

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,¹ PHILADELPHIA, PENNSYLVANIA]

Aliphatic Esters of the 9,10-Dihydroxystearic Acids

BY DANIEL SWERN AND E. F. JORDAN, JR.

Although the 9,10-dihydroxystearic acids, m. p. 95 and 130°, derivable from oleic and elaidic acids, are well-known compounds, a search of the literature revealed that only their methyl and ethyl esters had been reported.² Interest in plasticizers and high-melting waxes prompted us to prepare a series of esters of these hydroxy acids with aliphatic primary alcohols ranging in chain length from three to eighteen carbon atoms. The results are summarized in Tables I and II. The esters are white, crystalline solids, with very low vapor pressures. They are insoluble in water but

esters, the *n*-butyl ester has the minimum melting point, whereas in the series of high-melting esters, the *n*-amyl ester has the minimum melting point.

Experimental

Materials.—The 9,10-dihydroxystearic acids, m. p. 95 and 130°, were prepared from oleic acid by oxidation with hydrogen peroxide in acetic acid solution³ and with alkaline potassium permanganate,⁴ respectively. The 9,10-dihydroxyoctadecyl alcohol, m. p. 84.5–86°, was prepared from oleyl alcohol.⁵ The other alcohols were Eastman Kodak Company purest grade, and they were either crystallized to constant melting points or fractionally distilled before use.

TABLE I

PROPERTIES OF ESTERS OF 9,10-DIHYDROXYSTEARIC ACID, M. P. 130°

Ester ^a	Yield, ^b %	M. p., °C.	Saponification no.		Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -Propyl	51	92.5–93.5	156.4	156.0	70.4	70.2	11.8	11.5
<i>n</i> -Butyl	50	89–90	150.6	150.5	71.0	71.2	11.9	11.5
<i>i</i> -Butyl	18	89.5–90.5	150.6	150.3	71.0	71.0	11.9	11.6
<i>n</i> -Amyl	46	86.5–88	145.1	145.6	71.4	71.5	12.0	11.5
<i>n</i> -Hexyl	55	87–87.5	140.0	140.3	72.0	72.0	12.1	12.1
<i>n</i> -Octyl	54	88–89	130.9	131.6	72.9	73.0	12.2	11.6
<i>n</i> -Decyl	52	89.5–90.5	122.8	124.1	73.6	74.0	12.4	11.9
<i>n</i> -Dodecyl	59	91–92	115.7	116.0	74.3	73.9	12.5	12.0
<i>n</i> -Tetradecyl	65	92–93	109.4	109.7	75.0	74.8	12.6	12.0
<i>n</i> -Hexadecyl	69	94–95.5	103.7	104.4	75.5	75.5	12.7	12.5
<i>n</i> -Octadecyl	64	94–95	98.7	99.7	76.0	75.9	12.8	12.5
9,10-Dihydroxy-octadecyl	56	107–108.5	93.4	92.1	71.9	71.6	12.1	11.8

^a The methyl ester, m. p. 105°, and the ethyl ester, m. p. 99°, have been reported in the literature.² ^b Purified products.

TABLE II

PROPERTIES OF ESTERS OF 9,10-DIHYDROXYSTEARIC ACID, M. P. 95°

Ester ^a	Yield, ^b %	M. p., °C.	Saponification no.		Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -Propyl	25	57.5–58	156.4	156.4	70.4	69.8	11.8	11.7
<i>n</i> -Butyl	51	53–54	150.6	150.3	71.0	70.9	11.9	11.7
<i>n</i> -Amyl	30	58.5–59.5	145.1	145.2	71.4	71.5	12.0	12.0
<i>n</i> -Hexyl	46	64.5–65.5	140.0	140.4	72.0	72.0	12.1	11.5
<i>n</i> -Octyl	55	73–74	130.9	130.8	72.9	72.5	12.2	12.3
<i>n</i> -Decyl	63	72.5–73	122.8	123.2	73.6	73.6	12.4	12.2
<i>n</i> -Dodecyl	40	70–72	115.7	115.8	74.3	74.5	12.5	12.1
<i>n</i> -Tetradecyl	50	71.5–72	109.4	110.6	75.0	74.4	12.6	11.6
<i>n</i> -Hexadecyl	55	73–74	103.7	105.0	75.5	75.4	12.7	12.5
<i>n</i> -Octadecyl	63	76–77	98.7	99.9	76.0	75.8	12.8	12.5
9,10-Dihydroxy-octadecyl	60	96.5–97.5	93.4	92.1	71.9	72.3	12.1	12.1

^a The methyl ester, m. p. 71°, and the ethyl ester, m. p. 59°, have been reported in the literature.² ^b Purified products.

are soluble in most organic solvents. It is interesting to note that in the series of low-melting

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Hilditch, *J. Chem. Soc.*, 1828 (1926); Smit, *Rec. trav. chim.*, **49**, 675 (1930). Ishikawa and Kuroda [*Science Repts. Tokyo Bunrika Daigaku*, **A3**, 265 (1939)] have prepared a series of aliphatic esters from the dihydroxystearic acid isolable from castor oil.

Esterification Procedures.—The propyl and butyl esters were prepared by heating 15.8 g. (0.05 mole) of 9,10-dihydroxystearic acid, 32 ml. of the alcohol, and 0.316 g. of naphthalene- β -sulfonic acid for eight hours at 100°. The solution was poured into a large excess of hot water (90°), with stirring and the lower aqueous layer was discarded.

