A New Type of P-C and C-C Bond Cleavage Reactions in α-Trimethylsilyloxy-β-oxo Phosphonates and α-Ethoxy-β-oxo Phosphonates. The Synthesis of Unsymmetrical α-Hydroxy Ketones Utilizing 1:1 Carbonyl Adducts of Diethyl Trimethylsilyl Phosphite with Benzaldehyde

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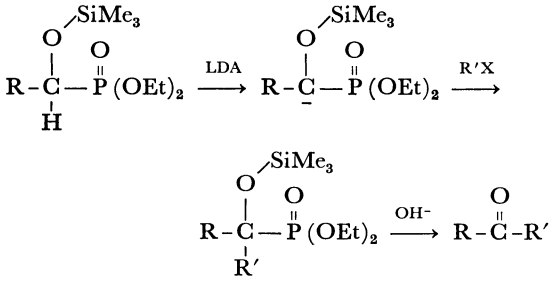
α-Lithiated diethyl α-(trimethylsilyloxy)benzylphosphonate underwent facile acylation with various acylating agents to afford the corresponding α-acylated products in good yields. On treatment of the α-acylated products with 1 M† NaOH–EtOH (1:1, v/v) the P–C bond was cleaved with elimination of diethyl phosphate to give α-hydroxy ketones predominantly. On the other hand, when diethyl α-acyl-α-ethoxybenzylphosphonates were treated under the same conditions, they were rather stable and recovered. However, the prolonged alkaline treatment or the use of 4 M NaOH–EtOH (1:1, v/v) resulted in the C–C bond cleavage giving carboxylic acids and diethyl α-ethoxybenzylphosphonate in quantitative yields, respectively. The mechanisms of the above two reactions were proposed and discussed in connection with the Perkow reaction and related reactions.

Our recent studies on the unsymmetrical ketone synthesis,[2,3] using 1:1 carbonyl adducts of diethyl trimethylsilyl phosphite with aldehydes, have shown that α-alkylated α-trimethylsilyloxy phosphonates were converted by one-step treatment with dilute sodium hydroxide solution to carbonyl compounds with elimination of diethyl phosphonate ion. The simultaneous



removal of the trimethylsilyl group and the tervalent phosphoryl group was considered to be the result of the neighboring participation of α-phosphoryl group where hydroxide ion attacked the phosphoryl center followed by intramolecular migration of the trimethylsilyl group from the α-oxygen to the phosphoryl oxygen so that trimethylsilanol could be eliminated.[2] Thus, it is now recognized that α-lithiated 1-(trimethylsilyloxy)alkylphosphonates can serve as a new type of acyl anion equivalents.

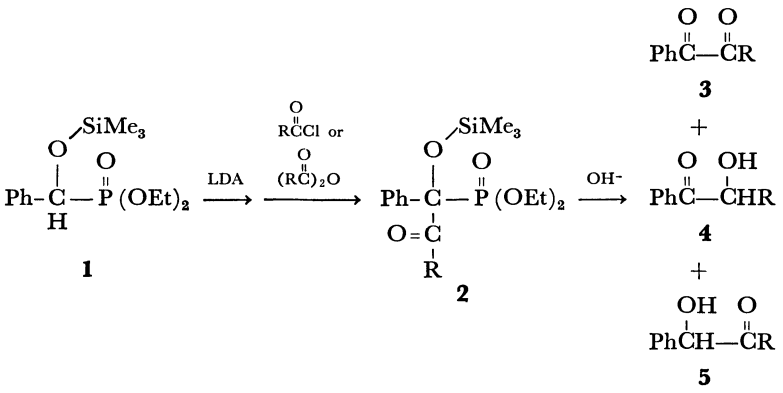
In this paper, we wish to report acylation of diethyl α-(trimethylsilyloxy)benzylphosphonate (**1**), conversion of the acylated products to α-hydroxy ketones, and also a novel type of C–C bond cleavage reactions in connection with the α-hydroxy ketone formation. A preliminary report of this work has already appeared.[5]

Table 1. Preparation of diethyl α-trimethylsilyloxy-α-acylbenzylphosphonates (**2**) from diethyl 1-(trimethylsilyloxy)benzylphosphonate (**1**)

