: C, 21.37; H, 5.75; N, 25.10.

This compound was converted to the picrate which melted at 221–223°. A mixed melting point with an authentic sample of 2-imino-1,3-diazacyclopentane picrate was not depressed. This picrate also gave the correct elemental analysis.

N-(2,2-Difluoroethyl)-phthalimide. This compound was prepared by a modification of the method of Childs and co-workers.⁵ 1,1-Difluoro-2-bromoethane, 6.05 g. (0.0417 mole, 10% excess), 6.966 g. (0.0376 mole) potassium phthalimide and 5 ml. of dimethylformamide were placed in a 22-ml. Parr bomb. The bomb was attached to a horizontal stirring shaft in such a manner that it would rotate end over end inside a furnace. The bomb was rotated and heated at 210° for 8 hr. After cooling, the contents of the bomb were removed, poured into water, and filtered. The precipitate was washed with water, dissolved in hot ethanol, and treated with decolorizing carbon. The carbon was removed and the product crystallized from the ethanol solution. After recrystallization from ethanol the product weighed 3.73 g. (47%) and melted at 116.5–117.5°.

Anal. Calcd. for C₁₀H₇F₂N₂O₂: C, 56.87; H, 3.34; N, 6.63. Found: C, 56.91; H, 3.02; N, 6.56.

2,2-Difluoroethylnitroguanidine. 2,2-Difluoroethylamine

(1.897 g., 0.0234 mole), prepared from *N*-(2,2-difluoroethyl)-phthalimide by the method of Childs and co-workers⁵ was placed in a 50-ml. flask fitted with a Teflon-coated magnetic stirrer and a reflux condenser. To this was added at once 1.458 g. (0.0108 mole) of 1-nitro-2-methyl-2-thiopseudourea. The flask was then placed in a water bath at 50° and the contents stirred. The reaction was allowed to proceed without heating until at the end of 20 min. the temperature of the bath was 34°. Ethyl ether (10 ml.) was then added through the condenser and the reaction heated at the reflux temperature of the ether for an additional 20 min. The reaction mixture was then cooled, filtered, and the precipitate washed with ether. The product weighed 1.66 g. (91%) and after two crystallizations from ethanol melted at 162.5–163.5°.

Anal. Calcd. for C₃H₅F₂N₂O₂: C, 21.43; H, 3.60; N, 33.33. Found: C, 21.66; H, 3.84; N, 33.00.

2,2-Difluoroethylguanidine picrate. The picrate was prepared by the hydrogenolysis procedure used to prepare 2,2,2-trifluoroethylguanidine picrate¹ and melted at 197–198°.

Anal. Calcd. for C₉H₁₀F₂N₄O₇: C, 30.69; H, 2.86; N, 23.86. Found: C, 30.88; H, 3.03; N, 23.82.

2,2-Difluoroethylguanidine nitrate. The nitrate salt was prepared from the picrate by the method used to prepare 2,2,2-trifluoroethylguanidine nitrate¹ and melted at 93.0–94.5°.

Anal. Calcd. for C₃H₅F₂N₃O₃: C, 19.36; H, 4.33; N, 30.10. Found: C, 19.24; H, 4.45; N, 29.51.

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Carbonyl Stretching Frequencies of Some Oxalate Esters

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Only a few references indicate the position of the carbonyl stretching frequencies of oxalate esters. Hampton and Newell reported only a single peak for di-*n*-butyl oxalate,¹ at 1746 cm.⁻¹ This information led Bellamy to conclude that interaction between adjacent carbonyl groups was small.² Miyazawa and Kurantani³ also reported only a single C=O stretching frequency for dimethyl oxalate, 1730 cm.⁻¹ More recently Bender observed two carbonyl stretching frequencies in a spectrum of diethyl oxalate.⁴ Our findings also show two carbonyl stretching frequencies in oxalate esters.

(1) R. R. Hampton and J. E. Newell, *Anal. Chem.*, **21**, 914 (1949).

(2) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley, New York, N. Y., 1954, p. 157.

