TABLE I

UNSATURATED ALCOHOL ESTERS OF 9,10-DIHYDROXYSTEARIC ACID

Ester	Melting point, 95° Yield,[a] %	M. p., °C.	Sapn. no. Calcd.	Sapn. no. Found	Iodine no. Calcd.	Iodine no. Found	Melting point, 130° Yield,[a] %	M. p., °C.	Sapn. no. Calcd.	Sapn. no. Found	Iodine no. Calcd.	Iodine no. 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

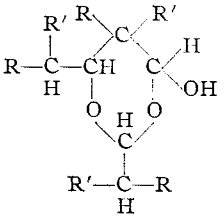
Glycol Esters from Aldehydes

BY FRANK J. VILLANI AND F. F. NORD

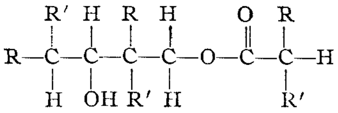
Investigations of several schools which were not fully independent have shown that products of aldehyde condensations lead sometimes to conflicting interpretations of the essential steps involved in their formation. Simple esters, polymers, aldols, glycol esters and 1,3-dioxanes are reported to have 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



$$R-\underset{H}{\overset{R'}{C}}-\underset{OH}{\overset{H}{C}}-\underset{R'}{\overset{R}{C}}-\underset{H}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-\underset{R'}{\overset{R}{C}}-H$$

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).

TABLE I

Aldehyde →		Acetaldehyde		Isobutyraldehyde	
Condensing agent		KOH + Et_2NH	$Mg(Al(C_2H_5)_4)_2$	KOH + Et_2NH	$Mg(Al(OC_4H_9)_4)_2$
Isolated product		2,6-Dimethyl-1,3-dioxane-4-ol	Monoacetate of 1,3-butanediol	2,6-Diisopropyl-5,5-dimethyl-1,3-dioxane-4-ol	Monoisobutyrate of 2,2,4-trimethyl-1,3-pentanediol
B. p.	°C.	68–72	85–89	90–95	103–105
	Mm.	2	11	4	2
n^{25}D		1.4380	1.4190	1.4463	1.4390
Benzoate B. p.	°C.	90–100	135–137	104–105	161–163
	Mm.	2	2	3^b	1^a
Benzoate M. p., °C.		92–93[3]	....	87–90	....
Benzoate n^{25}D		....	1.5045	....	1.5575
Benzoate d^{25}		....	1.0695	....	1.1200
Benzoate Yield, %		47.0	53.2	33.5	45.0
Benzoate Analyses, % Carbon	Calcd.	66.10	66.10	71.25	71.25
	Found	66.30	66.26	67.12	72.01
Benzoate Analyses, % Hydrogen	Calcd.	6.78	6.78	8.75	8.75
	Found	6.82	6.46	7.52	7.82

[a] A slight decomposition appeared to be unavoidable. The observed molar refraction of 92.26 is in agreement with the calculated value of 92.17. [b] Distilled over as a wax-like solid. This compound was partially solidified and was extremely hygroscopic, and as a result did not give a satisfactory analysis.

with water, drying over anhydrous sodium sulfate, the ethereal solution was finally rectified.

It is obvious from the data recorded that the benzoates prepared are entirely different and that depending on the nature of the catalyst, the products of the condensation are not identical. In the case of the acetaldehyde, we were able to isolate both the dioxane and the glycol ester. However, when the condensation of isobutyraldehyde was performed with our coördination catalyst, we obtained only the glycol ester.

COMMUNICATION NO. 46 FROM
THE DEPARTMENT OF ORGANIC CHEMISTRY
FORDHAM UNIVERSITY, NEW YORK 58, N. Y.

RECEIVED DECEMBER 29, 1945

COMMUNICATIONS TO THE EDITOR

IMPROVED PROCEDURES FOR THE PREPARATION OF SOME ORGANOSILICON COMPOUNDS

Sir:

The general methods used for the synthesis of R_4Si compounds have involved reaction of silicon tetrachloride with dialkylzinc[1] compounds, with RX compounds and sodium,[2] and with Grignard reagents.[3] The Wurtz modification was also used incidentally by Schumb and co-workers[4] to prepare R_4Si compounds from silicon hexachloride, an RX compound and sodium. In addition, tetra-*n*-butylsilane was prepared in 50% yield from ethyl orthosilicate with a 25% excess of *n*-butylmagnesium bromide and extensive heating.[5] These several procedures have given low to moderate yields or have involved relatively drastic conditions.

Incidental to a study of the preparation of some organosilicon compounds containing functional groups, we have examined the use of organolithium compounds. We have observed that silicon tetrachloride or ethyl orthosilicate or ethyl orthothiosilicate in ether react almost immediately with the simple alkyllithium and aryllithium compounds in ether to give excellent yields of R_4Si compounds.

$$SiCl_4 + 4RLi \longrightarrow R_4Si + 4LiCl$$

With silicon tetrachloride and the appropriate RLi compound, the yield of tetraethylsilane was 92%, the yield of tetra-*n*-butylsilane was 98%, and the yield of tetraphenylsilane was 99%. From ethyl orthosilicate the yield of tetra-*n*-butylsilane was 97%, and the yield of tetraphenylsilane was 98%. The yield of tetraphenylsilane from ethyl orthothiosilicate was also 98%. Color

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[1] Friedel and Crafts, *Ann.*, **127**, 28 (1863).

[2] Polis, *Ber.*, **18**, 1540 (1885).

[3] Kipping, *J. Chem. Soc.*, **91**, 209 (1907); Dilthey and Eduardoff, *Ber.*, **37**, 1140 (1904).

[4] Schumb, Ackerman and Saffer, THIS JOURNAL, **60**, 2486 (1938).

[5] Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940).