Acylating agent	Acylated product	R	Yield of **2** / %
$C_6H_5C(O)Cl$	**2a**	C_6H_5	81
$4\text{-}ClC_6H_4C(O)Cl$	**2b**	$4\text{-}ClC_6H_4$	88
$4\text{-}MeOC_6H_4C(O)Cl$	**2c**	$4\text{-}MeOC_6H_4$	83
$CH_3C(O)Cl$	**2d**	CH_3	39
$[CH_3C(O)]_2O$	**2d**	CH_3	68
$[(CH_3)_2CHC(O)]_2O$	**2e**	$(CH_3)_2CH$	74
$[CH_3(CH_2)_2C(O)]O$	**2f**	$CH_3(CH_2)_2$	71

Results and Discussion

In order to obtain α-diketones from α-acylated α-(trimethylsilyloxy)benzylphosphonates in a manner similar to that described in the synthesis of unsymmetrical ketones,[2,3] we examined the acylation of **1** and the alkaline treatment of the acylated products (**2**) which would be expected to give α-diketones. Acylation of lithiated **1** with various acylating agents is summarized



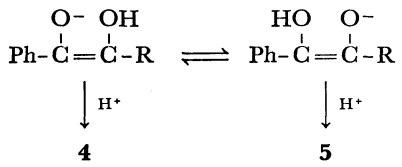
† 1 M = 1 mol dm^{-3}.

Table 2. Alkaline treatment of acylated products 2

Phosphonate	Time/min	Products	
		Yield of 3/%	Yields of 4 and 5/%[a]
2a	5	8	77 (**4a**)
2b	5	10	72 (**4b**)
2c	30	4	88 (**5c**)
2d	5	0	66 (**4d**:**5d**=1:2.8)
2e	10	0	83 (**4e**:**5e**=1:1.3)
2f	10	0	66 (**4f**:**5f**=1:2)

a) The ratio of **4** and **5** was determined by NMR spectra.

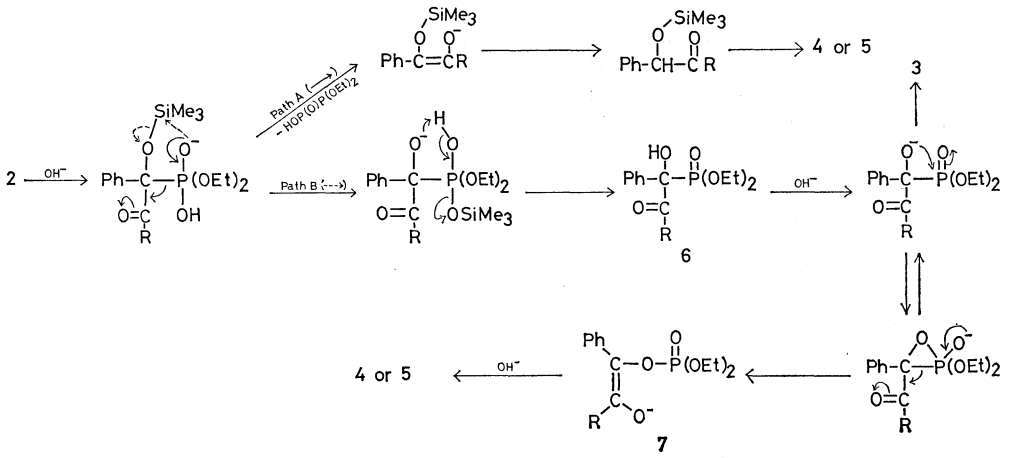
in Table 1. As in the case of the α-alkylation of lithiated **1**,[2,3] the acylation was also satisfactory. In the α-acylation of **1** with aliphatic acylating agents, acid anhydrides were found to be superior to acyl chlorides. The acylated products **2** were treated with 1 M NaOH–EtOH (1:1, v/v) under the same conditions as in the case of the unsymmetrical ketone synthesis. However, the alkaline treatment of **2a** resulted in the formation of benzil in only 8% yield. The main product in this reaction was found to be benzoin (**4a**) which was isolated in 77% yield. Similar results were obtained in the case of **2b** and **2c**. Especially, in the case of **2d**—**f**, α-hydroxy ketones were exclusively obtained. As shown in Table 1, the formation of **4** and/or **5** depends on the substituent of R. Under the alkaline conditions where α-hydroxy ketones were obtained, initially formed α-hydroxy ketones might be in equilibrium between the following two possible enediol enolates. In the case of **2b**, the equilibrium



lies so far to the left because *p*-chlorophenyl group, an electron-withdrawing group, stabilizes the anion of the left compound through the double bond so that **4b** was exclusively obtained. Contrary to this result, the alkaline treatment of **2c** gave **5c** owing to the resonance effect of *p*-methoxyphenyl group as the electron-donating group.

