

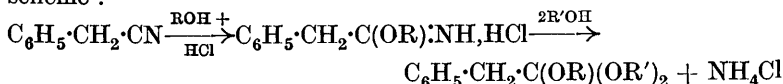
XL.—*Esters of Orthophenylacetic Acid.*

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ONE of the authors (Sah, *J. Amer. Chem. Soc.*, 1928, **50**, 516) reported the synthesis of a number of esters of orthoacetic acid by the action of alcohols on acetimido-ether hydrochlorides. Phenylacetimidoethyl ether hydrochloride has been synthesised by Pinner ["*Die Imido-äther*," Robert Oppenheim (Gustav Schmidt), Berlin, 1892, pp. 27, 66] and by Hill and Rabinowitz (*J. Amer. Chem. Soc.*, 1926, **48**, 734).

The present authors have successfully repeated Pinner's experiment and in addition have prepared phenylacetimidomethyl ether hydrochloride. By allowing various alcohols (methyl, ethyl, *n*-propyl, *isopropyl*, *n*-butyl, *isobutyl*, and *isoamyl*) to react with these imido-ether hydrochlorides, twelve new ortho-esters were isolated in

a very pure state. The reactions are represented by the following scheme :



EXPERIMENTAL.

Phenylacetimidomethyl Ether Hydrochloride.—While a solution of phenylacetonitrile and absolute methyl alcohol (1 mol. of each) in an equal volume of absolute ether was cooling in a freezing mixture, hydrogen chloride (1.25 mols.) was introduced. The reaction mixture, protected from moisture, was kept in the ice-box for about a week and the crystals were then filtered off and dried over soda-lime in a vacuum for 24 hours (yield, about 85%).

By using absolute ethyl alcohol in place of methyl alcohol, phenylacetimidoethyl ether hydrochloride was obtained in similar yield, but a longer time was required for its complete precipitation.

Formation of Orthophenylacetates (compare Sah, *loc. cit.*).—A mixture of the imido-ether hydrochloride (50 g.) and the absolute alcohol (500 c.c.) was kept in a closed bottle at room temperature for 2 weeks. The ammonium chloride was removed, and the filtrate fractionated (under about 40 mm.). The first fraction consisted mainly of unchanged alcohol together with some ortho-ester. The fraction boiling most constantly was refractionated at atmospheric pressure, kept for a week, during which more ammonium chloride separated, and distilled three times under reduced pressure (oil-pump) (yield, 40—45% of the theoretical).

The following esters of orthophenylacetic acid, like the alkyl orthoacetates, are colourless liquids with a pleasant odour; they are insoluble in water, soluble in acetic acid, carbon disulphide, chloroform, carbon tetrachloride, and very soluble in benzene, ethyl alcohol, ether, acetone, ethyl acetate, and light petroleum.

Orthophenylacetates, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{OR})(\text{OR}')_2$.

R.	R'.	B. p.	d_4^{20} .	n_D^{20} .	C, %.*	H, %.*
Me	Me	216—218°	1.0651	1.5075	67.2 (67.3)	8.0 (8.2)
Et	Me	217—219	1.0640	1.5080	68.7 (68.5)	8.3 (8.6)
Me	Et	224—226	1.0356	1.5000	70.2 (69.6)	8.4 (9.0)
Et	Et	225—227	1.0308	1.4997	70.3 (70.5)	9.1 (9.3)
Me	Pr ^α	239—242	1.0109	1.4950	71.4 (71.4)	9.7 (9.6)
Me	Pr ^β	227—229	1.0079	1.4913	70.75 (71.4)	9.2 (9.6)
Et	Pr ^α	238—241	1.0094	1.4967	72.0 (72.1)	9.5 (9.8)
Et	Pr ^β	228—230	1.0030	1.4908	72.65 (72.1)	9.4 (9.8)
Me	<i>n</i> -Bu	254—257	0.9953	1.4911	72.6 (72.8)	9.5 (10.1)
Me	<i>iso</i> -Bu	245—248	0.9929	1.4898	72.3 (72.8)	9.5 (10.1)
Et	<i>n</i> -Bu	254—257	0.9974	1.4916	73.3 (73.4)	10.2 (10.3)
Et	<i>iso</i> -Bu	248—251	0.9867	1.4883	73.2 (73.4)	9.8 (10.3)
Me	<i>iso</i> -Am	260—265	0.9880	1.4900	74.1 (74.0)	9.8 (10.5)
Et	<i>iso</i> -Am	260—265	0.9867	1.4887	73.9 (74.5)	10.8 (10.6)

* The theoretical percentages are given in parentheses.

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