Silyl Phosphites. XVIII. Versatile Utility of α-(Trimethylsilyloxy)-alkylphosphonates as Key Intermediates for Transformation of Aldehydes into Several Carbonyl Derivatives[1]

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Carbonyl addition compounds of diethyl trimethylsilyl phosphite (DTMSP) with aldehydes were converted, by treatment with lithium diisopropylamide (LDA) followed by the successive alkylation and alkaline hydrolysis, to carbonyl derivatives involving aldehydes, unsymmetrical ketones, β,γ-unsaturated ketones, and carboxylic acids. β-Substituted carboxylic esters and γ-substituted lactones were prepared by use of the carbonyl addition compounds of DTMSP with α,β-unsaturated aldehydes.

Since Corey and Seebach[2] introduced acyl anion equivalents by use of 1,3-dithianes in 1965, a number of reagents belonging to this category have appeared in the literature and have proved to be useful key intermediates in modern organic synthesis. A few years ago, Seebach advocated the concept of "Umpolung."[3k] These studies in this field have recently been reviewed.[3]

In this paper, we wish to report versatile utility of the carbonyl addition products of DTMSP with aldehydes in detail.[4]

In connection with our study, several related reactions have recently been reported.[5]

Results and Discussion

It is well known that the carbon-phosphorus bond of dialkyl α-hydroxy phosphonates is readily cleaved under alkaline conditions to give carbonyl compounds and dialkyl phosphonates.[6] This reaction pattern

$$R^1R^2\overset{OH}{\overset{|}{C}}\text{-P(O)(OR}^3)_2 \xrightarrow{OH^-} R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2 + \text{H-P(O)(OR}^3)_2$$

led us to study alkylation of the carbonyl addition compounds obtained by the reaction of silyl phosphites with aldehydes, since the formation of unsymmetrical ketones were expected on treatment of the α-alkylated products with acid followed by alkali.

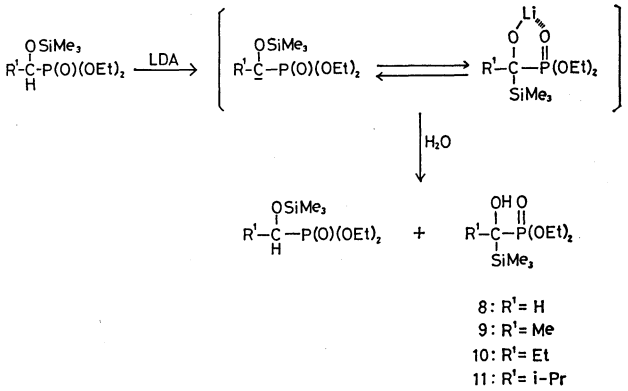
$$R^1\text{-}\overset{OSiMe_3}{\overset{|}{C}}\text{H-P(O)(OR}^3)_2 \xrightarrow{R^2X}$$

1—7

$$R^1\text{-}\overset{OSiMe_3}{\overset{|}{C}}(R^2)\text{-P(O)(OR}^3)_2 \xrightarrow{H^+} \xrightarrow{OH^-} R^1\text{-}\overset{O}{\overset{\|}{C}}\text{-}R^2$$

1: R^1=Ph **5**: R^1=*i*-Pr
2: R^1=H **6**: R^1=*n*-C_7H_{15}
3: R^1=Me **7**: R^1=$PhCH_2$
4: R^1=Et

It was found that metalation of diethyl α-(trimethylsilyloxy)benzylphosphonate (**1**) with LDA in THF proceeded quite easily to afford relatively stable α-carbanion species which reacted with alkyl halides to give the alkylated products (**18—30**) in good yields. However, in the case of addition compounds (**2—4**) of DTMSP with aliphatic aldehydes, the lithiation of **2—4** caused the Wittig rearrangement[7] (or the anti-Brook rearrangement[8]) of trimethylsilyl group.



Scheme 1.