If R is alkyl groups as in the case of the alkaline treatment of **2d**—**f**, the equilibrium lies to the right. Consequently, **5** was obtained predominantly over **4**. The ratio of **5**/**4** decreased in the order of methyl, isopropyl, butyl. This order, however, was reverse to that expected from the electronic effect of the alkyl substituents. Although the reason is not clear, in these cases probably the steric effects in the protonation of the endiol enolates might be more important factor than the electronic environment.

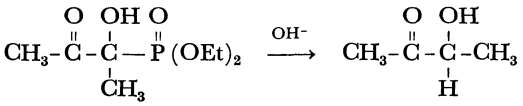
There might be two possible mechanisms for the predominant formation of α-hydroxy ketones. One of them is the mechanism involving an initial attack of hydroxide ion on the phosphorus followed by P–C bond cleavage with concomitant formation of enolate ion (see Path A in Scheme 1).[6] The other mechanism is as follows: The trimethylsilyl group was first eliminated according to a mechanism similar to that described in the case of the alkaline treatment of α-alkylated 1-(trimethylsilyloxy)alkylphosphonates[2,3] and the resulting α-hydroxy β-oxo phosphonate (**6**) is deprotonated followed by phosphoryl migration from carbon to oxygen and the subsequent hydrolysis of the resulting enediol phosphate (**7**) (see Path B in Scheme 1). The latter is closely related to the mechanisms of the Perkow reaction[7] and the Kukhtin-Ramirez oxyphosphorane formation[8] which are thought to proceed *via* an initial attack of the phosphorus on the carbonyl carbon followed by phosphoryl rearrangement.[9,10] In the present α-hydroxy ketone formation, the latter mechanism (Path B) was indirectly supported by the following experiment: Treatment of **2a** with a catalytic amount of *p*-toluenesulfonic acid in methanol–water (1:1, v/v) under reflux for 2 h gave diethyl α-benzoyl-α-hydroxybenzylphosphonate (**6**) in 66% yield. On treatment of **6** with 1 M NaOH–EtOH under the same conditions as with the alkaline treatment of **2a**, **3a**, and **4a** were obtained in 67 and 11% yields, respectively. The ratio of **3a** to **4a** was quite similar to that obtained from **2a**.



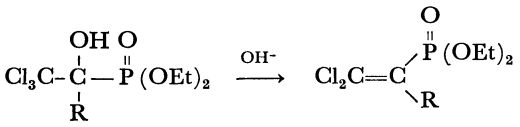
Scheme 1.

$$\mathbf{2a} \xrightarrow{H^+} \mathbf{6} \xrightarrow{OH^-} \mathbf{3a} + \mathbf{4a}$$

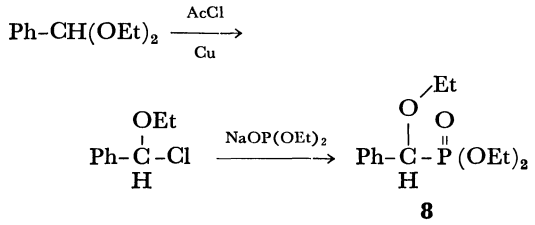
In connection with the mechanism *via* Path B, Kukhtin[11] reported a similar type of phosphoryl rearrangement in the alkaline treatment of the 1:1 carbonyl adduct of diethyl phosphonate with biacetyl.



Moreover, α-hydroxy-β,β,β-trichloro phosphonates were known to undergo phosphoryl rearrangement on treatment with alkali leading to the corresponding enol phosphates.[12]



In order to ascertain the mechanism *via* Path B, we prepared α-alkoxybenzylphosphonate (**8**) substituted with an ethoxy group in place of the trimethylsilyloxy group according to the following equation.

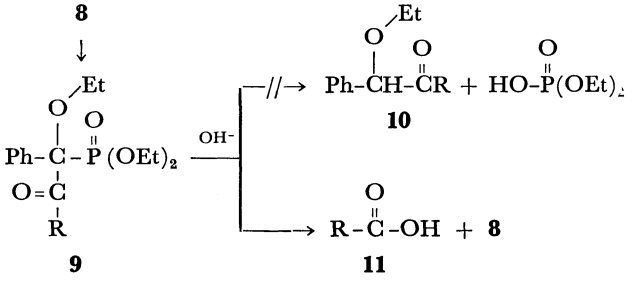


The acylation of **8** with acyl chlorides or acid anhydrides was essentially almost the same as that of **1**. The results are summarized in Table 3.

