[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

ESTERS OF ORTHO-ACETIC ACID[1]

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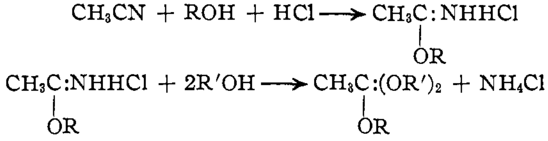
Although a number of esters of orthoformic acid, simple and mixed, were prepared by Pinner[2] through the action of alcohols on form-imino-ether hydrochlorides, their corresponding homologs, the various esters of ortho-acetic acid, with the exception of triethyl ortho-acetate, were not described in the literature. This only known ester of ortho-acetic acid was first synthesized by Geuther[3] in 1871 from methyl chloroform and sodium ethoxide. Since methyl chloroform is hard to prepare in available amounts in the laboratory, this method is only of theoretical interest. In 1907, Reitter and Hess[4] allowed ethyl alcohol to react with Pinner's acet-imino-ethyl-ether hydrochloride and isolated triethyl ortho-acetate. The reaction was not further developed and the various esters of ortho-acetic acid remained unknown. It is the purpose of this communication (1) to relate how triethyl ortho-acetate was prepared in large quantities in the laboratory by a simplified and improved procedure of Reitter and Hess and (2) to describe a few simple physical constants of the various new ortho-acetates produced by the following general reaction



$$CH_3CN + ROH + HCl \longrightarrow \underset{\textstyle OR}{CH_3C}:NHHCl$$

$$\underset{\textstyle OR}{CH_3C}:NHHCl + 2R'OH \longrightarrow \underset{\textstyle OR}{CH_3C}:(OR')_2 + NH_4Cl$$

Experimental Part

Acet-imino-ethyl-ether Hydrochloride.[5]—This was prepared according to Pinner's method. Into a cooled mixture of anhydrous acetonitrile (135 g., b. p. 82°), absolute ethyl alcohol (200 cc.) and absolute ether (120 cc.), there was introduced a slight molecular excess of dry hydrogen chloride. This mixture, after standing in the icebox overnight, solidified into a hard cake of white, shining plates. The ether was decanted. The hydrochloride was dried in a vacuum over soda lime for twenty-four hours to remove the excess of hydrogen chloride; yield, 86–95%. By using methyl alcohol in place of ethyl alcohol in the above reaction, **acet-imino-**

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[1] This paper was constructed from a thesis submitted by Peter P. T. Sah to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 21, 1926. The investigation was carried out under the direction of Professor Richard Fischer.

[2] Pinner, *Ber.*, **16**, 1644 (1883).

[3] Geuther, *Zeitschrift für Chemie*, **1871**, 128.

[4] Reitter and Hess, *Ber.*, **40**, 3020 (1907).

[5] Hill and Rabinowitz, THIS JOURNAL, **48**, 732 (1926).

methyl-ether hydrochloride was obtained as white, shining plates; yield, 71.6%.

Triethyl Ortho-Acetate.—Three hundred and fifty g. of acet-imino-ethyl-ether hydrochloride, absolutely dry and free from hydrogen chloride, was treated with 750 cc. of absolute ethyl alcohol. The mixture was allowed to stand in a tightly stoppered bottle in a dry place for two weeks with occasional shaking. The ammonium chloride separating out was filtered. This was preserved, since the reaction of alcohol with imino-ether hydrochloride was very slow and the solid precipitate still contained a large amount of the unreacted hydrochloride. The filtrate was treated with 2 g. of fused potassium carbonate to remove any trace of free hydrogen chloride. The solution was then fractionated under reduced pressure of 40–60 mm. The first fraction boiled over between 25 and 35°, consisted of absolute alcohol with some ortho-acetate and was used again in the further treatment of the precipitate of ammonium chloride as well as the fresh portion of acet-imino-ethyl-ether hydrochloride. The fraction from 55 to 75° at 50 mm. was collected and refractionated at atmospheric pressure. Pure triethyl ortho-acetate boiled very constantly at 144 to 146° at atmospheric pressure without any decomposition. From four runs 750 cc. of pure product was obtained.