The product distributions of **2—4**/**8—10** after quenching with 1 M† NH_4Cl at −78 °C or at room temperature are summarized in Table 1. Table 1 implies that the equilibrium between the carbanion and the oxido ion is affected by both the alkyl substituent and the temperature. The ratio of the carbanion to the oxido ion grows up with a rise in temperature and also with an increase in the bulkiness of the α-substituent. The equilibrium between **4** and **10** in 1,2-dimethoxyethane (DME) is in favor of **10** as compared with THF (see Table 1). The above-mentioned facile Wittig rearrangement of the trimethylsilyl group can be explained as follows; the *O*-lithio derivatives (oxido ion) can be stabilized by an intramolecular chelation with the neighboring group of $P(O)(OEt)_2$. The Wittig rearrangement of this type has been known little.[9] Only one example has been reported by West where benzyl trimethylsilyl ether underwent the Wittig rearrangement under special conditions using an excess amount of strong lithiating agents such as *t*-butyllithium.[9a]

Hünig[10a-e] reported that synthesis of aromatic ketones utilizing the addition compounds of aldehydes with trimethylsilyl cyanide. In connection with the Wittig rearrangement of α-trimethylsilyloxy phosphonates mentioned above, alkylation of 2-(trimethylsilyloxy)propionitrile (**12**) was conducted. However, all attempts to obtain the alkylated products (**13**) were unsuccessful. It is likely that the lithiated intermediate decomposes *via* the Wittig rearrangement to an acylsilane and cyanide ion which in turn react

† 1 M = 1 mol dm^{-3}.

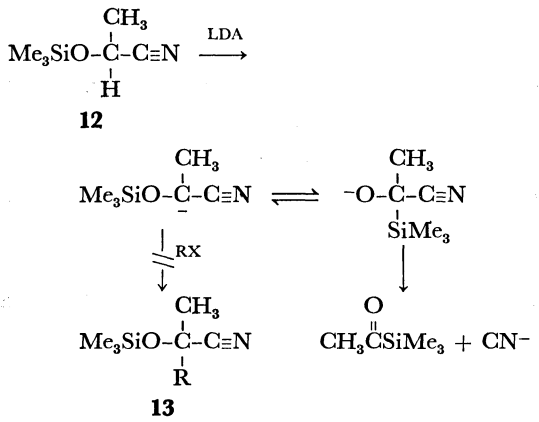
Table 1. Product distributions of α-trimethylsilyloxy phosphonates (**2**—**5**) and α-hydroxy-α-trimethylsilyl phosphonates (**8**—**11**)

Phosphonate		**2**		**3**		**4**				**5**	
Condition for lithiation	solv.	THF		THF		THF	THF	DME		THF	
	time/h	0.5		0.5		0.5	5	1		0.5	
Temp[a]		−78 °C	r.t.	−78 °C	r.t.	−78 °C	r.t.	−78 °C	−78 °C	−78 °C	r.t.
Product (%)	**2**	0	0	**3** 0	22	**4** 45	40	45	22	**5** 85	35
	8	87	78	**9** 91	42	**10** 37	0	31	58	**11** 0	0

a) Temperature at which the lithiation mixture was quenched with 1 M NH_4Cl.

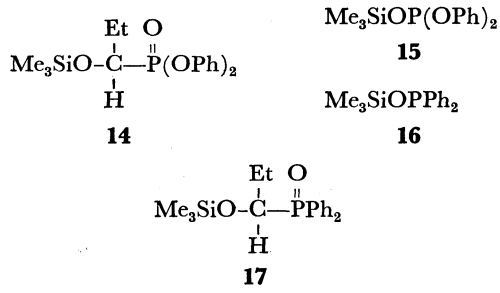
Table 2. Elemental analyses and spectral data of **8**—**10**

Compound	Molecular formula	Found (%)	Calcd (%)	IR(NaCl) $\tilde{\nu}$/cm^{-1}	^{1}H-NMR(CCl_4) δ
8	$C_8H_{21}O_4PSi$	C: 40.12 H: 8.56	39.98 8.81	1035, 1100, 1215(νP=O), 1250, 1370, 1392, 1445, 2890, 2970, 3290(OH)	0.12(9H, s, Me_3Si), 1.37(6H, t, J=7 Hz, CH_3), 3.55(1H, dd, J=6 Hz, J=14 Hz, CHP), 3.80—4.38(4H, m, CH_2-O), 5.10 (1H, d, J=6 Hz, OH)
9	$C_9H_{23}O_4PSi$	C: 42.91 H: 9.53	42.50 9.11	1030, 1055, 1104, 1170, 1222(νP=O), 1252, 1370, 1394, 1448, 2890, 2965, 3280(OH)	0.11(9H, s, Me_3Si), 1.31(6H, t, J=7 Hz, CH_3), 1.39(3H, d, J=19.2 Hz, CH_3CP), 3.80—4.38(4H, m, CH_2-O), 4.38(1H, br. OH)
10	$C_{10}H_{25}O_4PSi$	C: 44.51 H: 9.56	44.76 9.39	1027, 1057, 1228(νP=O), 1248, 1380, 1442, 2910, 2966, 3290(OH)	0.11(9H, s, Me_3Si), 1.01(3H, t, J=7 Hz, CH_3), 1.29(6H, t, J=7 Hz, CH_3), 1.30—2.23(2H, m, CH_2C), 3.80—4.43(5H, m, CH_2-O and OH)