We considered that, if the α-hydroxy ketone formation from **2** was attributed to Path A, the alkaline treatment of the acylated products (**9**) would give α-ethoxy ketones (**10**). On the other hand, if Path B was the real process, **9** would be recovered unchanged since the ethyl group could not be migrated to the phosphoryl oxygen under these conditions owing to the stable Et–O bond. Therefore, we examined the hydrolysis of **9a** under the same alkaline conditions as described in the alkaline treatment of **2a**. When **9a** was treated with 1 M NaOH–EtOH (1:1, v/v) for 5 min, no reaction took place and 96% of **9a** was recovered. Similar results were obtained also in the case of **9b**—**d**. These results are summarized in Table 4. From these results, we concluded that **4** or **5** was formed *via* Path B.

Table 3. Acylation of diethyl α-ethoxybenzylphosphonates (**8**)

Acylating agent	Acylated product R		Yield of **9** %
$C_6H_5C(O)Cl$	**9a**	C_6H_5	81
$4\text{-}ClC_6H_4C(O)Cl$	**9b**	$4\text{-}ClC_6H_4$	63
$4\text{-}MeOC_6H_4C(O)Cl$	**9c**	$4\text{-}MeOC_6H_4$	81
$CH_3C(O)Cl$	**9d**	CH_3	61



C–C Bond Cleavage of **9**. In connection with the above alkaline treatment of **9**, we found a new type of C–C bond cleavage reactions. When the alkaline treatment of **9a** was prolonged or more concentrated sodium hydroxide solution was employed, some reaction occurred. However, the reaction observed was not P–C bond but C–C bond cleavage reaction. When **9a** was treated with 1 M NaOH–EtOH (1:1, v/v) for 5 h, benzoic acid and **8** were obtained in quantitative yields, respectively. The above C–C bond cleavage reaction is regarded as a

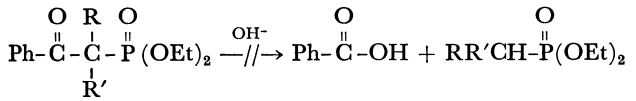
Table 4. Alkaline treatment of acylated products **9**

Phosphonate	Conditions[a]		Yields/% of products		Recovery of **9** %
	Alkali	Time	**8**	**11**	
9a	1 M NaOH-EtOH	5 min	0	0	96
	1 M NaOH-EtOH	5 h	quant.	quant.	0
	4 M NaOH-EtOH	5 min	62	63	31
	4 M NaOH-EtOH	30 min	quant.	quant.	0
	2 M HCl, 60 °C	1 h	0	0	98
9b	1 M NaOH-EtOH	5 min	33	33	62
	1 M NaOH-EtOH	1 h	95	90	0
9c	1 M NaOH-EtOH	5 min	0	0	99
	1 M NaOH-EtOH	30 min	10	10	90
	1 M NaOH-EtOH	24 h	99	92	0
9d	1 M NaOH-EtOH	5 min	0	0	96
	1 M NaOH-EtOH	5 h	b)	quant.	0

a) The ratio of NaOH and EtOH was 1:1 (v/v) and the reaction was carried out at room temperature. b) No efforts to isolate acetic acid were made.

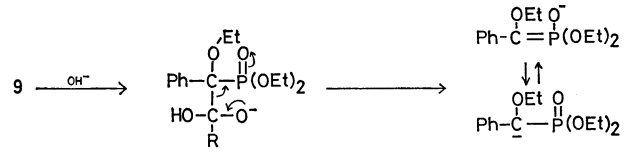
similar type of "acid degradation" to that in acetoacetate synthesis.[13] The conditions and results of the alkaline treatment of **9a**—**d** are summarized in Table 4. Table 4 implies that the reaction rate of the C–C bond cleavage is increased by an electron-withdrawing group substituted at the *p*-position of the benzoyl group and retarded by an electron-donating group. Although a numerous examples have appeared of C–C bond cleavage reactions in acetoacetate synthesis, the present type of fragmentation has not been reported in the chemistry of β-oxo phosphonates to our knowledge. This is substantially because alkoxycarbonyl groups in acetoacetates can stabilize α-carbanions more effectively than dialkoxyphosphoryl groups so that the C–C bond cleavage of acetoacetate derivatives takes place easily.

