

in vacuo at 35° bath temperature, there remained 7.4 g. of sulfur-free, white, crystalline substance, representing 87%. This material is evidently a mixture of alpha and beta *l*-arabinomethylosides. Once recrystallized from chloroform and petroleum ether it gave $[\alpha]_D -73.9^\circ$ in chloroform. Since at constant rotation the product showed $[\alpha]_D -129.2^\circ$, the latter is the more levorotatory form, and according to the nomenclature of Hudson¹⁶ is to be considered the alpha glycoside.

The substance dissolves readily in water (hygroscopic), methanol, ethanol, ethyl acetate, chloroform and ether. It can be recrystallized from chloroform with addition of petroleum ether or from hot carbon tetrachloride. From the latter a constant rotation is reached more quickly. $[\alpha]_D^{31^\circ} -129.2^\circ$ ($\alpha -18.37^\circ$; 0.925 g. in 26.02 cc. of U. S. P. CHCl₃, 4-dm. tube); m. p. 89–90°; b. p. 133–137° (5 mm.).

Anal. Calcd. for C₆H₉O₅(OCH₃): methoxyl, 20.95. Found: 20.7.

2,3-Dimethylmethyl-*l*-arabinomethyloside.—The mixed alpha- and beta-glycosides from the Pacsu reaction (4.77 g.), after one recrystallization from chloroform and petroleum ether, were methylated with 45 g. of methyl sulfate, 52 cc. of sodium hydroxide (56%), 16 cc. of carbon tetrachloride, and 2 cc. of water according to the directions of West and Holden¹⁷ for the methylation of glucose. On distillation there was obtained 2.5 g. of a light, mobile liquid of pungent, mint-like odor. It reduced Benedict's solution only after boiling with acid; b. p. 60–65° (6 mm.).

Anal. Calcd. for C₈H₁₇O(OCH₃)₂: methoxyl, 52.85. Found: 53.4.

2,3 - Dimethyl - *l* - arabinomethylose.—2,3 - Dimethylmethyl-*l*-arabinomethyloside (4 g.) was heated for two hours on the boiling water-bath with 20 cc. of sulfuric acid (2%). The solution was neutralized with barium carbonate, filtered and extracted with 100 cc. of chloroform in three portions. After drying over Drierite, the chloro-

(16) C. S. Hudson, *THIS JOURNAL*, **31**, 66 (1909).

(17) E. S. West and R. F. Holden, *ibid.*, **56**, 930 (1934).

form was distilled off at ordinary pressure. The remaining yellow liquid was distilled, and gave a colorless, odorless, mobile liquid which readily reduced Benedict's solution; b. p. 97–99° (6 mm.), $[\alpha]_D^{24^\circ} -43.8^\circ$ ($\alpha -2.00^\circ$; 0.457 g. in 10.00 cc. of U. S. P. chloroform, 1-dm. tube).

Anal. Calcd. for C₈H₁₇O₂(OCH₃)₂: methoxyl, 38.3. Found: 37.6.

Oxidation of Dimethyl-*l*-arabinomethylose.—Two grams of dimethyl-*l*-arabinomethylose was oxidized with 20 cc. of nitric acid (*d* 1.2)¹⁸ and the resulting acid-free sirup esterified with methyl alcohol containing 3% of hydrochloric acid. The resulting dimethyl ester of dimethoxy-*l*(+)-succinic acid was not distilled. After removal of hydrochloric acid with barium carbonate, the methyl alcohol was evaporated *in vacuo*, the remaining barium chloride removed by dissolving the residue in ether and filtering, and the resulting sirup, after evaporation, dissolved in 20 cc. of methyl alcohol. This solution was then saturated with dry ammonia and allowed to stand. After thirty-six hours there had crystallized 0.7 g. of dimethoxy-*l*(+)-succinic diamide;¹⁹ long needles, m. p. 270°, dec. 284°; $[\alpha]_D^{30^\circ} +91^\circ$, *c*, 0.46, H₂O.

Summary

1. The first methyltetroside, alpha-methyl-*l*-arabinomethyloside, has been prepared, characterized and the furanoside structure proved.