to give a complex mixture. In this respect, the utility of α-trimethylsilyloxy phosphonates should be emphasized since α-oxido phosphonates do not decompose owing to the stable chelation as shown in Scheme 1 and exist in equilibrium with the reactive carbanion species so that the alkylation proceeds under certain conditions. In this sense, it is interesting that Stork[11] and other groups[12—14] reported the usefulness of anions of protected cyanohydrins as acyl carbanion equivalents which were also stabilized through intramolecular chelations.

In order to avoid the Wittig rearrangement of α-trimethylsilyloxy phosphonates, we attempted the preparation of diphenyl α-trimethylsilyloxy phosphonates (**14**) substituted by an electron-withdrawing group such as $P(O)(OPh)_2$ group in place of diethoxyphosphinyl group. However, diphenyl trimethylsilyl phosphite (**15**) could not be prepared as a pure material. We failed also to prepare the corresponding carbonyl addition compound (**14**) by the *in situ* reaction of diphenyl phosphonate with propionaldehyde in the presence of sodium followed by trimethylsilylation. On the other hand, trimethylsilyl diphenylphosphinite (**16**) could be prepared according to the reported procedure.[15] The phosphinite (**16**) underwent facile addition reaction with propionaldehyde to afford the corresponding adduct (**17**). However, this adduct was



found to be rather unstable compared with **4**. During the isolation of **17** by means of silica gel column chromatography, its decomposition to α-hydroxypropylphosphinite was observed to a considerable extent. Moreover, the lithiation of **17** led to a complex mixture.

From the above results, we finally chose the diethyl esters **1**—**7** as the precursors of acyl anion equivalents for transformation of aldehydes to ketones. The alkylation of **1** was satisfactory and a variety of alkyl halides could be employed. Since Table 1 suggested that at higher temperatures the equilibrium between the α-carbanion and the α-oxido ion was in favor of the former, the alkylation of **2**—**6** was carried out by

TABLE 3. ALKYLATION OF α-TRIMETHYLSILYLOXY PHOSPHONATES (**1**—**7**)

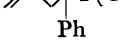
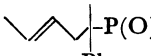
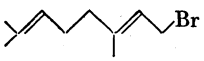
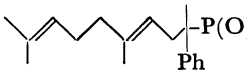
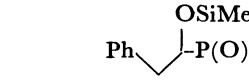
Phosphonate	Conditions for lithiation Solvent	LDA(equiv.)	Time/h	Conditions for alkylation RX (equiv.)	Temp/°C	Time/h	Product	Compd No.	Yield/%
1	THF	(1.15)	0.5	MeI (1.15)	−78	0.5	Me-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**18**	90
1	THF	(1.15)	0.5	EtI (1.2)	−78	0.7	Et-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**19**	87
1	THF	(1.15)	0.5	*n*-PrI (1.25)	−78	1.3	*n*-Pr-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**20**	81
1	THF	(1.15)	0.5	*n*-BuI (1.3)	−78	0.8	*n*-Bu-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**21**	84
1	THF	(1.15)	0.5	*i*-PrI (1.35)	−78→r.t.	24	*i*-Pr-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**22**	80
1	THF	(1.15)	0.5	$PhCH_2Br$ (1.15)	−78	0.5	Ph-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**23**	85
1	THF	(1.1)	0.5	$PhCH_2CH_2Br$ (1.15)	−78→r.t.	5	Ph-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**24**	67
1	THF	(1.1)	0.5	 (1.25)	−78	1.3		**25**	88
1	THF	(1.2)	0.5	 (1.25)	−78	0.7		**26**	67
1	THF	(1.2)	0.5	 (1.25)	−78	1.0		**27**	68
1	THF	(1.1)	0.5	Me-S-S-Me (1.05)	−78	0.8	CH_3S-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**28**	69
1	THF	(1.1)	0.5	Ph-S-S-Ph (1.2)	−78	0.5	PhS-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**29**	81
1	THF	(1.1)	0.5	Me_3SiCl (1.2)	−78→r.t.	20	Me_3Si-C(OSiMe$_3$)(Ph)-P(O)(OEt)$_2$	**30**	71
2	THF	(1.05)	0.5	MeI (1.05)	−78→r.t.	12	**3**		86
2	THF	(1.1)	0.5	EtI (1.2)	−78→r.t.	1.0	**4**		77
2	THF	(1.1)	0.7	$PhCH_2Br$ (1.15)	−78→r.t.	12		**31**	80