In order to study the effect of α-substituents of phosphonates in the C–C bond cleavage reaction, the following three compounds were treated with alkali: As a consequence, α-unsubstituted benzoylmethylphosphonate (**12**), α-monoalkylated and dialkylated benzoylmethylphosphonates (**13**) and (**14**) were found to



12: R=R′=H
13: R=H, R′=CH_3
14: R=R′=CH_3

be quite stable under the alkaline conditions where the fission of the C–C bond of **9** took place. The facile cleavage of the C–C bond of **9** might be due to both ethoxy and phenyl substituents which could stabilize the α-carbanion (**15**) of **8** and hence assist the fission of the C–C linkage at the stage of the transition state.



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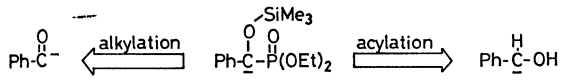
Conclusion. It is noted that the α-carbanion of diethyl α-(trimethylsilyloxy)benzylphosphonate can serve as the benzyl anion equivalent when it was allowed to react with acylating agents followed by the successive alkaline treatment. The α-hydroxy ketone synthesis has proved to involve a phosphoryl rearrangement where the phosphoryl group was eliminated as diethyl phosphate. This is in contrast to the unsymmetrical ketone synthesis from the same carbanion where the phosphoryl group was removed as diethyl phosphonate.



In summary, the compounds having both benzoyl and diethoxyphosphoryl groups on a quarternary carbon undergo C–C bond cleavage reactions with alkali, while the P–C bond cleavage occurs especially when a hydroxyl group is substituted on the quarternary carbon. The ease of the former cleavage reaction depended on the substituents on the quarternary carbon.

Experimental

Melting points and boiling points were uncorrected. IR spectra were recorded on a Hitachi 124 spectrophotometer. ^1H NMR spectra were recorded on a Hitachi R-24B spectrometer. Tetrahydrofuran (THF) was purified by distillation from NaOH pellets followed by redistillation from sodium ribbon and used finally after distillation from benzophenone ketyl. All lithiation and acylation reactions were carried out under argon atmosphere. Lithium diisopropylamide (LDA) was prepared by treatment of diisopropylamine with one equivalent of butyllithium (1.8 M solution in hexane) in THF at −78 °C for 30 min under argon atmosphere.

*General Procedure for Acylation of Lithiated Diethyl α-Trimethylsilyloxybenzylphosphonate (**1**).* To a cooled solution (−78 °C) of LDA (3.3 mmol) in THF (10 ml) was added dropwise diethyl α-trimethylsilyloxybenzylphosphonate (**1**) (928 mg, 3.0 mmol). The mixture was stirred for 0.5 h and then an appropriate acylating agent (3.3 mmol) was added at −78 °C. After being stirred for 0.5 h, the resulting mixture was warmed to room temperature and poured into a mixture of 1 M NH_4Cl (20 ml) and CH_2Cl_2 (20 ml) with vigorous stirring. The organic layer and further extracts with CH_2Cl_2 (3×20 ml) were combined, dried over Na_2SO_4, and evaporated *in vacuo*. The residual oil was chromatographed on silica gel with hexane–ether to afford the corresponding **2**.

*Diethyl α-Trimethylsilyloxy-α-benzoylbenzylphosphonate (**2a**).* The structure of this compound was confirmed by direct comparison with an authentic sample prepared previously.[14]

*Diethyl α-Trimethylsilyloxy-α-(4-chlorobenzoyl)benzylphosphonate (**2b**).* Mp 49—52 °C; NMR (CCl_4) δ 0.12(9H, s, Me_3Si), 1.20(3H, t, $J_{H-H}=J_{H-P}=7$ Hz, one of CH_3C–O), 1.24(3H, t, $J_{H-H}=J_{H-P}=7$ Hz, one of CH_3C–O), 3.76—4.42(4H, m, CH_2O), 7.15(2H, d, $J_{H-H}=8.5$ Hz, ArH), 7.25(3H, m, ArH), 7.52(2H, m, ArH), 7.72(2H, d, $J_{H-H}=8.5$ Hz, ArH).

Found: C, 55.68; H, 6.12%. Calcd for $C_{21}H_{28}O_5ClPSi$: C, 55.44; H, 6.20%.