2. The sugar has been removed from its reaction mixture as the ethyl mercaptal following a suggestion of Emil Fischer.²⁰

3. The yield of *l*-arabinomethylose from calcium rhamnonate by hydrogen peroxide degradation has been increased from 6.1 to 18%.

(18) E. L. Hirst and A. K. Macbeth, *J. Chem. Soc.*, 22–26 (1926).

(19) E. L. Hirst, *ibid.*, 350 (1926).

(20) E. Fischer, *Ber.*, **27**, 673 (1894).

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The Fries Reaction with α -Naphthol Esters^{1,2}

By R. W. STOUGHTON

The Fries rearrangement of naphthyl esters offers a means of preparation of the hydroxy-naphthyl ketones which can be reduced to alkyl-naphthols. Lederer³ has investigated the low temperature rearrangement of a few α -naphthyl esters in nitrobenzene solution and found that the principal product is the *p*-hydroxy ketone. As the *o*-ketones were desired, a study of the reaction

(1) Presented before the Organic Division of the American Chemical Society at the Cleveland, Ohio, Meeting, September, 1934.

(2) The funds for carrying out this work were given by the International Health Division of the Rockefeller Foundation.

(3) Lederer, *J. prakt. Chem.*, **136**, 49 (1932).

to higher temperatures was made. Previously, only the acetate⁴ has been studied in this manner but now the series has been extended through the valerate.

It was found that when a fatty acid ester of α -naphthol is heated with aluminum chloride under optimum conditions there is found 50–60% of the *o*- and 5–10% of the *p*-hydroxy ketone. The relative proportions of these isomers are similar to those obtained from a phenol substituted in the ortho and meta positions rather than from

(4) Fries, *Ber.*, **54**, 709 (1921).

phenol itself. In addition to these normal products there is usually formed 1–5% of a 2,4-diacetyl-1-naphthol. Fries⁴ observed the formation of 2,4-diacetyl-1-naphthol in the rearrangement of α -naphthyl acetate but Lederer³ made no mention of any such compound. As the molecular weight of the acid increased the yield of both the *p*-acyl and diacyl derivatives decreased and no divaleryl-naphthol was obtained.

The formation of such small amounts of diacyl compounds gives no indication as to whether this reaction is intramolecular in nature or not. In view of the drastic conditions employed in the formation of these compounds, they might have been formed from some side reaction or from a secondary rearrangement of one of the initial products. That such a rearrangement can take place was shown experimentally by heating 4-acetyl-1-naphthol with aluminum chloride. The same three products were formed in the same proportions as obtained from the original rearrangement of α -naphthyl acetate. No rearranged products could be obtained from the ortho compound.

Von Auwers,⁵ in rearranging of *sym-m*-xylenyl acetate to 2-acetyl-3,5-dimethylphenol, obtained a little 2,6-diacetyl-3,5-dimethylphenol as a by-product. This case is interesting because no para acetyl derivative was isolated, and therefore it is unlikely that it could have been formed from such a secondary rearrangement. Information regarding these compounds is too limited to draw any conclusions as to the mechanism of their formation.

The reduction of the *o*-ketones is described and the physical properties of the resulting alkylnaphthols are recorded.

Experimental

Preparation of Esters.—A convenient amount (50–100 g.) of α -naphthol was treated with a 10% excess of the proper acyl chloride in a flask equipped with a reflux condenser. Usually hydrogen chloride was evolved at once but if the reaction seemed slow a drop of concd. sulfuric acid was added as a catalyst. After standing for two hours at room temperature the mixture was heated for one hour on the steam-bath and then poured into ice water. The product was taken up in ether, washed with sodium bicarbonate solution and vacuum distilled. The yields varied from 90–95%. Two of these esters are reported for the first time and their physical properties are recorded below.

α -Naphthyl propionate: yellow oil; b. p. (2 mm.) 134–135°; d_{20}^{20} 1.1186; n_D^{25} 1.5811. *Anal.* Calcd. for $C_{15}H_{12}O_2$: C, 78.0; H, 6.1. Found: C, 78.3; H, 6.5.

(5) Von Auwers, *Ber.*, **48**, 90 (1915).

