uct, was difficult. Only by repeated recrystallizations from alcohol under nitrogen was an analytically pure sample obtained. The oxazine was stable in the solid state, but was unstable in certain solutions (*e.g.*, benzene or hexane), particularly in the presence of oxygen. No pure compounds have been isolated from this decomposition.

Compound **2** was unreactive toward $NaBH_4$ and reacted only partially with $LiAlH_4$ in pyridine or boiling alcoholic KOH. As expected, reaction with acid occurred readily. However, acid hydrolysis did not result in the expected regeneration of starting material. Instead, under a variety of conditions, the only substance isolated was a high molecular weight compound of complex structure.

The evidence at hand does not allow a definite structure for this compound or a mechanism for its formation. However, the compound was shown not to arise from diphenacylaniline, since, under the same conditions in which **2** was hydrolyzed (boiling acetic acid), diphenacylaniline reacted only partially and did not produce any of the hydrolysis product. The reactions of **2** will be the subject of future investigations.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Spectral data were obtained from a Perkin-Elmer Model 137 ir spectrophotometer, a Varian A-60 nmr spectrometer, and a Hitachi Perkin-Elmer Model 139 uv-visible spectrophotometer. Analyses were performed by the Chemical Analytical Services, Berkeley, Calif.

Diphenacylaniline (1).—A mixture of 3.00 g (15 mmol) of phenacyl bromide, 15 ml of 95% ethanol, 3.15 g of Na_2CO_3, and 0.60 ml (7.5 mmol) of aniline was stirred and heated under reflux for 3 hr. After cooling to room temperature, the solid was filtered and triturated with H_2O for 15 min, then refiltered and recrystallized from pyridine to give 1.40 g (57%) of **1**: mp 237–239° (lit.[3] mp 236–240°); uv λ_{max} (dioxane) 252 nm (ϵ 26,600), 282 (3600); ir 1680 cm^{-1} (Nujol mull).

2,4,6-Triphenyl-1,4-oxazine (2).—A mixture of 1.55 g (4.7 mmol) of **1** and 0.87 ml (9.4 mmol) of $POCl_3$ in 30 ml of pyridine (dried over CaH_2) was heated with occasional swirling at 100° for 45 min. The deep red solution was poured onto 50 ml of crushed ice and the resulting solid was filtered. Two recrystallizations from isopropyl alcohol gave 0.81 g (55%) of red needles, mp 167–180°. This material was 80–90% pure and contained an impurity with a carbonyl peak at 1680 cm^{-1}. Use of a nitrogen atmosphere for the reaction did not materially affect the yield or purity of the product. However, repeated recrystallization from alcohol under nitrogen gave a small amount (72 mg) of an analytically pure sample: mp 183–185°; uv (EtOH) λ_{max} 238 nm (ϵ 19,800), 348 (20,400), 440 (3100); ir (CS_2) strong absorption at 1640, 1250, 1040, 750, and 685 cm^{-1}; nmr (CS_2) δ 6.44 (s, 2 H), 6.83 (m, 1 H), 6.95 (m, 2 H), 7.30 (m, 12 H). *Anal.* Calcd for $C_{22}H_{17}NO$: C, 84.85; H, 5.51; N, 4.50. Found: C, 84.68; H, 5.40; N, 4.71.

Acid Hydrolysis of 2.—A mixture of 298 mg (0.96 mmol) of **2**, 35 ml of 95% ethanol, and 4 ml of concentrated HCl was heated to reflux for 30 min. The light yellow solid, which formed on cooling, was filtered and crystallized from 40% isopropyl alcohol–cyclohexane to give 71 mg (0.125 mmol) of colorless crystals with a waxy appearance, mp 231–234°. Recrystallization gave crystals: mp 236–238° uv (EtOH) λ_{max} 240 nm (sh, ϵ 17,200), 330 (36,500); ir (CS_2) strong absorption at 1655, 1240, 755, and 690 cm^{-1}; nmr (CS_2) δ 6.50 (m, 2 H), 6.75 (m, 4 H), 7.14 (m, 24 H). *Anal.* Calcd for $C_{40}H_{30}N_2O_2$: C, 84.19; H, 5.30; N, 4.91; mol wt, 572. Found: C, 84.39; H, 5.44; N, 4.76; mol wt 545 (Rast).

Registry No.—**1**, 41120-12-1; **2**, 41120-13-2; phenacyl bromide, 532-27-4; aniline, 62-53-3.

