only by bubbling through sulfuric acid gave a satisfactory production of product at 125° with a pressure of 180 pounds per square inch without the use of added catalyst. A sample prepared from carbon monoxide and chlorine, and purified from excess chlorine by amalgamated mossy tin, required a temperature of 145° for an unsatisfactorily slow rate. The addition of 3 cc. of antimony pentachloride increased the rate so that satisfactory production was obtained at 80°.

Distillation of the condensate in the liquid air traps gave a middle fraction of relatively pure carbonyl chlorofluoride, representing about 25% of the initial phosgene. Redistillation of this fraction gave a material with the properties:

Melting point, °C.		−138
Boiling point (760 mm.), °C.		− 42
Vapor pressure to ±5%		$\log P_{\text{mm.}} = 7.93 - (1165/T)$
Molecular weight (by vapor density)		82.5
% Chlorine		43.6
Theoretical for COClF	Molecular weight	82.5
	% Chlorine	43.6

The gas has an odor similar to but distinguishable from that of phosgene. It is readily adsorbed by sodium hydroxide or soda lime. It shows no tendency to react with glass. Yields of approximately 50% COClF were obtained in some of the later preparations.

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[CONTRIBUTION FROM THE
EASTERN REGIONAL RESEARCH LABORATORY[1]]

Unsaturated Alcohol Esters of the 9,10-Dihydroxystearic Acids. Preparation of Elaidyl Alcohol

BY DANIEL SWERN, E. F. JORDAN, JR., AND H. B. KNIGHT

During a recent investigation it was necessary to identify a series of by-products which appeared to be unsaturated alcohol esters of 9,10-dihydroxystearic acid. A search of the literature revealed that none of these compounds had been described previously. To facilitate their identification, we have prepared the allyl, methallyl, β-chloroallyl, furfuryl, cinnamyl, oleyl and elaidyl esters of both 9,10-dihydroxystearic acids, m. p. 95 and 130°, respectively.

Elaidyl alcohol is not a very well-known compound, since its preparation is extremely tedious. It is usually prepared by reduction of purified methyl or ethyl elaidate with metallic sodium and absolute alcohol, and purified by fractional distillation and crystallization.[2] We have worked out a convenient method for its preparation in fair yield from commercial or highly purified oleyl alcohol. Elaidyl alcohol, m. p. 36–37°, is obtained as glistening plates.

Experimental

Materials.—Low melting 9,10-dihydroxystearic acid (m. p. 95°) and its high-melting isomer (m. p. 130°), and their methyl esters (m. p. 70 and 104°, respectively) were prepared as previously described.[3,4] Purified oleyl alcohol was prepared from the commercial grade by low temperature solvent crystallization and fractional distillation.[5] The allyl, methallyl, β-chloroallyl, cinnamyl and furfuryl alcohols were the purest commercial grades and were fractionally distilled before use.

Two alternative procedures were employed for the preparation of elaidyl alcohol.

1. Commercial oleyl alcohol (oleyl alcohol content, 60 to 70%) was distilled through an 18-inch Vigreux column, and the fraction boiling at 165–205° (4.3 mm.), which amounted to about 85% of the starting material, was retained. Six hundred grams was dissolved in 9000 ml. of acetone, and the solution was cooled to −20° to precipitate solid (saturated) alcohols. The liquid alcohols (470 g.), obtained from the filtrate, were heated and stirred for two hours in a nitrogen atmosphere at 220–225° with 0.3% of powdered selenium.[6] The cooled reaction mixture was dissolved in 4700 ml. of acetone, treated with active carbon and filtered, and the filtrate was cooled to −20°. The precipitate, m. p. about 30°, consisted mainly of elaidyl alcohol and weighed 200 g. Pure elaidyl alcohol, m. p., 36–37° (lit. 35–35.5°),[2] was obtained after one additional crystallization from acetone at −20° and two at 0°. The yield was 56 g. *Anal.* Iodine number: Calcd., 94.5; Found, 93.4.

2. Purified oleyl alcohol[5] (270 g., oleyl alcohol content, 97%) was isomerized as described above. Crystallization from acetone at −20°, after treatment of the solution with active carbon, yielded 164 g. of fairly pure elaidyl alcohol m. p. about 33°; iodine number, about 91. Pure elaidyl alcohol, m. p., 36–37°, was obtained after two additional crystallizations from acetone at 0 to −5°. The yield was 110 g. Iodine number was 93.6.

Esterification Procedures.—The allyl, β-chloroallyl, oleyl and elaidyl esters were prepared by direct esterification of the corresponding alcohol with the dihydroxystearic acids, previously reported methods being employed.[3] In these preparations, with the exception of the allyl esters, the azeotropic method was used. Approximately 2–3 ml. of allyl and β-chloroallyl alcohol per gram of acid were employed, as compared with 20% molar excesses of oleyl and elaidyl alcohols. Yields of crude esters were quantitative.

The methallyl, furfuryl and cinnamyl esters were prepared by alcoholysis of methyl 9,10-dihydroxystearate with the appropriate alcohol. A typical preparation is as follows: To 0.5–1.0 mole of the freshly distilled alcohol, 0.4 g. (0.017 mole) of metallic sodium was added slowly at room temperature. When the sodium was completely dissolved, 0.05 mole of methyl 9,10-dihydroxystearate was added, and the mixture was heated on the steam-bath for three hours in a nitrogen atmosphere, with occasional shaking. The methyl alcohol formed in the reaction was permitted to escape. The reaction mixture was poured into a large quantity of hot water, and the aqueous layer was separated and discarded. The product was washed with hot water and cooled to room temperature. The solid product obtained was crystallized to constant melting point from 95% ethyl alcohol (2 to 5 ml./g.).

