

# THE PREPARATION OF ESTERS

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IN the course of investigations carried out in these laboratories, a considerable number of different esters has been required. A simple method, resulting in very satisfactory yields, has been described by Clinton and Laskowski<sup>1</sup> involving the refluxing of a mixture of the acid, commercial methyl alcohol, ethylene dichloride and sulphuric acid for from 6 to 15 hours. This method has the advantage of not requiring the separation of water formed during the reaction.

We have employed this method with success in the preparation of several methyl esters not described by Clinton and Laskowski, and have investigated the extension of the method to include other alcohols. Ethyl esters have been prepared from the following acids:—9-undecylenic, sebacic, oxalic, tartaric and citric. Equally successful preparations of *n*-butyl esters have been carried out from sebacic and citric acids. Citrates have been obtained in satisfactory yield from both  $\beta$ -chloroethyl and  $\beta$ -bromoethyl alcohols, and a good yield of cinnamic ester has been obtained from tetrahydrofuryl alcohol.

TABLE I

ESTER	B.pt. or M.pt. °C.	YIELD Per Cent.
Methyl sebacate ... ..	B.pt. 164° to 168°/12 mm. ... ..	89
Ethyl sebacate ... ..	B.pt. 192° to 197°/25 mm. ... ..	80 to 84
<i>iso</i> Propyl sebacate ... ..	B.pt. 181° to 183°/10 mm. ... ..	55
<i>n</i> Butyl sebacate ... ..	B.pt. 216° to 220°/14 mm. ... ..	92
<i>tert</i> Butyl sebacate ... ..	Olefine evolved ... ..	
Methyl oxalate ... ..	B.pt. 163° ; m.pt. 51° ... ..	44 to 47
Ethyl oxalate ... ..	B.pt. 182° to 192° ... ..	48 to 51
Methyl citrate ... ..	M.pt. 79° ... ..	56
Ethyl citrate (a) ... ..	B.pt. 136° to 138°/2 mm. ... ..	55
Ethyl citrate (b) ... ..	B.pt. 179° to 180°/12 mm. ... ..	40
Ethyl citrate (c) ... ..	B.pt. 176° to 178°/10 mm. ... ..	35
$\beta$ Chloroethyl citrate ... ..	B.pt. 215° to 216°/0.5 mm. ... ..	32
$\beta$ Bromoethyl citrate ... ..	B.pt. 226° to 228°/0.4 mm. ... ..	30
<i>n</i> Butyl citrate ... ..	B.pt. 170° to 172°/0.5 mm. ... ..	65
Ethyl tartrate ... ..	B.pt. 158° to 160°/12 mm. ... ..	39 to 41
Ethyl 9-undecylenate ... ..	B.pt. 137° to 139°/13 mm. ... ..	88
Methyl (p-methoxyphenyl)-propionate ... ..	B.pt. 154° to 156°/16 mm. ; m.pt. 38° ... ..	86
Methyl (m-methoxyphenyl)-propionate ... ..	B.pt. 154° to 156°/16 mm. ... ..	76
	M.pt. 29° to 30° ... ..	
Methyl p-hydroxybenzoate* ... ..	M.pt. 128° ... ..	85
Tetrahydrofuryl cinnamate ... ..	B.pt. 207° to 209°/11 mm. ... ..	67
Methyl piperonylate*... ..	B.pt. 146°/11 mm. ; m.pt. 52° ... ..	71

Standard conditions : 1 mol. of aliphatic carboxyl group, 3 mol. of the alcohol, 300 ml. of ethylene dichloride and 3 ml. of concentrated sulphuric acid heated under a reflux condenser for 15 hours.

\* —aromatic acid, as above but with 15 ml. of concentrated sulphuric acid per mol. of carboxyl group.

(a) anhydrous ethyl alcohol.

(b) ethyl alcohol (95 per cent.)

(c) industrial methylated spirit used.

Primary alcohols appear to react with readily esterifiable acids in a satisfactory manner by this method. An attempted esterification of benzoic acid by benzyl alcohol gave a product containing so high a

proportion of dibenzyl ether as to render the method unsuitable for the preparation of benzyl esters: it is possible that the use of other catalysts than sulphuric acid might eliminate this difficulty.

In the case of the one secondary alcohol examined there are indications that esterification proceeds rather less readily, since, under the standard conditions, a mixture of products was obtained from sebacic acid with *isopropyl* alcohol. The yield of di-*isopropyl* sebacate was 55 per cent., and a considerable quantity of mono-*isopropyl* sebacate was also formed. Attempted esterification of readily dehydrated alcohols by this method, in the presence of sulphuric acid, leads to the formation of the olefine. While dibasic acids, in which the carboxyl groups are widely separated, appear to esterify very readily, in the special case of oxalic acid, with two vicinal carboxyl groups, it does not appear possible appreciably to exceed a yield of 50 per cent. The general yield of 50 per cent. of ethyl oxalate is unaltered whether hydrated or anhydrous acid be employed, and the yield is not reduced by halving the amount of alcohol in the reaction mixture. Whereas we were able to obtain consistent yields of 55 per cent. of methyl citrate, using the standard method, and a similar yield of ethyl citrate when anhydrous ethyl alcohol was used, the yield of ester from industrial methylated spirit was of the order of 35 per cent. Using ethyl alcohol (95 per cent.) a yield of 40 per cent. was obtained.

It would appear that, in general, this method of esterification is of considerable value, and is of much wider application than is at present indicated in the literature.

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#### REFERENCE

1. Clinton and Laskowski, *J. Amer. chem. Soc.*, 1948, **70**, 3135.