*Diethyl α-Trimethylsilyloxy-α-(4-methoxybenzoyl)benzylphosphonate (**2c**).* Mp 92—98 °C; IR(NaCl) 968, 1027, 1055, 1146, 1192, 1255 (νP=O), 1320, 1516, 1579, 1604, 1672 (C=O), 2800, 2900, and 3065 cm^{-1}; NMR(CCl_4) δ 0.14(9H, s, Me_3Si), 1.19(3H, t, $J_{H-H}=J_{H-P}=7$ Hz, one of CH_3C–O), 1.23(3H, t, $J_{H-H}=J_{H-P}=7$ Hz, one of CH_3C–O), 3.68(3H, s, CH_3O), 4.02(4H, m, CH_2O), 6.67(2H, d, $J_{H-H}=10$ Hz, ArH), 7.25(3H, m, ArH), 7.58(2H, m, ArH), 7.78(2H, d, $J_{H-H}=10$ Hz, ArH).

Found: C, 59.09; H, 6.85%. Calcd for $C_{22}H_{31}O_6PSi$: C, 58.65; H, 6.94%.

*Diethyl α-Trimethylsilyloxy-α-acetylbenzylphosphonate (**2d**).* Oily substance: NMR(CCl_4) δ 0.20(9H, s, Me_3Si), 1.16 (3H, t, $J_{H-H}=J_{H-P}=7$ Hz, one of CH_3C–O), 1.25(3H, t, $J_{H-H}=J_{H-P}=7$ Hz, one of CH_3C–O), 2.22(3H, s, CH_3C(O)), 3.73—4.32(4H, m, CH_2O), 7.30(3H, m, ArH), 7.65(2H, m, ArH).

Found: C, 53.65; H, 7.81%. Calcd for $C_{16}H_{27}O_5PSi$: C, 53.61; H, 7.59%.

*Diethyl 1-Trimethylsilyloxy-3-methyl-2-oxo-1-phenylbutylphosphonate (**2e**).* Oily substance: NMR(CCl_4) δ 0.20(9H, s, Me_3Si), 0.70(3H, d, $J_{H-H}=7$ Hz, one of $(CH_3)_2C$), 0.99 (3H, d, $J_{H-H}=7$ Hz, one of $(CH_3)_2C$), 1.16(3H, t, $J_{H-H}=$

7 Hz, one of CH_3C–O), 1.28(3H, t, J_{H-H}=7 Hz, one of CH_3C–O), 3.42(1H, m, CH), 3.70—4.33(4H, m, CH_2O), 7.25(3H, m, ArH), 7.70(2H, m, ArH).

Found: C, 55.96; H, 8.21%. Calcd for $C_{18}H_{31}O_5PSi$: C, 55.94; 8.09%.

*Diethyl 1-Trimethylsilyloxy-2-oxo-1-phenylpentylphosphonate (**2f**).* Oily substance: NMR(CCl_4) δ 0.20(9H, s, Me_3Si), 0.80(3H, t, J_{H-H}=7 Hz, CH_3C), 1.14(3H, t, J_{H-H}=7 Hz, one of CH_3C–O), 1.24(3H, J_{H-H}=7 Hz, one of CH_3C–O), 1.50(2H, m, $CH_2CC(O)$), 2.57(2H, m, $CH_2C(O)$), 3.70—4.30(4H, m, CH_2O), 7.25(3H, m, ArH), 7.61(2H, m, ArH).

Found: C, 55.45; H, 7.92%. Calcd for $C_{18}H_{31}O_5PSi$: C, 55.94; H, 8.09%.

*Conversion of Acylated Compounds (**2**) into Acyloins (**4** and **5**) under Alkaline Conditions.* An appropriate acylated compound **2** was dissolved in ethanol (20 ml) at room temperature. To the solution was added 1 M sodium hydroxide (20 ml). The resulting solution was stirred at room temperature until **2** had disappeared and then poured into a mixture of 1 M NH_4Cl (20 ml) and CH_2Cl_2 (20 ml) with stirring. The organic layer was collected, combined with further extracts with CH_2Cl_2 (3×20 ml), dried over Na_2SO_4, and evaporated to dryness. The residual oil was chromatographed on silica gel with hexane–ether to afford the corresponding **4** and **5** as listed Table 2.

