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Short Communications

A Method for Condensations of Esters with Diethyl Oxalate

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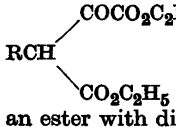
A general method for the preparation of α-ethoxalyl esters of the formula



is the condensation of an ester with diethyl oxalate using sodium ethoxide as a condensation agent [1,2]. As these esters readily undergo pyrolysis when heated to above about 150°, only the first relatively lowboiling esters have been prepared in a state of purity by distillation.

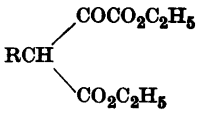
In the present investigation, where the reaction was forced by distilling off the alcohol formed using toluene as a solvent, good yields of rather pure esters with constant boiling points were obtained from esters which are not branched in the α- or β-positions. From the most simple ester branched in the β-position, ethyl *iso*-valerate, the yield was only about 20 % and from the highly branched ethyl *t*-butylacetate no condensation product could be obtained. All the esters prepared were fractionated at a pressure of 1–4 mm. At this pressure no appreciable decomposition of the ethoxalyl esters took place.

The ethoxalyl esters with at least one α-hydrogen atom are sufficiently strong acids to be titrated with standard sodium hydroxide solution, using a mixture of one part of thymol blue and three parts of phenolphthalein as an indicator. The somewhat high equivalent weights are probably due to a slight decomposition during the distillation.

Experimental. 0.25 mole of sodium ethoxide suspended in 250 ml of dry toluene was prepared from 5.75 g of sodium and 11.5 g of absolute alcohol in a three-necked round-bottomed flask, fitted with a dropping funnel, a mercury sealed stirrer, and a 30-cm Widmer column with a total reflux variable take off still head. The suspension was cooled in ice-water and a mixture of 0.25 mole of diethyl oxalate and 0.25 mole of the ester added. The flask was then heated with an electrical heating mantle and the alcohol formed carefully distilled off. When no more alcohol could be obtained, the flask with the deeply coloured solution was cooled in ice-water, and an ice cold solution of 0.25 mole of glacial acetic acid in 100 ml of water added as rapidly as possible. The mixture was stirred for five minutes and then transferred to a separatory funnel. Sufficient water was added to dissolve the salt eventually precipitated. The toluene layer was separated and the water layer extracted with ether. The combined ether and toluene layers were washed with water and then with a solution of sodium bicarbonate. After drying over a little anhydrous sodium sulphate, the ether and toluene were removed under reduced pressure, and the residue fractionated at a pressure of 1–4 mm.

The yields, boiling points and equivalent weights of the ethoxalyl esters are given in Table 1.

Table 1. Preparation of ethoxalyl esters



R	Yield %	B.p.	Equivalent weights Calc.	Found
Ethyl	60	104/4 mm	216.2	217.7
*Iso*propyl	20	100/2 mm	230.3	236.5
n-Propyl	63	99/1.5 mm	230.3	232.4
*Iso*butyl	57	102/1.5 mm	244.3	250.2
n-Butyl	61	116/2 mm	244.3	249.4

1. Adickes, F., and Andresen, G. *Ann.* **555** (1943) 48.
2. *Organic Syntheses* **II** (1943) 272.

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On the Action of Bacterial L-lysine Decarboxylase on Hydroxylysine

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Gale [1] has shown that various bacteria possess an enzyme capable of specifically decarboxylating L-lysine. He also tested the purified enzyme against different lysine derivatives and found it inactive in all cases except when hydroxylysine was the substrate. The hydroxylysine used was an impure preparation (85 % periodate-ammonia, $(\alpha)_D + 4.7$ in *N* HCl) that was decarboxylated to about 60 per cent although at a slower rate than lysine.

However, Zittle and Eldred [2] have claimed that L-lysine decarboxylase does not decarboxylate hydroxylysine. This question is obviously of importance for the quantitative determination of L-lysine with this enzyme.

Using pure hydroxylysine prepared according to Bergström and Lindstedt [3,4] we have reinvestigated this question. The results plotted in Fig. 1 show that hydroxylysine was decarboxylated to the same extent as lysine, although at a considerably slower rate. It is evident, therefore, that any hydroxylysine present will give an error in the determination of lysine with the usual preparation of bacterial decarboxylase as the carbon dioxide evolved represents the sum of L-lysine and hydroxylysine present.

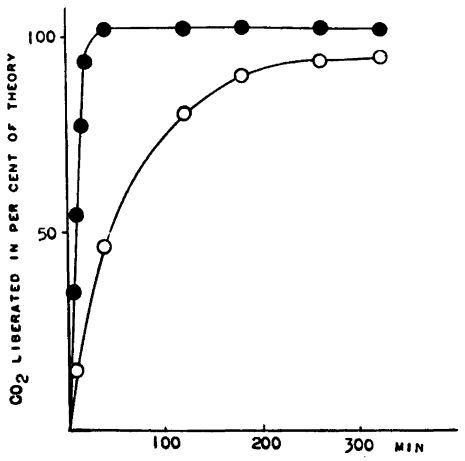

Fig. 1. ○ *hydroxylysine.* ● *lysine. The values are corrected for* CO_2 *retention in the solution.*

We have obtained one mole of carbon-dioxide per mole hydroxylysine on preparations from fish skin. The analytically pure samples from some commercial gelatines give less, possibly due to partial racemization in the manufacturing process. Synthetic hydroxylysine prepared according to Touster [5] was decarboxylated to 25 per cent while a synthetic L-hydroxylysine obtained from Dr. J. Weissiger showed 50 per cent decarboxylation. This work will be reported in detail in a subsequent publication.

Experimental. *Bacterium cadaveris* (strain no. 6578 Natural collection of type cultures, London) were grown and acetone dried as described by Zittle and Eldred. 5 μM of the amino acid in 0.5 ml water