α -Naphthyl valerate: yellow oil; b. p. (6 mm.) 172–176°; d_{20}^{20} 1.0992; n_D^{25} 1.5698. *Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 78.8; H, 7.5.

Rearrangement of Esters.—The ester was treated with an equal weight of powdered aluminum chloride with cooling and after the initial reaction had subsided it was heated at a temperature of 100° for two hours and finally at 120° for one hour. The reaction mixture was decomposed carefully by adding cold dilute hydrochloric acid and subsequent heating on the steam cone. The *o*-hydroxy ketone was separated by steam distillation or, in the case of the higher members, by careful fractional recrystallization from alcohol or dilute acetic acid. It was finally obtained in the form of pale yellow needles which gave a green color with alcoholic ferric chloride.

For isolation of the *p*-hydroxy ketone the residue from the steam distillation or recrystallization was stirred with 5% sodium hydroxide and the filtered solution acidified. The precipitate was recrystallized from dilute alcohol or benzene as white needles giving no color with ferric chloride.

The residue from the sodium hydroxide extraction was washed with hydrochloric acid and the crude 2,4-diacetyl-1-naphthol recrystallized from dilute alcohol in the form of white needles which gave a violet color with ferric chloride. Only negative results were obtained in attempts to isolate a divaleryl-naphthol in the way outlined above.

The physical constants and analyses of these compounds are given in Table I.

TABLE I

α -Naphthyl ester used	Acyl-1-naphthol formed	Yield, %	M. p., °C., corr.	Formula	Analyses, %			
					Calcd.		Found	
					C	H	C	H
Acetate ^a	2-Acetyl ^b	61	98–99	$C_{12}H_{10}O_2$				
	4-Acetyl ^b	5	197–198	$C_{12}H_{10}O_2$				
	2,4-Diacetyl ^b	4	140–141	$C_{14}H_{12}O_3$	73.6	5.3	73.3	5.6
Propionate	2-Propionyl ^c	54	83–84	$C_{13}H_{12}O_2$	78.0	6.1	78.0	6.4
	4-Propionyl ^c	6	188–189	$C_{13}H_{12}O_2$	78.0	6.1	78.3	6.5
	2,4-Dipropionyl ^c	2	100–101	$C_{15}H_{14}O_3$	75.0	6.3	75.0	6.5
Butyrate ^d	2-Butyryl ^d	55	84–85	$C_{14}H_{14}O_2$				
	4-Butyryl ^d	3	166–167	$C_{14}H_{14}O_2$				
	2,4-Dibutyryl ^d	2	101–102	$C_{16}H_{16}O_3$	76.0	7.1	75.6	7.1
Valerate	2-Valeryl ^e	40	75–76	$C_{15}H_{16}O_2$	78.9	7.1	78.9	7.5
	4-Valeryl ^e	2	168–169	$C_{15}H_{16}O_2$	78.9	7.1	78.9	7.2

^a Schaeffer, *Ann.*, **152**, 287 (1869). ^b Fries, *Ber.*, **54**, 709 (1921). ^c Hantzsch, *ibid.*, **39**, 3096 (1916). ^d Lederer, *J. prakt. Chem.*, **135**, 49 (1932).

Oxidation of Diacyl-1-naphthols.—To a hot solution of 0.5 g. of the diacylnaphthol in 30 cc. of water and 0.7 cc. of 20% potassium hydroxide, solid potassium permanganate was added slowly. As soon as a pink color developed that was permanent for fifteen minutes, the solution was cooled, filtered, acidified and evaporated to about 10 cc. On cooling a yellowish solid was deposited which was shown to be phthalic acid by a mixed melting point and conversion into the anhydride. This shows that the acyl groups are in the same ring as the hydroxyl and therefore they must be ortho and para to it.

Rearrangement of Acetyl-1-naphthols.—A mixture composed of 5 g. of 4-acetylnaphthol and an equal weight of aluminum chloride was heated at 100–120° for three hours.

The product was decomposed and worked up in the same manner as that from the rearrangement of the esters. From it there was obtained 3 g. (60%) of 2-acetyl-1-naphthol; 0.2 g. (4%) of 2,4-diacetyl-1-naphthol and about 0.2 g. (4%) of recovered 4-acetyl-1-naphthol.