TABLE 3. (Continued)

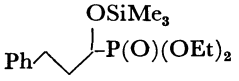
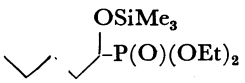
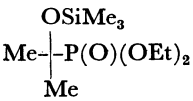
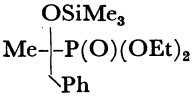
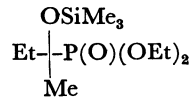
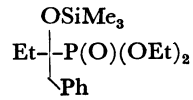
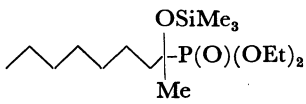
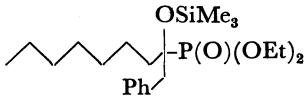
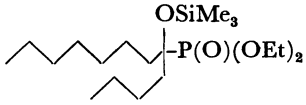
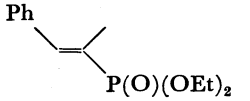
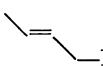
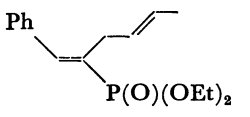
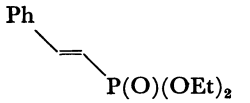
Phosphonate	Conditions for lithiation Solvent	Time/h	LDA(equiv.)	Conditions for alkylation RX (equiv.)	Temp/°C	Time/h	Product	Compd No.	Yield/%
2	THF	0.5	(1.1)	$PhCH_2CH_2I$ (1.2)	−78→r.t.	3		**32**	48
2	THF	0.8	(1.1)	*n*-BuI (1.15)	−78→r.t.	4		**33**	41
3	THF	0.5	(1.1)	MeI (1.2)	−78→r.t.	3		**34**	95
3	THF	0.5	(1.15)	$PhCH_2Br$ (1.15)	−78→r.t.	12		**35**	76
3	THF	0.7	(1.15)	$PhCH_2CH_2Br$ (1.15)	−78→r.t.	1.0	—		0
4	THF	5	(1.2)	MeI (1.2)	−78→r.t.	1.5		**36**	84
4	THF	5	(1.15)	$PhCH_2Br$ (1.15)	−78→r.t.	3		**37**	58
5	THF	15	(1.2)	MeI (1.2)	−78→r.t.	3	74% of **5** was recovered		0
5	DME	1	(1.1)	MeI (1.1)	−78→r.t.	1.5	63% of **5** was recovered		0
6	DME	1	(1.0)	MeI (1.05)	−78→r.t.	1.5		**38**	86
6	DME	1	(1.1)	$PhCH_2Br$ (1.1)	−78→r.t.	1.3		**39**	29
6	DME	1	(1.1)	*n*-BuI (1.1)	−78→r.t.	2.5		**40**	13
7	THF	0.5	(1.15)	MeI (1.2)	−78→r.t.	0.8		**41**	57
7	THF	0.5	(1.1)	 (1.05)	−78→r.t.	4		**42**	19
7	THF	1	(1.2)	H_2O (3.7)	−78	3 min		**43**	41

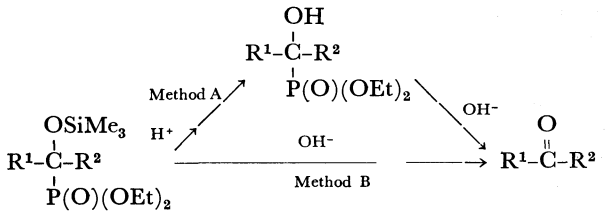
TABLE 4. ELEMENTAL ANALYSES AND ^{1}H-NMR DATA OF α-ALKYLATED PHOSPHONATES (**18**—**43**)