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[3] G. K. Almstrom, *Justus Liebigs Ann. Chem.*, **411**, 350 (1916).

A Double Perkow Reaction. 1,3-Butadiene-2,3-diol Bis(dialkyl phosphate)

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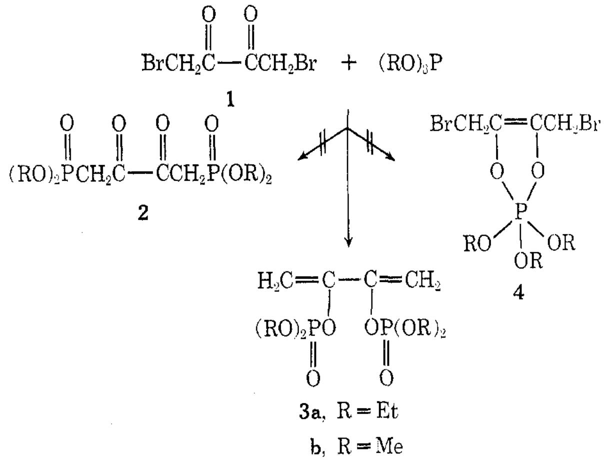
Trialkyl phosphites are known to react with α-halo ketones to yield β-ketophosphonates and/or vinyl phosphates (Arbuzov[1] and Perkow[2] products, respectively) and with nonhalogenated ketones and α diketones to yield phosphoranes.[3] In view of these results, an examination of the reactions of trialkyl phosphites with 1,4-dibromo-2,3-butanedione (**1**) was of interest. This ketone is capable of yielding all of these types of product, *i.e.*, phosphonates (**2**), phosphates (**3**), and phosphoranes (**4**), and allows an assessment of the competition between the three processes.



The addition of 2 mol of triethyl phosphite to a 1 *M* ethereal solution of **1** gave **3a** (98%) in an exothermic reaction. The ir spectrum of **3a** exhibited a characteristic olefinic stretching band (1602 cm^{-1}), but was transparent in the carbonyl region. The ^1H nmr spectrum consisted of a methyl triplet at τ 8.70, a methylene octet at 5.88, and a vinyl multiplet at 4.82. A broadened quintet at +6.8 ppm was observed in the ^{31}P nmr spectrum. These data are only consistent with structure **3a** and are inconsistent with either structure **2** or **4**. Similar results were obtained in the reaction of **1** with trimethyl phosphite; the ir and nmr data obtained for **3b** were similar to those cited for **3a**.

Further evidence for the proposed structure was provided by the absorption of 2 equiv of hydrogen by **3b** (atmospheric pressure, Pd/C). Reduction of the ethyl analog **3a** was inexplicably more difficult but was accomplished at 60 psi in methanol using 5% Ru/C–

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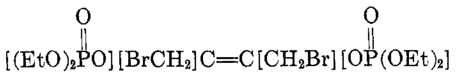
[1] (a) G. M. Kosolapoff, "Organo-Phosphorus Compounds," Wiley, New York, N. Y., 1950; (b) P. C. Crofts, *Quart. Rev., Chem. Soc.*, **12**, 341 (1958); (c) M. Grayson and E. J. Griffith, "Topics in Phosphorus Chemistry," Wiley, New York, N. Y., 1964; (d) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, London, 1965.

[2] (a) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961); (b) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965).

[3] (a) F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); (b) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

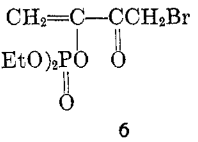
$PdCl_2$ as catalyst. Bromination of **3a** afforded the 1,4-addition product **5** as a white solid.



$$[(EtO)_2\overset{O}{\overset{\|}{P}}O][BrCH_2]C{=}C[CH_2Br][O\overset{O}{\overset{\|}{P}}(OEt)_2]$$

5

Reaction of an equimolar mixture of triethyl phosphite and **1** was also exothermic and afforded, exclusively, the mono Perkow product **6** (96%). Hence,

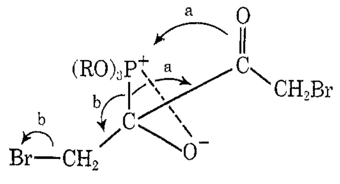


6

the double Perkow product **3a** must arise sequentially with the rate of formation for the first vinyl phosphate group being considerably faster than that for the second.

