

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).

the yield up to 30% by carrying out the reaction in the presence of a catalytic amount of triethylamine or pyridine under refluxing conditions. In their synthesis, labeled silver carbonate was prepared from sodium carbonate-C¹⁴, which in turn was obtained by liberation of carbon dioxide from barium carbonate-C¹⁴ followed by absorption in sodium hydroxide solution.

We have now found that silver carbonate is obtained in about 90% yield by stirring barium carbonate with aqueous silver nitrate. This simplified the whole procedure very much by eliminating the need of intermediate preparation of labeled sodium carbonate. Silver carbonate and excess of ethyl iodide in dry ether at room temperature in the dark gave diethyl carbonate in about 40% yield based on the barium carbonate used.

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Silver carbonate-C¹⁴. Since silver carbonate is unstable in the light and darkens when exposed even to diffuse room light for several hours, it had to be prepared and handled in the dark. Silver nitrate (4.3 g.) in 10 cc. of water was added gradually to a stirred suspension of 2.473 g. of barium carbonate-C¹⁴ (0.0538 ± 0.0006 mc./mole) in 10 cc. of water. After stirring for 30 min., the pale yellow precipitate formed was filtered off with a sintered-glass filter, and washed with water until silver ion was no more detected, then with ethanol, and finally with dry ether. The dried material weighed 3.4 g. In a preliminary experiment with ordinary barium carbonate, silver carbonate prepared was analyzed for silver by dissolving it in dilute nitric acid followed by precipitation and weighing of silver chloride (Found: Ag, 70.60. Calcd. for Ag₂CO₃: Ag, 78.23).

Diethyl carbonate-(carbonyl-C¹⁴). Silver carbonate-C¹⁴ (3.4 g.), 5.0 g. of ethyl iodide, and 20 cc. of ether were placed in a 100-cc. Erlenmeyer flask, and the mixture was allowed to stand for 50 hr. in the dark with occasional agitation. It was, after addition of 1.405 g. of non-labeled diethyl carbonate, filtered with a sintered-glass filter, and the residue was washed with two portions of 10 cc. of ether. The filtrate and washings were combined and distilled through a Vigreux column, yielding 1.8 g. of diethyl carbonate-(carbonyl-C¹⁴), b.p. 122-126°.

A half gram of the diluted labeled ester obtained above and 0.7 g. of hydrazine hydrate were heated at 120° for 6 hr. in an oil bath. The solid precipitate, on 3 crystallizations from ethanol, gave carbonylhydrazide-C¹⁴ of a constant activity of 0.0167 = 0.0006 mc./mole, m.p. 152.0-152.5°. The diluted ester, therefore, had an activity of 0.0167 mc./mole, and this value indicated that 0.630 g. of diethyl carbonate-(carbonyl-C¹⁴) had been formed before the dilution corresponding to a yield of 42.8% based on the barium carbonate-C¹⁴ used. The total recovery of radioactivity in the product from the active barium carbonate was 37.9%.

Radioactivity determinations. The carbonylhydrazide-C¹⁴ (40 mg.) was oxidized according to the method of Van Slyke and Folch,³ and the liberated carbon dioxide was converted into barium carbonate and counted on an "infinitely thick" layer with an end-window Geiger-Müller counter. The count was corrected for background and compared with a standard barium carbonate-C¹⁴ of a known activity.

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(3) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940).

Further Experiments on the Alkylation of Benzene with C¹⁴-Labeled Ethyl Chloride

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In a previous paper,² we reported alkylation of benzene with C¹⁴-labeled ethyl chloride and aluminum chloride in which no isomerization of the ethyl group occurred. We also found that C¹⁴-labeled ethyl chloride was extensively isomerized by treatment with aluminum chloride in the absence of benzene. The latter result raised the question of why no isomerization of the ethyl group occurred during the alkylation, since the two processes probably involve the same intermediate, whether it is a carbonium ion³ or a complex.⁴

We have now carried out further experiments with C¹⁴-labeled ethyl chloride with the aim of learning more about the relationship of isomerization and alkylation. In the previous work,² ethyl-2-C¹⁴ chloride was mixed with aluminum chloride and kept at room temperature for one hour. In two experiments, the degree of isomerization was found to be 84% and 92%, respectively. In order to obtain a better estimate of the rate of the isomerization, we have now allowed ethyl-1-C¹⁴ chloride to stand over aluminum chloride for *six minutes* and then determined the extent of isomerization as before by recovering the ethyl chloride and adding it to benzene in the presence of fresh aluminum chloride. The ethylbenzene produced was found to contain all the C¹⁴ in the α -position, hence no detectable isomerization of ethyl-1-C¹⁴ chloride occurred in six minutes. One may estimate that the rate of isomerization of ethyl-1-C¹⁴ chloride by aluminum chloride is probably faster but of the same order of magnitude as the rate of isomerization of ethyl-1-C¹⁴ bromide by aluminum bromide;⁵ however, the former system is heterogeneous and the latter is homogeneous, so comparison is difficult.

Assuming that the same intermediate is involved in isomerization and alkylation, the fact that no isomerization was observed when alkylation with labeled ethyl chloride was carried out at 80° may be attributed to the fact that the intermediate reacted with benzene much faster than it underwent

(1) Taken from the M.A. thesis of Stellakis G. Panayides, University of Texas, 1957.

(2) R. M. Roberts, G. A. Ropp, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 1764 (1955).

(3) (a) C. C. Price, *Org. Reactions*, Vol. III, 7 (1946); (b) L. M. Nash, T. I. Taylor, and W. v. E. Doering, *J. Am. Chem. Soc.*, **71**, 1516 (1949).

(4) H. C. Brown and W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6279 (1953).

(5) F. L. J. Sixma and H. Hendriks, *Rec. trav. chim.*, **75**, 169 (1956), reported that at 25° the isomerization of ethyl-1-C¹⁴ bromide containing 0.045 mole aluminum bromide per mole of organic halide was 63% complete in 48 hr.