(3) T. Miyazawa and K. Kurantani, *J. Chem. Soc. Japan* (Pure Chemistry Section), **72**, 804 (1951). *Chem. Abstr.*, **47**, 43d (1953).

(4) M. L. Bender, *J. Am. Chem. Soc.*, **75**, 5986 (1953).

(4) All melting points were measured on a Kofler micro hot stage.

(5) A. F. Childs, L. J. Goldsworthy, G. F. Harding, F. E. King, A. W. Nineham, W. L. Norris, S. G. P. Plant, B. Shelton, and A. L. L. Tompsett, *J. Chem. Soc.*, 2174 (1948).

EXPERIMENTAL

Ethyl chloroglyoxylate was prepared by the method of Southwick and Seivard⁶ in 75.5% yield. Octyl chloroglyoxylate and phenyl chloroglyoxylate were obtained from the reaction of oxalyl chloride and 1-octanol or phenol, respectively.⁸ Dioctyl oxalate could be isolated as a high-boiling fraction in the synthesis of octyl chloroglyoxylate. The preparation of hydroquinone bis-ethoxalyl ester illustrates the method used in synthesizing the mixed esters.

Hydroquinone bis-ethoxalyl ester. A stirred solution of 2.2 g. (0.02 mole) hydroquinone in 25 ml. peroxide-free dioxane⁷ was treated with 5.7 g. (0.042 mole) ethyl chloroglyoxylate. The solution was cooled in an ice bath and 5.2 g. (0.04 mole) quinoline⁹ was added dropwise. After stirring thirty minutes more in the ice bath, water was added to dissolve the quinoline hydrochloride and precipitate the product. The white crystalline solid was filtered, washed twice with 20 ml. methanol, and dried to yield 2.9 g. hydroquinone bis-ethoxalyl ester whose m.p., 80–81°,⁹ was not changed by recrystallization from methanol.

Anal. Calcd. for C₁₄H₁₄O₈: C, 54.2; H, 4.5. Found: C, 54.3; 54.3; H, 4.6, 4.5.¹⁰

Diethyleneglycol bis-ethoxalyl ester. Diethyleneglycol, 7.95 g. (0.075 mole) treated with 21.8 g. (0.16 mole) ethyl chloroglyoxylate and 19.3 g. (0.15 mole) quinoline yielded the diethoxalate, 12.7 g., b.p. 165–172°/0.3 mm.

Anal. Calcd. for C₁₂H₁₈O₈: C, 47.1; H, 5.9. Found: C, 47.2; H, 5.8.

Diphenyl oxalate. Phenol, 3.76 g. (0.04 mole), oxalyl chloride, 2.52 g. 1.7 ml. (0.02 mole), and 5.0 g. 2.4 ml. (0.04 mole) quinoline yielded white needles, m.p. 135–137° (hexane).

Anal. Calcd. for C₁₄H₁₀O₄: C, 69.4; H, 4.2. Found: C, 69.5; H, 4.3.

Ethyl octyl oxalate was not isolated. The sample used for obtaining the spectrum was prepared by dissolving octyl chloroglyoxylate in chloroform containing ethanol.

Ethyl phenyl oxalate. Phenol, 2.83 g. (0.03 mole), ethyl chloroglyoxylate 4.5 g. (0.032 mole), and 3.87 g. (0.03 mole) quinoline yielded the mixed oxalate, b.p. 97–99°/4 mm.

Octyl chloroglyoxylate. 1-Octanol, 13.0 g. (0.1 mole), was added dropwise with stirring to 12.7 g. (0.01 mole) oxalyl chloride, and the mixture was heated on the steam bath for 3 hr. to drive off hydrogen chloride. Fractionation yielded 15.0 g. octyl chloroglyoxylate, b.p. 117–119°/12 mm. and 2.0 g., b.p. 150–157°/0.6 mm. of *dioctyl oxalate*.

*Phenyl chloroglyoxylate.*¹¹ Phenol, 2.82 g. (0.03 mole) in ether was added to an ether solution of 3.2 ml. (0.037 mole) oxalyl chloride and the ether solution was stirred two days at room temperature. Fractionation yielded the chloride, b.p. 87–89°/6 mm., white needles, m.p. 56–57°. (Lit. b.p. 97°/12 mm., m.p. 57°.)