Vinyl phosphates **3a**, **3b**, and **6** were thermally labile to the extent that purification was not possible by either gas chromatographic or distillation techniques. **3a** and **3b** were nevertheless storage stable for several months at −10°, while **6** decomposed within 1 week at that temperature.

Recent studies suggest that the formation of both vinyl phosphates[4] and phosphoranes[5] proceeds by a mechanism involving initial attack of phosphorus on carbonyl carbon. By applying such a scheme to **1** the corresponding β-ketophosphonium intermediate **7** is generated which may undergo cyclization (route a) as



7

occurs with 2,3-butanedione[6] or bromine elimination (route b) as occurs with bromoacetone.[7] That in fact vinyl phosphates (route b) exclusively arise can be rationalized in terms of the entropy factor. A pathway involving loss of alkyl bromide is favorable because it would result in an entropy increase, whereas cyclization to phosphorane would further constrain the system.

Arbuzov products (**2**) might be expected to arise by direct S_N2 displacement of bromine by phosphorus. Because the carbonyl carbon in **1** is the most electrophilic site, a result of the electron-withdrawing groups $BrCH_2$– and –$COCH_2Br$, direct nucleophilic displacement of bromine cannot compete successfully. Thus, while other pathways are seemingly available, the preference of **1** to form double Perkow products is noteworthy.

Experimental Section

Melting points are corrected. Ir spectra were scanned on the neat smears (KBr or NaCl plates) using Perkin-Elmer 257 and 521 spectrophotometers. Nmr spectra were obtained with Varian Associates A-60A (^{1}H) and XL-100-15 (^{31}P) spectrometers operating at ambient temperature. Chemical shifts are in parts per million relative to internal TMS (τ 10) and external 85% orthophosphoric acid for the ^{1}H and ^{31}P resonances, respectively. The ^{31}P spectra were stabilized with ^{2}H internal lock. Elemental analysis were performed by Galbraith Laboratories, Knoxville, Tenn. High resolution mass spectra were obtained on an AEI MS 902S spectrometer with a DS 30 Data System.

1,3-Butadiene-2,3-diol Bis(diethyl phosphate) (3a).—To a magnetically stirred solution of 1,4-dibromo-2,3-butanedione (12.2 g, 0.050 mol) in 50 ml of absolute diethyl ether was added dropwise triethyl phosphite (16.6 g, 0.10 mol). An ice–water bath was used to maintain the reaction temperature below 10°. After the mixture stirred for 2 hr at 10°, the solvent was removed *in vacuo* and 17.7 g (0.049 mol. 98%) of an orange liquid (**3a**) was obtained: ir bands at 1602 (m, C=C), 1276 (s, P=O), 878 (m) cm^{-1}; ^{1}H nmr (CCl_4) τ 8.70 (12 H, t, J^3_{PH} = 7.5 Hz, CH_3CH_2O), 5.88 (8 H, octet, J^3_{PH} = 8.5 Hz, CH_2CH_2OP), 4.82 (4 H, m, vinyl); ^{31}P nmr (CCl_4) +6.8 ppm (br quintet, J_{PH} = 8.0 Hz); mass spectrum (70 eV) *m/e* calcd for $C_{12}H_{24}O_8P_2$, 358.0970 (found, 358.0993).

1,3-Butadiene-2,3-diol Bis(dimethyl phosphate) (3b).—In a procedure similar to that described above, reaction of 1,4-dibromo-2,3-butanedione (12.2 g, 0.050 mol) and trimethyl phosphite (12.4 g, 0.10 mol) gave 12.9 g (0.042 mol, 85%) of an orange liquid (**3b**): ir bands at 1602 (m, C=C), 1276 (s, P=O), 883 (m), 852 (m), 822 (m) cm^{-1}; ^{1}H nmr (CCl_4) τ 6.21 (12 H, d, J^3_{PH} = 11 Hz, CH_3OP), 4.80 (6 H, m, vinyl); ^{31}P nmr (CCl_4) +4.4 ppm (br septet, J_{PH} = 11 Hz); mass spectrum (70 eV) *m/e* calcd for $C_8H_{16}O_8P_2$, 302.0319 (found, 302.0313).