*Diethyl α-Benzoyl-α-hydroxybenzylphosphonate (**6**).* To a solution of **2a** (1.846 g, 4.39 mmol) in methanol–water (1:1, v/v, 30 ml) was added a catalytic amount of *p*-toluenesulfonic acid monohydrate (50 mg). The solution was refluxed for 2 h and diluted with water (30 ml) after cooling. The aqueous solution was extracted with CH_2Cl_2 (4×30 ml) and the organic layers were combined, dried over Na_2SO_4, and evaporated *in vacuo* to dryness. The residue was chromatographed on silica gel with hexane–ether to afford **6** (1.014 g, 66%): Mp 76—78 °C; NMR($CDCl_3$) δ 1.15(3H, t, J_{H-H}=J_{H-P}=7 Hz, one of CH_3C–O), 1.27(3H, t, J_{H-H}=J_{H-P}=7 Hz, one of CH_3C–O), 3.67—4.40(6H, m, CH_2O and CH_2Cl), 3.85(1H, s, OH), 7.27(3H, m, ArH), 7.48 (2H, m, ArH).

Found: C, 61.17; H, 6.29%. Calcd for $C_{18}H_{21}O_5P\cdot 1/4H_2O$: C, 61.27; H, 6.14%.

*Diethyl α-Ethoxybenzylphosphonate (**8**).*[15] Diethyl phosphonate (7.95 g, 57.6 mmol) was added dropwise to sodium (1.50 g, 65.2 mmol) in dry ether (25 ml) at 10 °C. After evolution of hydrogen gas ceased, the mixture was refluxed for an additional 5 h and cooled in an ice bath to 0 °C. To the cooled solution was added dropwise α-chlorobenzyl ethyl ether (10.2 g, 59.8 mmol) and the mixture was stirred at room temperature for 1 h. The resulting solution was poured into a mixture of 1 M NH_4Cl (30 ml) and CH_2Cl_2 (30 ml). The organic phase was collected and the aqueous layer was further extracted with CH_2Cl_2 (3×30 ml). The extracts were combined, dried over Na_2SO_4, evaporated *in vacuo*, and chromatographed on silica gel with hexane–ether to afford **8** (10.7 g, 68%): Bp 121—136 °C/0.49—0.53 mmHg; IR(NaCl) 960, 1023, 1050, 1094, 1160, 1254 (νP=O), 1388, 1450, 1490, 2900, and 2960 cm^{-1}; NMR (CCl_4) δ 1.14(3H, t, J_{H-H}=J_{H-P}=7 Hz, one of CH_3C–O), 3.46(2H, q, J_{H-H}=7 Hz, CH_2O–C), 3.67—4.21(4H, m, CH_2O–P), 4.45(1H, d, J_{H-P}=15.5 Hz, CH), 7.27(5H, m, ArH).

Found: C, 57.16; H, 7.99%. Calcd for $C_{13}H_{21}O_4P$: C, 57.35; H, 7.7%.

*General Procedure for Acylation of Diethyl α-Ethoxybenzylphosphonate (**8**).* To a cooled (−78 °C) solution of LDA (8.8 mmol) in dry THF (20 ml) was added **8** (2.18 g, 8 mmol). After stirring at −78 °C for 0.5 h, an appropriate acyl chloride (9.6 mmol) was added dropwise to the mixture. The usual work-up described in the case of acylation of **1** afforded the corresponding **9**.

*Diethyl α-Ethoxy-α-benzoylbenzylphosphonate (**9a**).* Oily substance: IR(NaCl) 965, 1045, 1100, 1162, 1182, 1240 (νP=O), 1260, 1392, 1448, 1485, 1597, 1680, 2915, 2970, and 3020 cm^{-1}; NMR(CCl_4) δ 1.07(3H, t, J_{H-H}=7 Hz, CH_3C–O–C), 1.22(3H, t, J_{H-H}=J_{H-P}=7 Hz, one of CH_3C–O), 1.26(3H, t, J_{H-H}=J_{H-P}=7 Hz, one of CH_3C–O), 3.05—3.65(1H, m, one of CH_2–O–C), 3.72—4.45(5H, m, one of CH_2–O–C and CH_2O–P), 7.25(5H, m, ArH), 7.25(3H, m, ArH), 7.67—7.90(2H, m, ArH).

Found: C, 63.48; H, 6.83%. Calcd for $C_{20}H_{24}O_5ClP$: C, 63.82; H, 6.70%.