Compound	Molecular formula	Found (%)	Calcd (%)	^{1}H-NMR δ
18	$C_{15}H_{27}O_4PSi$[25]			($CDCl_3$) 0.27(9H, s, Me_3Si), 1.30(3H, t, J=7 Hz, CH_3), 1.38 (3H, t, J=7 Hz, CH_3), 2.05(3H, d, J=16 Hz, CH_3CP), 4.10 (4H, m, CH_2-O), 7.40(3H, m, ArH), 7.61(2H, m, ArH)
19	$C_{16}H_{29}O_4PSi$	C: 55.51 H: 8.57	55.79 8.49	(CCl_4) 0.28(9H, s, Me_3Si), 0.72(3H, t, J=7 Hz, CH_3), 1.08 (3H, t, J=7 Hz, CH_3C-O), 1.30(3H, t, J=7 Hz, CH_3C-O), 2.29(2H, m, CH_2CP), 3.29—4.32(4H, m, CH_2OP), 7.17—7.41 (3H, m, ArH), 7.41—7.85(2H, m, ArH)
20	$C_{17}H_{31}O_4PSi$	C: 56.93 H: 8.78	56.96 8.78	($CDCl_3$) 0.27(9H, s, Me_3Si), 0.06—1.47(11H, m, CH_3CH_2 and CH_3C-O), 1.98—2.48(2H, m, CH_2CP), 3.30—4.30(4H, m, CH_2-O), 7.05—7.34(3H, m, ArH), 7.34—7.63(2H, m, ArH)
21	$C_{18}H_{33}O_4PSi$	C: 58.36 H: 9.07	58.03 8.93	($CDCl_3$) 0.27(9H, s, Me_3Si), 0.67—1.50(13H, m, $CH_3CH_2CH_2C$ and CH_3C-O), 2.27(2H, m, CH_2CP), 3.33—4.38(4H, m, CH_2-O), 7.30(3H, m, ArH), 7.98(2H, m, ArH)
22	$C_{17}H_{31}O_4PSi$	C: 56.56 H: 8.72	56.96 8.72	($CDCl_3$) 0.25(9H, s, Me_3Si), 0.77(3H, d, J=7 Hz, CH_3), 0.98 (3H, d, J=7 Hz, CH_3), 0.92(3H, t, J=7 Hz, CH_3C-O), 1.31 (3H, t, J=7 Hz, CH_3), 2.18—2.85(1H, m, CH), 3.00—4.32 (4H, m, CH_2-O), 7.08—7.31(3H, m, CH), 7.31—7.64(2H, m, ArH)
23	$C_{22}H_{33}O_4PSi$	C: 63.15 H: 8.14	62.83 7.91	($CDCl_3$) 0.25(9H, s, Me_3Si), 0.96(3H, t, J=7 Hz, CH_3), 1.18 (3H, t, J=7 Hz, CH_3), 1.83—2.80(4H, m, CH_2CH_2), 3.08—4.25(4H, m, CH_2-O), 6.98(5H, s, ArH), 6.77—7.63(5H, m, ArH)
24	$C_{21}H_{31}O_4PSi$	C: 61.64 H: 7.87	62.04 7.69	($CDCl_3$) 0.19(9H, s, Me_3Si), 1.05(3H, t, J=7 Hz, CH_3), 1.31 (3H, t, J=7 Hz, CH_3), 3.30—4.34(6H, m, CH_2Ph and CH_2-O), 6.90(5H, s, ArH), 6.95—7.29(3H, m, ArH), 7.29—7.62 (2H, m, ArH)