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(2) Toyama, *Chem. Umschau Fette, Öle, Wachse Harze*, **31**, 13 (1924).

(3) Swern and Jordan, THIS JOURNAL, **67**, 902 (1945).

(4) Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).

(5) Swern, Knight and Findley, *Oil & Soap*, **21**, 133 (1944).

(6) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

TABLE I

UNSATURATED ALCOHOL ESTERS OF 9,10-DIHYDROXYSTEARIC ACID

	Melting point, 95°						Melting point, 130°					
			Sapn. no.		Iodine no.				Sapn. no.		Iodine no.	
Ester	Yield,[a] %	M. p., °C.	Calcd.	Found	Calcd.	Found	Yield,[a] %	M. p., °C.	Calcd.	Found	Calcd.	Found
Allyl	30	59.8-60.7	157.4	158.1	71.2	70.0	46	98.8-99.1	157.4	157.1	71.2	71.4
Methallyl	58	60.5-61.0	151.4	151.9	68.4	68.4	53	92.8-93.3	151.4	151.4	68.4	67.6
β-Chloroallyl[b]	52	67.3-67.7	...	...	..	..	59	98.2-98.4	...	...	..	..[c]
Furfuryl	36	69.9-70.2	141.5	143.0	..	..	51	99.0-99.3	141.5	142.5	..	..
Oleyl	50	52.0-52.4	98.9	101.3	44.8	43.6	67	79.9-80.2	98.9	100.2	44.8	43.8
Elaidyl	53	70.2-70.7	98.9	101.3	44.8	43.9	70	84.7-85.2	98.9	101.0	44.8	44.6
Cinnamyl	42	74.4-74.9	129.7	130.1	..	..	34	101.1-101.4	129.7	131.5	..	..

[a] Purified products, after at least three crystallizations from 95% ethanol. [b] (Low melting point) Calcd.: C, 64.6; H, 10.1. Found: C, 64.8; H, 9.8. (High melting point) Calcd.: C, 64.6; H, 10.1. Found: C, 64.8; H, 9.9. [c] The theoretical iodine number could not be obtained (*cf.* Shriner, "Quantitative Analysis of Organic Compounds, 2nd ed., 1941, p. 51).

Results and Discussion

The results are summarized in Table I. With the exception of the furfuryl ester, which becomes slightly yellow after exposure to light and air, the products are white, crystalline solids. The esters prepared from the low-melting form of 9,10-dihydroxystearic acid are insoluble in water and Skellysolve B, and soluble in 95% ethanol, acetone, toluene, ethyl acetate and nitropropane. The esters prepared from the high-melting form of 9,10-dihydroxystearic acid are also insoluble in water and Skellysolve B, but only slightly soluble at room temperature in the other solvents mentioned. On gentle warming, however, they dissolve readily. Preliminary investigation indicated that some of these compounds may be good plasticizers for ethyl cellulose and cellulose acetate.

PHILADELPHIA 18, PA. RECEIVED MAY 13, 1946

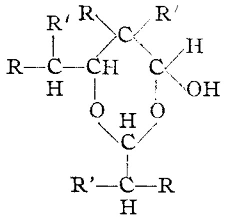
Glycol Esters from Aldehydes

BY FRANK J. VILLANI AND F. F. NORD

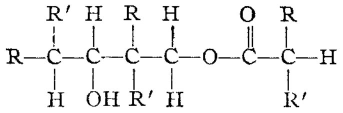
Investigations of several schools which were not fully independent have shown that products of aldehyde condensations lead sometimes to conflicting interpretations of the essential steps involved in their formation. Simple esters, polymers, aldols, glycol esters and 1,3-dioxanes are reported to have been isolated, depending on the nature of the condensing agent used.[1] Raman spectra which might support the contention that a number of isolated glycol esters[2] should be regarded as 1,3-dioxanes failed to do so because the carbonyl line does not appear in, or disappears from, the spectrum. It is also suggested that although the refractive indices and the densities of the glycol esters differ considerably from those of the isomeric 1,3-dioxanes, the corresponding boiling points are very close.

To finally clarify this question we have prepared the dioxanes and the corresponding glycol esters as described in the literature,[2,3] and we have also examined the physical and chemical properties of both.

Both compounds, the 1,3-dioxanes



and the glycol esters



$$R{-}C(R')(H){-}CH(OH){-}C(R)(R'){-}CH_2{-}O{-}C(=O){-}C(R)(R'){-}H$$

give the same breakdown products on proper treatment with alcoholic alkali.

Accordingly the benzoates[4] were prepared, which resulted in the following observations (Table I).

Experimental.—A representative procedure for the preparation of the glycol esters is as follows:

To a mole of the aldehyde is added a quantity of the coordination catalysts equal to 5% of the weight of the aldehyde. The flask is quickly stoppered and cooled under the tap. After the initial reaction has subsided, the mixture was permitted to stand for twenty-four hours at room temperature. Without further treatment the contents of the flask are fractionated.

The procedure for the preparation of the dioxanes[5] is as follows:

To a mixture of equal volumes of aldehyde and ether, in the presence of a few drops of diethylamine, 10% potassium hydroxide was added dropwise with vigorous stirring, maintaining the temperature at 5-10°. The reaction is complete when the temperature fails to rise on the addition of further alkali. After separation, washing thoroughly

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[1] Owen, "Ann. Rep. on the Progress of Chem.," **41**, 139-148 (1945).

[2] Kulpinski and Nord, *J. Org. Chem.*, **8**, 256-270 (1943).

[3] Späth, Lorenz and Freund *Ber.*, **76**, 57 (1943).

[4] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1945, p. 137.

[5] Saunders, Murray and Cleveland, THIS JOURNAL, **65** (1943).