On heating 10 g. of 2-acetyl-1-naphthol with 20 g. of aluminum chloride in the same manner, 9.5 g. (95%) of the starting material was recovered but no other crystalline compound could be isolated from the accompanying tar.

2-Alkyl-1-naphthols.—The *o*-hydroxy ketones were reduced with zinc amalgam and hydrochloric acid using the detailed procedure of Coulthard, Marshall and Pyman.⁶

TABLE II

2-Alkyl-1-naphthol	Yield, %	°C.	B. p.	Mm.	M. p. °C.
Ethyl- ^a	60	128-133		(3)	69-70
Propyl-	50	133-136		(2)	51-52
Butyl-	63	145-149		(4)	71-72
Amyl-	50				55-56

Formula	Analyses, %			
	Calcd.		Found	
	C	H	C	H
C ₁₂ H ₁₂ O	83.7	7.0	83.3	7.2
C ₁₃ H ₁₄ O	83.8	7.6	83.9	7.8
C ₁₄ H ₁₆ O	84.0	8.1	84.1	8.4
C ₁₅ H ₁₈ O	84.1	8.5	84.3	8.4

^a Lévy [*Compt. rend.*, **194**, 1749 (1932)] prepared this compound by the dehydrogenation of 2-ethyltetrone and gives the melting point as 68-68.5°.

(6) Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

After refluxing from fifteen to twenty-five hours, a test portion gave no color with alcoholic ferric chloride. After cooling, the product was extracted with ether and vacuum distilled. On recrystallization from petroleum ether, fine white needles were obtained. A varying amount of a non-volatile red oil remained in the distilling flask which solidified to a brittle glass. This polymerized or oxidized material probably accounts for the low yields obtained in these reductions. It was also noted that the pure alkyl-naphthols on standing in the air slowly turned to a red oil and their preservation was difficult. The physical constants of these compounds are given in Table II.

Summary

1. The fatty acid esters of α -naphthol on heating with aluminum chloride yield 2-acyl- with a little 4-acyl-1-naphthol. The lower members of the series also give small amounts of 2,4-diacyl-1-naphthol.

2. It has been pointed out that the formation of these diacyl derivatives is not evidence against an intramolecular reaction since they might have been formed from a side reaction or by a secondary rearrangement of the initial products.

3. The preparation of some 2-alkyl-1-naphthols by the reduction of the *o*-hydroxy ketones has been described.

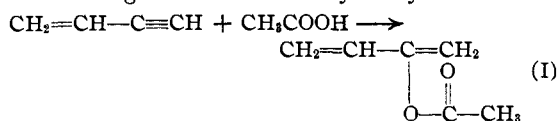
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The Addition of Organic Carboxylic Acids to Vinylacetylene¹

BY JAMES H. WERNTZ

Chloro-2-butadiene-1,3 (chloroprene) is obtained by the addition of hydrogen chloride to vinylacetylene.² The present paper is concerned with analogs of chloroprene obtained by the addition of organic acids to vinylacetylene.



1,3-Butadienyl-2-acetate (I) is formed when vinylacetylene is added to acetic acid containing a mercuric salt or boron trifluoride. The condensation is attended by side reactions which lead to the formation of resinous substances and lower the conversion to the desired product. The ester, like chloroprene, polymerizes under normal con-

ditions, or under high pressures, or in emulsions to form a rubber-like material. The rate of polymerization is intermediate between that of chloroprene and isoprene. Unlike chloroprene, the ester polymerizes under the influence of peroxide catalysts to form resinous polymers. The ester and its rubber-like polymer have a tendency to decompose slowly and to liberate free acid, particularly at increased temperatures.

The addition of organic carboxylic acids to vinylacetylene appears to be a general reaction. Esters obtained in this manner are listed in Table I.

Proof of Structure of 1,3-Butadienyl-2-acetate.—The boiling range, 38-40°, at 20 mm. of 1,3-butadienyl-2-acetate indicates it to be a mono ester since the diacetates of butenediol that are described in the literature all boil above 100° at

(1) Paper XXII in the series "Acetylene Polymers and their Derivatives." Paper XXI, *THIS JOURNAL*, **56**, 1625 (1934).

(2) Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932)