25	$C_{17}H_{29}O_4PSi$	C: 57.00 H: 8.24	57.28 8.20	($CDCl_3$) 0.28(9H, s, Me_3Si), 1.10 and 1.29(3H and 3H, t and t, J=7 Hz, CH_3C-O), 3.08(2H, dd, J=7 Hz, J=7 Hz, CH_2CP), 3.38—4.37(4H, m, CH_2O), 4.86—5.26(2H, m, CH_2=C), 5.28 —5.80(1H, m, C=CH), 7.30(3H, m, ArH), 7.58(2H, m, ArH)
26	$C_{18}H_{31}O_4PSi$	C: 58.84 H: 8.35	58.35 8.43	($CDCl_3$) 0.21(9H, s, Me_3Si), 1.06 and 1.23(3H and 3H, t and t, J=7 Hz, CH_3), 1.50(3H, d, J=5 Hz, CH_3-C=C), 2.95(2H, m, CH_2CP), 3.30—4.27(4H, m, CH_2-O), 4.77—5.63(2H, m, CH=CH), 7.20(3H, m, ArH), 7.47(2H, m, ArH)
27	$C_{24}H_{41}O_4PSi$	C: 63.42 H: 9.01	63.68 9.13	($CDCl_3$) 0.25(9H, s, Me_3Si), 1.10(3H, t, J=7 Hz, CH_3), 1.32 (3H, t, J=7 Hz, CH_3), 1.60(9H, s, CH_3-C=C), 1.95(4H, b, CH_2CH_2), 3.05(2H, dd, J=7 Hz, J=7 Hz, CH_2CP), 3.40—4.40 (4H, m, CH_2-O), 4.98(2H, m, C=CH), 7.28(3H, m, ArH), 7.52 (2H, m, ArH)
28	$C_{15}H_{27}O_4PSSi$	C: 49.36 H: 7.46 S: 8.74	49.70 7.51 8.84	($CDCl_3$) 0.27(9H, s, Me_3Si), 1.15 and 1.27(3H and 3H, t and t, J=7 Hz, CH_3), 2.03(3H, s, CH_3S), 3.60—4.33(4H, m, CH_2-O), 7.13—7.37(3H, m, ArH), 7.50—7.75(2H, m, ArH)
29	$C_{20}H_{29}O_4PSSi$	C: 56.42 H: 7.03 S: 7.72	56.58 6.88 7.55	($CDCl_3$) 0.33(9H, s, Me_3Si), 1.11 and 1.30(3H and 3H, t and t, J=7 Hz, CH_3), 3.47—4.37(4H, m, CH_2-O), 6.99(5H, s, ArH), 6.80—7.70(5H, m, ArH)
30	$C_{17}H_{30}O_4PSi$	C: 52.48 H: 8.40	52.55 8.56	(CCl_4) 0.05(9H, s, Me_3Si), 0.23(9H, s, Me_3Si), 1.05 and 1.36 (3H and 3H, t and t, J=7 Hz, CH_3) 3.36—4.50(4H, m, CH_2-O), 7.10—7.80(5H, m, ArH)
31	$C_{15}H_{27}O_4PSi$[26]			(CCl_4) 0.17(9H, s, Me_3Si), 1.33(6H, t, J=7 Hz, CH_3), 2.37—3.37(2H, m, CH_2CP), 3.73—4.37(5H, m, CH and CH_2-O), 7.17 (5H, s, ArH)
32	$C_{16}H_{29}O_4PSi$	C: 55.72 H: 8.60	55.79 8.49	(CCl_4) 0.15(9H, s, Me_3Si), 1.28(6H, t, J=7 Hz, CH_3), 1.50—2.20(2H, m, CH_2CP), 2.20—3.09(2H, m, CH_2CCP), 3.33—4.32 (5H, m, CH and CH_2-O), 7.10(5H, m, ArH)

