Diethyl 1-Bromoacetylvinyl Phosphate (6).—Triethyl phosphite (8.3 g, 0.050 mol) was added dropwise to a solution of 1,4-dibromo-2,3-butanedione (12.2 g, 0.050 mol) in 50 ml of absolute diethyl ether. The reaction exotherm was moderated with an ice–water bath keeping the temperature below 10°. After the solution had stirred for 1.5 hr at 10°, the solvent was removed *in vacuo*. An orange liquid (14.5 g, 0.048 mol, 96% yield) remained which was identified as **6**: ir bands at 1701 and 1691 (m, C=O), 1612 (m, C=C), 1274 (s, P=O), 830 (m) cm^{-1}; ^{1}H nmr (CCl$_4$) τ 8.67 (6 H, t, J^3_{HH} = 7 Hz, CH$_3$CH$_2$O), 5.80 (4 H, octet, J^3_{PH} = 8.5 Hz, CH$_3$CH$_2$OP), 5.58 (2 H, s, CH$_2$Br), 4.27, 3.99 (2 H, pair of t, J^2_{HH} = 3 Hz, J^4_{PH} = 3 Hz, vinyl); mass spectrum (70 eV) *m/e* calcd for $C_8H_{14}BrO_5P$, 299.9760 (found, 299.9769).

Acknowledgment.—We are indebted to Professor C. E. Griffin for critical review of the manuscript and for helpful discussions. We thank Professor R. W. Parry for use of his spectrometer (XL-100-15).

Registry No.—**3a,** 41189-14-4; **3b,** 41189-15-5; **5,** 41189-16-6; **6,** 41189-17-7; 1,4-dibromo-2,3-butanedione, 6305-43-7; triethyl phosphite, 122-52-1; trimethyl phosphite, 121-45-9.

Novel Synthesis of γ-Keto Esters

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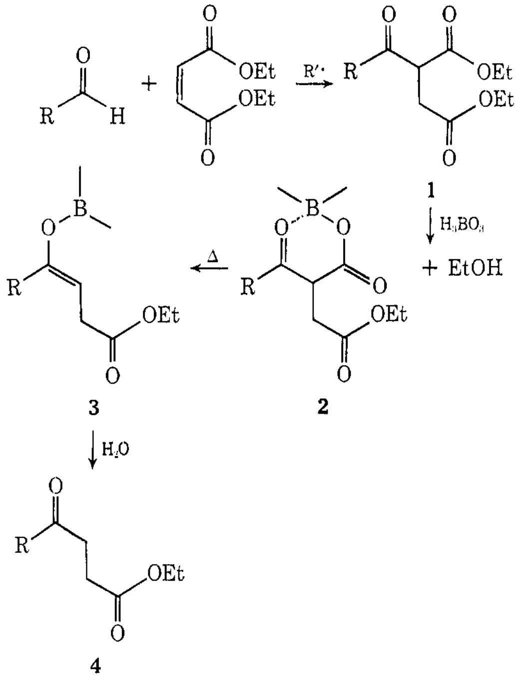
One method for the preparation of γ-keto esters proceeds *via* acid[1] or alkaline[2] saponification of an acylated succinic diester followed by decarboxylation and reesterification to the desired γ-keto ester. The attractive feature of this process is the ready availability of a variety of acylated succinic diesters.[3] The disadvantages of the process are the relatively low overall yield and the fact that the intermediate γ-keto acid has to be reesterified to the desired γ-keto ester.

We now wish to report a high yield, direct conversion of acylated diethyl succinates to the corresponding γ-keto esters.

The starting materials, acylated diethyl succinates, are readily available *via* radical-induced addition of aldehydes to diethyl maleate.[3] These keto diesters, when heated in the presence of boric acid, yield, after aqueous work-up, the desired γ-keto ester in one step (Scheme I).

Indications are that the reaction proceeds to a complexed borate ester intermediate **2** *via* a selective transesterification process. It is reasonable to assume that the ability of the ketocarbonyl group to complex to the boron atom is responsible for the high selectivity in the transesterification step. This type of reaction sequence is experimentally supported by the collection of ethanol[4] prior to the onset of decarboxylation. The intermediate borate ester **2** thus formed would appear to be ideally suited to undergo decarboxylation and this indeed takes place readily at temperatures around 160–170°. The product, after decarboxylation, is an enol borate of type **3**, from which the free γ-keto ester **4** is liberated by an aqueous work-up procedure.

SCHEME I



The yields obtained for the transformations **1** → **4** are summarized in Table I.

TABLE I

1	Registry no.	4 (% isolated yield[a])	Registry no.
R = ethyl	41117-76-4	77	3249-33-0
R = *n*-propyl	41117-77-5	80	14369-94-9
R = *n*-hexyl	41117-78-6	80	14294-63-4

[a] Satisfactory physical data have been obtained for all isolated γ-keto esters **4**.

Experimental Section[5]

Since the procedure is general, only the preparation of 4-oxohexanoic acid ethyl ester (**4**, R = ethyl) is described.

Diethyl propionylsuccinate[3] (92.0 g, 0.4 mol) and boric acid (24.6 g,[6] 0.4 mol) were heated to 150° (oil bath, magnetic stirring, Claisen condenser connected with a gas measuring device). Within 1 hr, 11.7 g of distillate (mainly ethanol) and ~0.75 l. of gas were collected. As the temperature was raised to 170°, the rate of CO$_2$ evolution increased and a total of 8.3 l. of gas was collected after 1.5 hr. At this time, CO$_2$ evolution was almost at a standstill and the reaction mixture had a clear, light yellow appearance (total reaction time, 2.5 hr; vpc analysis of a sample showed the reaction mixture to contain only very little starting material). The contents of the flask were cooled to room temperature, poured onto ice–water (550 ml), and extracted with toluene (3 × 180 ml). After the combined organic layers were dried over anhydrous MgSO$_4$, the solvent was removed *in vacuo* and the residue was distilled through a 10-cm Vigreux apparatus. A main fraction of 48.6 g (77%), bp 109–112° (18 mm[7]), was collected. Vpc analysis indicated the material to be of 99.2% purity (area comparison).

Acknowledgment.—We thank the staff of our Physical Chemistry Department (Direction, Dr. R. P. W. Scott) for the determination of spectral data.

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[1] A. Franke and A. Kroupa, *Monatsh.*, **69**, 167 (1936).

[2] E. Friedman, *J. Prakt. Chem.*, **146**, 159 (1936).

[3] T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1009, (1952).

[4] As characterized by comparative vpc and mass spectrometry.

[5] Vpc conditions: Hewlett-Packard Model 5720 with dual flame detector; column 6 ft × 0.125 in o.d. stainless steel; 10% UCW-98 on Diatoport 5, programmed at 30°/min from 50 to 250°.

[6] No attempts were made to use <1 mol of boric acid/mol of **1**.

[7] Bp 95–98° (11 mm): M. I. Ushakov and V. F. Kucherov, *J. Gen. Chem. USSR*, **14**, 1073 (1944); *Chem. Abstr.*, 7185 (1946).