Hydrogenation of 3a.—A solution of 6.9 g (19 mmol) of **3a** in 150 ml of absolute methanol was placed in a Parr hydrogenation apparatus along with a catalyst system comprising 5% ruthenium on charcoal (1.5 g) and palladium chloride (0.1 g). Reduction proceeded over a 6-day period under 50–60-psi hydrogen gas pressure. Work-up consisted of filtration through Celite and solvent evaporation from the filtrate. A sweet-odored liquid (6.1 g) was obtained. The ir spectrum of this product was transparent in the olefinic region.

Hydrogenation of 3b.—A magnetically stirred solution of **3b** (1.5 g, 5.0 mmol) in 25 ml of ethyl acetate was reduced with gaseous hydrogen over 5% rhodium on charcoal in a typical microhydrogenation apparatus. The extent of hydrogen absorption (10 mmol) corresponded to the reduction of two double bonds. The solution was subsequently filtered through Celite and the solvent was removed *in vacuo* from the filtrate. The product (1.25 g) exhibited an ir spectrum devoid of olefinic bands in the 1600-cm^{-1} region.

1,4-Dibromo-2-butene-2,3-diol Bis(diethyl phosphate) (5).—Bromine (4.8 g, 0.030 mol) was added dropwise to a solution of **3a** (10.7 g, 0.030 mol) in 50 ml of carbon tetrachloride. The reaction appeared to be facile as noted by the rate of disappearance of the 1602-cm^{-1} band. After the mixture stirred for 0.5 hr, the solvent was removed *in vacuo* to give an orange liquid that crystallized at room temperature within several hours. The product was recrystallized from a small amount of ether at −78° followed by rapid collection and drying on a sintered-glass funnel. A white powder (6.1 g, 0.012 mol, 39% yield) was obtained and identified as **5**: mp 64–65°; ir bands at 1670 (w, C=C), 1272 (s), 1218 (s), 1025 (s) cm^{-1}; ^{1}H nmr (CCl_4) τ 8.61 (12 H, t, J^3_{HH} = 7.5 Hz, CH_3CH_2O), 5.80 (8 H, octet, J^3_{PH} = 7 Hz, CH_3CH_2OP), 5.66 (4 H, s, CH_2Br); ^{31}P nmr (CCl_4) +37.3 ppm (quintet, J_{PH} = 7 Hz).

Anal. Calcd for $C_{12}H_{24}Br_2O_8P_2$: C, 26.80; H, 4.65; Br, 30.80; P, 12.00. Found: C, 27.03; H, 4.62; Br, 31.06; P, 11.92.

Decomposition of **5** was noticeable when it was left standing overnight at room temperature.

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[4] (a) I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967); (b) I. J. Borowitz, S. Firstenberg, G. B. Borowitz, and D. Schuessler, *J. Amer. Chem. Soc.*, **94**, 1623 (1972).

[5] Y. Ogata and M. Yamashita, *J. Amer. Chem. Soc.*, **92**, 4670 (1970).

[6] F. Ramirez and N. B. Desai, *J. Amer. Chem. Soc.*, **92**, 2652 (1960).

[7] A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **105**, 735 (1955); *Chem. Abstr.*, **50**, 11230*g* (1956).

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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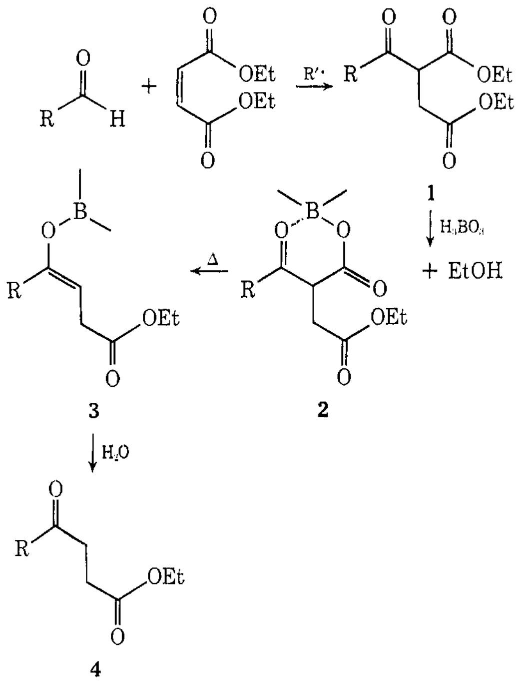
One method for the preparation of γ-keto esters proceeds *via* acid[1] or alkaline[2] saponification of an acylated succinic diester followed by decarboxylation and reesterification to the desired γ-keto ester. The attractive feature of this process is the ready availability of a variety of acylated 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).