*Diethyl α-Ethoxy-α-(4-chlorobenzoyl)benzylphosphonate (**9b**).* Oily substance: NMR(CCl_4) δ 0.98—1.40(9H, m, CH_3), 3.06—4.58(6H, m, CH_2), 7.05—7.60(5H, m, ArH), 7.18 (2H, d, J_{H-H}=9 Hz, ArH), 7.75(2H, d, J_{H-H}=9 Hz, ArH).

Found: C, 58.36; H, 6.17; Cl, 9.06%. Calcd for $C_{20}H_{24}O_5ClP$: C, 58.47; H, 5.89; Cl, 8.63%.

*Diethyl α-Ethoxy-α-(4-methoxybenzoyl)benzylphosphonate (**9c**).* Oily substance: NMR(CCl_4) δ 0.99—1.04(9H, m, CH_3), 3.10—4.48(6H, m, CH_2), 3.75(3H, s, CH_3O), 6.65(2H, d, J_{H-H}=9 Hz, ArH), 7.00—7.57(5H, m, ArH), 7.87(2H, d, J_{H-H}=9 Hz, ArH).

Found: C, 61.88; H, 6.73%. Calcd for $C_{21}H_{27}O_6P$: C, 62.06; H, 6.70%.

*Diethyl α-Ethoxy-α-acetylbenzylphosphonate (**9d**).* Oily substance: NMR(CCl_4) δ 1.07—1.63(9H, m, CH_3), 2.01 (3H, s, $CH_3C(O)$), 3.23—4.30(6H, m, CH_2), 7.03—7.60 (5H, m, ArH).

Found: C, 57.12; H, 7.32%. Calcd for $C_{15}H_{23}O_5P$: C, 57.32; H, 7.37%.

*Reaction of Diethyl α-Ethoxy-α-acylbenzylphosphonate (**9**) with Alkali.* An appropriate diethyl 1-ethoxy-2-oxobenzylphosphonate (**9**) (2 mmol) was dissolved in ethanol (20 ml) and 20 ml of 1 M NaOH was added at once with stirring. The reaction conditions are summarized in Table 4. After the reaction was complete, the mixture was poured into a mixture of 1 M NH_4Cl (30 ml) and CH_2Cl_2 (30 ml) put in a separatory funnel. The organic phase was collected and the aqueous layer was extracted with CH_2Cl_2 (2×30 ml). The extracts were combined, dried over Na_2SO_4, evaporated *in vacuo*, and chromatographed on silica gel with hexane–ether to afford **8** and/or the starting material **9**. The aqueous layer was acidified to pH 1.0 by concd HCl and then extracted with CH_2Cl_2 (3×20 ml). The extracts were combined and dried over Na_2SO_4. Removal of the solvent gave a carboxylic acid. The structures of the products were confirmed by comparison with authentic samples.

*Preparation of Diethyl 1-Benzoylethylphosphonate (**13**) and Diethyl 1-Benzoyl-1-methylethylphosphonate (**14**).* To a suspension of sodium hydride (50%, 144 mg, 3 mmol) in dry THF (6 ml) was added diethyl benzoylmethylphosphonate (587 mg, 2.3 mmol) at room temperature. After stirring for 18 h, the resulting homogeneous solution was treated with 1 M NH_4Cl (20 ml) and extracted with CH_2Cl_2 (3×20 ml). The extracts were combined, dried over Na_2SO_4, evaporated, and chromatographed on silica gel with benzene–ethyl acetate to afford **13**[16] (260 mg, 42%) and **14** (228 mg, 35%): NMR($CDCl_3$) δ 1.29(6H, t, J_{H-H}=7 Hz, CH_3C–O), 1.68(6H, d, J_{H-P}=17 Hz, CH_3C–P), 4.08(2H, t, J_{H-H}=J_{H-P}=7 Hz, one of CH_2O), 4.19(2H, t, J_{H-H}=J_{H-P}=7

† 1 mmHg≈133.322Pa.

Hz, one of CH_2O), 7.42(3H, m, ArH), 7.97(2H, m, ArH).

Found: C, 59.08; H, 7.43%. Calcd for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.45%.

Stability of ***12***, ***13***, *and* ***14*** *under Alkaline Conditions.* Compound **12**, **13**, or **14** (0.5 mmol) was dissolved in ethanol (5 ml) and 5 ml of 1 M NaOH was added. TLC after 1 h showed that these compounds were stable under these conditions and remained as single spots.

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