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ESTERS OF ALPHA-TETRAHYDROFURFURYL ALCOHOL

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As α -tetrahydrofurfuryl alcohol will shortly be available on a commercial scale from the catalytic reduction of furfural, it seemed desirable to investigate the properties of its esters, especially in regard to their stability as compared with those of α -furfuryl alcohol investigated some time ago in this Laboratory.¹

The introduction of four hydrogen atoms in the furfuran ring produces a remarkable stability in the derivatives of the hydrogenated ring. For example, α -tetrahydrofurfuryl alcohol is a very stable compound, remaining colorless indefinitely, whereas α -furfuryl alcohol cannot be kept colorless even in the dark for more than a few weeks. The sensitivity of α -furfuryl alcohol to mineral acids is entirely absent from the hydrogenated alcohol and thus it becomes possible to use the ordinary esterification reactions for the preparation of its esters.

Methods of Preparation.—The use of hydrochloric acid gas and of sulfuric acid dissolved in the alcohol together with the acid whose ester is desired, the action of acid chlorides and anhydrides were all employed in the preparation of the esters described in this paper. The yields were uniformly good (80% or above) except in the preparation of the α -tetrahydrofurfuryl furoate by using sulfuric acid as a condensing agent, when much tar was obtained and only a 50% yield of the ester. This may be ascribed to the instability of the furfuran ring of the furoic acid.

Properties of the Esters.—The esters are all colorless liquids with very faint odors characteristic of the acids employed. The benzoate and the furoate are odorless. They are insoluble in water, with the exception of the acetate which is miscible with water in all proportions, but miscible with alcohol, ether and chloroform.

These esters are very stable and can be distilled under atmospheric pressure. If the boiling point is much over 200°, however, the samples thus distilled will color on standing, showing that some decomposition was initiated by the heating. For this reason the high boiling esters were distilled under reduced pressure. Thus purified they show no decomposition or coloration after two months with the exception of the furoate which, in common with all other esters of furoic acid, will color slightly on standing.

As α -tetrahydrofurfuryl furoate has a higher boiling point than α -furfuryl furoate, which is a dimorphous solid (m. p. 19.5 and 27.5°), it was thought that it might also be obtained in a crystalline form. This,

¹ Zanetti, *THIS JOURNAL*, **47**, 535 (1925); **47**, 1452 (1925); Zanetti and Kerr, *ibid.*, **48**, 794 (1926).

however, was not found to be the case. When cooled in a freezing mixture to -15° , the ester became a thick liquid of the consistency of glycerine. When cooled in a solid carbon dioxide-ether mixture, it assumed the consistency of Canada balsam and when finally cooled in liquid air it went suddenly and with great contraction in volume into a glassy solid without any trace of crystallization whatever. The solidified ester had the appearance of a block of shattered glass and even by keeping it at the temperature of liquid air for some time no crystals appeared. The benzoate and valerianate behaved similarly.

The physical constants and analyses of the esters prepared are given in Table I.

TABLE I
ESTERS OF α -TETRAHYDROFURFURYL ALCOHOL

Compound	B. p., $^{\circ}\text{C}$.	Press., mm.	D_{20}^{20}	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Acetate, $\text{C}_7\text{H}_{12}\text{O}_3$	194-195	753	1.061	58.33	58.57	8.33	8.71
					58.78		8.85
Propionate, $\text{C}_8\text{H}_{14}\text{O}_3$	204-207	756	1.044	60.79	60.36	8.86	8.92
					60.27		8.49
Butyrate, $\text{C}_9\text{H}_{16}\text{O}_3$	225-227	759	1.012	62.79	62.61	9.30	9.57
					62.31		9.38
Valerianate, $\text{C}_{10}\text{H}_{18}\text{O}_3$	238-240	756	0.999	64.51	64.36	9.68	9.68
					64.25		9.78
Benzoate, $\text{C}_{12}\text{H}_{14}\text{O}_3$	300-302	750	1.137	69.90	69.25	6.99	6.94
					69.80		6.55
Furoate, $\text{C}_{11}\text{H}_{12}\text{O}_4$	136-138	3	1.194	60.60	60.39	6.06	6.06
					60.59		6.08

The writer is indebted to the Miner Laboratories for kindly supplying him with α -tetrahydrofurfuryl alcohol.

Summary

1. The acetate, propionate, butyrate, valerianate, benzoate and furoate of α -tetrahydrofurfuryl alcohol have been prepared and their properties reported.

NEW YORK, N. Y.

NOTE

Luminescence of Aliphatic Grignard Compounds.—The purpose of this note is to clear up a disagreement in which the writer had a share. In studying the luminescence of Grignard compounds in ether solution when reacting with oxygen, especially of aliphatic compounds, we find on the one hand Möller¹ recording light from ethylmagnesium bromide, propylmagnesium bromide, *iso*-amylmagnesium bromide and benzylmagnesium bromide; and Evans and Diepenhorst² reporting light from several

¹ Möller, *Arch. Pharm. Chem.*, **21**, 449 (1914).

² Evans and Diepenhorst, *THIS JOURNAL*, **48**, 715 (1926).