Infrared spectra were obtained using a Perkin-Elmer Model No. 21 Spectrophotometer equipped with a sodium chloride prism. Liquid samples were measured as meniscus layers between sodium chloride disks or in chloroform solution. Concentrations were adjusted empirically to result in 30–50% transmission in the carbonyl band regions. Solid samples were measured in chloroform solution or KBr pellets. The ratio of 0.5 to 1 mg. in 500 mg. KBr gave well defined carbonyl bands.

(5) P. L. Southwick and L. L. Seivard, *J. Am. Chem. Soc.*, **71**, 2532 (1949). The potassium salt was prepared as in L. Claissen, *Ber.*, **24**, 127 (1891).

(6) G. v. Frank and W. Caro, *Ber.*, **63B**, 1532 (1930).

(7) L. F. Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Co., Boston, Mass., 1955, p. 282, Method b.

(8) Freshly distilled from zinc dust.

(9) Melting points are not corrected.

(10) Analyses were done by Dr. C. Fitz, Needham, Mass.

(11) R. Stolle and E. Knebel, *Ber.*, **54**, 1215 (1921).

RESULTS

Table I lists the carbonyl stretching frequencies for the diesters and ester chlorides.

TABLE I

Compound	C=O Frequencies	Medium
Diethyl oxalate	1740, 1765 cm. ⁻¹	Liquid film
Dioctyl oxalate	1740, 1762	CHCl ₃ solution
	1743, 1765	Liquid film
Ethyl octyl oxalate	1740, 1763	CHCl ₃ solution
Diethyleneglycol bis-ethoxalyl ester	1742, 1767	Liquid film
	1744, 1765	CHCl ₃ solution
Ethyl phenyl oxalate	1748, 1775	Liquid film
Hydroquinone bis-ethoxalyl ester	1752, 1775	KBr pellet
	1751, 1778	CHCl ₃ solution
Diphenyl oxalate	1758, 1775–1780	KBr pellet
	1760, 1787	CHCl ₃ solution
Ethyl chloroglyoxylate	1757, 1793	Liquid film
Phenyl chloroglyoxylate	1770, 1785	CCl ₄ solution
Octyl chloroglyoxylate	1762, 1795	Liquid film

Two strong intensity peaks attributed to carbonyl stretching are present in every compound examined. The four dialkyl oxalates of this study absorb at 1740–1744 cm.⁻¹ and 1762–1767 cm.⁻¹ in either liquid phase or chloroform solution. Both peaks of the two alkyl aryl oxalates are at higher frequency, 1748–1752 and 1775–1778 cm.⁻¹ while the peaks of diphenyl oxalate are at still slightly higher frequency, 1757–1760 and 1775–1787 cm.⁻¹ The two alkyl chloroglyoxylates peak at 1757–1762 and 1793–1795 cm.⁻¹ while phenyl chloroglyoxylate absorbs at 1770 and 1785 cm.⁻¹ The peak at lower frequency is a little stronger except in the spectra of diphenyl oxalate in chloroform and octyl chloroglyoxylate where the higher frequency band is the stronger.

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A Simple Method for the Preparation of Diethyl Carbonate-(carbonyl-C¹⁴) from Barium Carbonate-C¹⁴

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Diethyl carbonate-(carbonyl-C¹⁴) was required in connection with other work being carried out in this laboratory. Eisenhauer and his co-workers¹ have synthesized this ester according to the method of de Clermont² by heating ethyl iodide and silver carbonate-C¹⁴. They obtained a 9% yield by the original procedure, but they were able to improve

(1) H. R. Eisenhauer, J. M. Pepper, L. B. Jaques, and J. W. T. Spinks, *Can. J. Chem.*, **30**, 245 (1952).

(2) P. de Clermont, *Ann.*, **91**, 375 (1854); *Ann. chim et phys.*, [3] **44**, 330 (1855).