(3) Scanlan and Swern, *This Journal*, **62**, 2305 (1940).

(4) Le Sueur, *J. Chem. Soc.*, **79**, 1313 (1901).

(5) Swern, Findley and Scanlan, *This Journal*, **66**, 1925 (1944).

The crude ester was washed once with hot water. The dry crude ester, obtained in nearly quantitative yield, was recrystallized to a constant melting point from 95% ethanol (5 ml./g.).

The higher alcohol esters were prepared by refluxing 15.8 g. of 9,10-dihydroxystearic acid, 0.06 mole of the alcohol, 200 ml. of benzene, and 0.316 g. of naphthalene- β -sulfonic acid for eight hours. The water formed during the reaction was removed azeotropically, and the benzene was returned to the reaction mixture. The quantitative amount of water was liberated. The benzene solution was evaporated to dryness, and the crude ester was melted and washed once with hot water. The aqueous layer was discarded, and the dried product, obtained in quantitative

yield, was recrystallized to a constant melting point from 95% ethanol (5 ml./g.).

Summary

The 9,10-dihydroxystearic acids, m. p. 95° and 130°, have been esterified with twelve saturated aliphatic primary alcohols. The products are fairly high melting solids with very low vapor pressures. They may be useful as plasticizers or high-melting waxes.

PHILADELPHIA, PA.

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Cinnamamides. I. α,β -Diamino Derivatives

BY NORMAN H. CROMWELL AND JOHN A. CAUGHLAN¹

Although cinnamamide and various N-substituted derivatives have been known for many years, only a few studies have been made of the chemistry of these α,β -unsaturated carbonyl compounds. It seemed of interest to carry out several experiments to compare the reactivity of such compounds with that of the α,β -unsaturated ketones with which we have been concerned in this Laboratory.²

Vorländer³ showed that N-substituted cinnamamides added sodiummalonate in the normal way and added bromine at the olefinic double bond. Also Kohler⁴ found this α,β -unsaturated carbonyl system to be reactive in the usual manner toward the Grignard reagent.

In the present investigation cinnamoyl chloride was treated with various secondary amines to give excellent yields of cinnampiperidide (I), cinnammorpholide (II), cinnamdiethylamide (III) and cinnamtetrahydroisoquinolide (IV). These unsaturated amides were readily converted into their corresponding dibromides (V), (VI), (VII) and (VIII) in carbon tetrachloride solution.

It was of interest to compare the reactivity of these dibromides with secondary amines, with similar studies that have been made with dibromo ketones.⁵ The dibromide (V) reacted with piperidine in pyridine solution or without solvent to give the α,β -diamino amide (IX), while (VI) reacted with morpholine to form (X) and with piperidine to give (XI). All three of these products⁶ resulted in low yields and it seemed apparent that a large portion of the dibromides had engaged in a parallel reaction.

(1) A Parke, Davis and Company research fellow, 1943-1944.

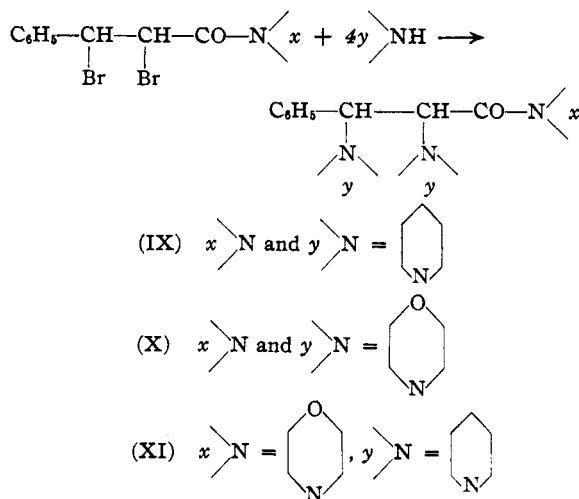
(2) See (a) THIS JOURNAL, **67**, 124 (1945); (b) **66**, 872 (1944); and preceding papers.

(3) Vorländer, *Ann.*, **320**, 66 (1902).

(4) Kohler and Heritage, *Am. Chem. J.*, **33**, 31 (1905).

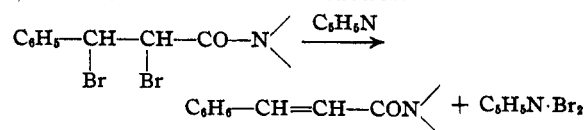
(5) See Cromwell, Harris and Cram, THIS JOURNAL, **66**, 134 (1944), and preceding papers.

(6) These α,β -diamino amides are of a new type and thus are being "screen tested" for pharmacological activity by the Parke, Davis and Company, Detroit, Michigan.



When the dibromides (VII) and (VIII) were treated in the same way with diethylamine and tetrahydroisoquinoline, respectively, no diamino amides could be isolated. The only products resulting from these latter reactions were the unsaturated amides (III) and (IV), respectively. Moreover, it was found that refluxing the dibromides (V) and (VI) with pyridine alone gave from 25-35% yields of the corresponding unsaturated amides (I) and (II), respectively.

The formation of the α,β -dibromo amides is reversible, and in the presence of a strong halogen acceptor such as pyridine⁷ the equilibrium is forced toward the α,β -unsaturated amide. In this respect the dibromo amides differ from the dibromo ketones. It is this reaction



(7) It has long been known that amines form some sort of addition compounds with halogens under anhydrous conditions; see Hantzsch and Graf, *Ber.*, **38**, 2157 (1905).