TABLE I

PREPARATION AND ANALYSIS OF ORTHO-ACETATES

		Analysis						
					% H		% C	
Formula	Synthetic reagents	Subs., g.	H_2O, g.	CO_2, g.	Calcd.	found	Calcd.	found
$CH_3C(OCH_3)_3$ or $C_5H_{12}O_3$	$CH_3C{:}NHHCl$ | OCH_3 $+2CH_3OH$	0.1009	0.0914	0.1844	10.07	10.14	49.96	49.84
		.1012	.0922	.1862		10.19		50.18
		.1017	.0918	.1857		10.10		49.80
$CH_3C(OCH_3)_2$ | OC_2H_5 or $C_6H_{14}O_3$	$CH_3C{:}NHHCl$ | OC_2H_5 $+2CH_3OH$	.1014	.0952	.1988	10.52	10.51	53.69	53.47
		.1028	.0964	.1990		10.49		52.79
		.1025	.0967	.2002		10.55		53.27
$CH_3C—OCH_3$ || $(OC_2H_5)_2$ or $C_7H_{16}O_3$	$CH_3C{:}NHHCl$ | OCH_3 $+2C_2H_5OH$	.0946	.0985	.1967	10.89	11.65	56.71	56.71
		.1006	.0976	.2088		10.86		56.61
		.1013	.0982	.2106		10.84		56.70
$CH_3C—OC_2H_5$[6] || $(OC_3H_7)_2$ or $C_{10}H_{22}O_3$	$CH_3C{:}NHHCl$ | OC_2H_5 $+2C_3H_7OH$	.0950	.1004	.2232	11.66	11.83	63.10	64.08
		.0943	.0999	.2222		11.86		64.26
		.1042	.1098	.2445		11.79		63.99
$CH_3C—OC_2H_5$[6] || $(OC_4H_9)_2$ or $C_{12}H_{26}O_3$	$CH_3C{:}NHHCl$ | OC_2H_5 $+2C_4H_6OH$	.1002	.1148	.2457	12.01	12.82	65.99	66.88
		.1496	.1735	.3678		12.98		67.05
		.1150	.1343	.2816		13.07		66.78

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[6] The slightly high values of molecular refraction and carbon content of these two ortho-esters seemed to indicate that they were contaminated, respectively, by traces of tri-*n*-propyl and tri-*n*-butyl ortho-acetates from which they could not be separated by fractional distillation.

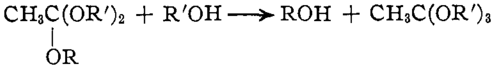
TABLE II

PHYSICAL PROPERTIES OF ORTHO-ACETATES

Ortho-acetates	B. p., °C.	d_4^{25}	n_D^{25}	Mol. ref. (G. and D.) Obs.	Mol. ref. (G. and D.) Calcd.	Mol. ref. (L. and L.) Obs.	Mol. ref. (L. and L.) Calcd.
Trimethyl	107–109	0.94375	1.38585	49.10	49.14	29.88	30.166
Dimethylethyl	123–126	.91915	1.38885	56.73	56.79	34.49	34.769
Methyldiethyl	135–136	.90085	1.39185	64.43	64.44	39.14	39.372
Ethyldi-*n*-propyl[6]	190–194	.87129	1.40635	88.70	87.39	53.66	53.181
Ethyldi-*n*-butyl[6]	220–225	.86461	1.41485	104.70	102.69	63.18	62.387

The ester is a colorless liquid with a pleasant odor, similar to that of ethyl acetate but stronger. The following constants were noted: b. p. 144–146°; n_D^{25}, 1.39485; d_4^{25}, 0.8847; molecular refraction (Gladstone and Dale), 72.33 (obs. val.), 72.09 (calcd. val.); molecular refraction (Lorenz and Lorentz), 43.91 (obs. val.), 43.975 (calcd. val.). The liquid is insoluble in cold water, but is miscible with ethyl alcohol, ether, ethyl acetate, chloroform and carbon tetrachloride. It is highly volatile with ethyl alcohol when distilled with the latter at atmospheric pressure.

By allowing various alcohols to react with acet-imino-ether hydrochloride, five new esters of ortho-acetic acid were isolated. Their method of preparation and physical properties are described in the following tables. In the case of a higher alcohol reacting on a lower alcohol derivative of imino-ether hydrochloride, there was always observed, in perfect accord with Pinner's experiments,[2] the formation of a by-product, a simple ortho-ester, in small amounts. The lower alcohol radical had a tendency toward being replaced by the higher alcohol, which was in excess.



$$\underset{\displaystyle \mathrm{OR}}{\mathrm{CH_3C}}\mathrm{(OR')_2} + \mathrm{R'OH} \longrightarrow \mathrm{ROH} + \mathrm{CH_3C(OR')_3}$$

Summary

1. A simple procedure for the preparation of triethyl ortho-acetate is described.

2. Five new esters of ortho-acetic acid were prepared through similar reactions and their physical constants studied

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