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A HIGH YIELD ROUTE TO ETHYL ESTERS OF CARBOXYLIC ACIDS

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Abstract—Diethyl trichloromethylphosphonate reacts with carboxylic acids to yield their ethyl esters, via transesterification; even the hindered mesitoic acid is esterified in high yield.

A carboxylic acid can react at high temperatures (110–170°) with triethyl phosphite to yield the ethyl ester of the carboxylic acid, and diethyl phosphite.[1,2] Further, it has been shown that diethyl phosphite, itself, will convert carboxylic acids into their ethyl esters, but somewhat more reluctantly[3] (temperatures ranging up to 205° being required). Frank[4] reported that diethyl trichloromethylphosphonate will slowly convert boiling ethanol into diethyl ether, and phenol into the corresponding ether at 150°. Thus it seemed to us that the use of this ester might give good yields of ethyl carboxylates, at a lower temperature than is required with diethyl phosphite, due to the strong $-I$ effect of the CCl_3 group present.

EXPERIMENTAL

A typical procedure for the preparation of ethyl esters of carboxylic acids

The starting material, diethyl trichloromethylphosphonate, was prepared by the method of Kosolapoff.[5] Triethyl phosphite (100 g), and carbon tetrachloride (500 ml) were heated under reflux overnight. After removal of excess carbon tetrachloride the residue yielded on distillation diethyl trichloromethylphosphonate 143 g (92%), b.p. 174–178°/40 mm, n_D^{25} 1.4610 (lit.[6] n_D^{25} 1.4610).

The typical reaction is that by which ethyl benzoate was prepared. Benzoic acid (12.2 g; 0.1 mol) and diethyl trichloromethylphosphonate (25.6 g; 0.1 mol) were heated at 120° for one day. Distillation of the mixture gave ethyl benzoate; yield: 14.4 g (96%); b.p. 120–124°/24 mm; IR spectrum identical to that of an authentic sample of ethyl benzoate.

Table 1. Preparation of ethyl esters

Carboxylic acid	pK_a	b.p. (760 mm) of ester	Isolated yield %	Max. temp. reached	Duration of reaction in hours
Trifluoroacetic acid	0.23	59–62°	52	90°	24
Trichloroacetic acid	0.63	76–80°/18 mm	77	120°	24
Salicylic acid*	2.74	125–130°/18 mm	72	120°	24
Mesitoic acid	3.44	128–130°/12 mm	93	120°	24
Formic acid	3.74	54–60°	82	120°	24
o-Toluic acid	3.91	106–112°/18 mm	94	120°	24
Benzoic acid	4.20	120–124°/24 mm	96	120°	24
Acetic acid	4.76	77–80°	93	120°	24
Acetic acid	4.76	77–80°	77	120°	8
iso-Butyric acid	4.86	110–112°	98	120°	24
Propionic acid	4.87	98–102°	98	120°	24

*It should be noted that this acid is selectively esterified without accompanying ether formation involving the phenolic group; higher temperatures are required for this reaction.[4]

With one exception the reactions were carried out at 120° using equimolar amounts of the carboxylic acid and diethyl trichloromethylphosphonate. The carboxylic acids are listed in order of increasing pK_a as there appears to be some correlation between decreasing acid strength and reactivity, though the low yield in the case of trifluoroacetic acid could be attributed to the lower reaction temperature.

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