Table 4. (Continued)

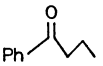
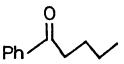
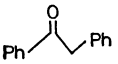
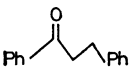
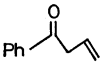
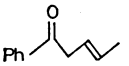
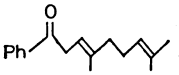
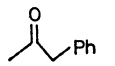
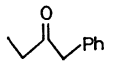
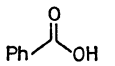
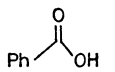
Compound	Molecular formula	Found (%)	Calcd (%)	^{1}H-NMR δ
33	$C_{12}H_{29}O_4PSi$	C: 48.71 H: 9.82	48.62 9.86	(CCl_4) 0.17(9H, s, Me_3Si), 0.91(3H, t, J=7 Hz, CH_3), 1.28(6H, t, J=7 Hz), CH_3), 1.05—1.90(6H, m, (CH_2),) 3.50—3.88(1H, m, CH), 3.70—4·28(4H, m, CH_2-O)
34	$C_{10}H_{25}O_4PSi$	C: 44.70 H: 9.40	44.76 9.39	(CCl_4) 0.15(9H, s, Me_3Si), 1.30(6H, t, CH_3), 1.37(6H, d, J= 14.5 Hz, CH_3CP), 3.79—4.32(4H, m, CH_2-O)
35	$C_{16}H_{29}O_4PSi$	C: 55.96 H: 8.52	55.79 8.49	(CCl_4) 0.16(9H, s, Me_3Si), 1.18(3H, d, J=14 Hz, CH_3CP), 1.18(6H, t, J=7 Hz, CH_3), 2.74(2H, m, CH_2CP), 3.94(4H, m, CH_2-O), 7.01(5H, s, ArH)
36	$C_{11}H_{27}O_4PSi$[22]			(CCl_4) 0.13(9H, s, Me_3Si), 0.91(3H, J=7.2 Hz, CH_3) 1.30(6H, t, J=7 Hz, CH_3), 1.34(3H, d, J=16 Hz, CH_3CP), 1.40—2.00 (2H, m, CH_2CP), 4.08(4H, m, CH_2-O)
37	$C_{17}H_{31}O_4PSi$	C: 56.47 H: 8.87	56.96 8.72	(CCl_4) 0.12(9H, s, Me_3Si), 0.89(3H, t, J=6.5 Hz, CH_3), 1.05 (3H, t, J=7 Hz, CH_3), 1.12(3H, t, J=7 Hz, CH_3), 1.65(2H, m, CH_2C), 2.80(1H, d, J=12 Hz, one of CH_2Ph), 2.82(1H, d, J=10 Hz, one of CH_2Ph), 3.85(4H, m, CH_2-O), 6.99(5H, s, ArH)
38	$C_{16}H_{37}O_4PSi$	C: 54.07 H: 11.02	54.51 10.58	(CCl_4) 0.19(9H, s, Me_3Si), 0.89(3H, t, J=5.8 Hz, terminal CH_3), 1.10—1.95(21H, m, $(CH_2)_6$ and CH_3 and CH_3CP), 4.00 (4H, m, CH_2-O)
39	$C_{22}H_{41}O_4PSi$	C: 61.33 H: 9.73	61.65 9.64	($CDCl_3$) 0.15(9H, s, Me_3Si), 0.60—1.77(21H, m, CH_3C-O and heptyl), 2.82(2H, d, J=10 Hz, CH_2Ph), 3.83(4H, m, CH_2-O), 6.96(5H, s, ArH)
40	$C_{19}H_{43}O_4PSi$	C: 58.13 H: 11.19	57.83 10.98	(CCl_4) 0.18(9H, s, Me_3Si), 0.70—2.05(30H, m, heptyl and butyl and CH_3C-O), 3.77—4.30(4H, m, CH_2-O)
41	$C_{13}H_{19}O_3P$	C: 61.51 H: 7.72	61.41 7.53	(CCl_4) 1.31(6H, t, J=7 Hz, CH_3), 1.98(3H, dd, J=14.5 Hz, J=1.2 Hz, C=CCH_3), 3.78—4.28(4H, m, CH_2-O), 7.21(5H, s, ArH), 7.28(1H, dd, J=24 Hz, J=1.2 Hz, CH=C)
42	$C_{16}H_{23}O_3P(\frac{1}{4}H_2O)$	C: 64.44 H: 7.90	64.31 7.93	(CCl_4) 1.30(6H, t, J=7 Hz, CH_3), 1.65(3H, m, C-CCH_3), 3.07 (2H, d, J=19 Hz, C=CCH), 3.98(4H, m, CH_2-O), 5.41(2H, m, CH=CH), 7.21(5H, s, ArH), 7.32(1H, d, J=25 Hz, CH=CP)
43	$C_{12}H_{17}O_3P$[27]			(CCl_4) 1.29(6H, t, J=7Hz, CH_3), 4.01(4H, m, CH_2-O), 6.10 (1H, dd, J=17 Hz, J=17 Hz, C=CHP), 7.33(1H, dd, J=22 Hz, J=17 Hz, PhCH=), 7.30(5H, m, ArH)

raising the temperature from −78 °C to room temperature. Consequently, the alkylated products **3**, **4**, and **31**—**40** were obtained in good yields. When the alkylation was performed at −78 °C, the alkylated product was not obtained and the Wittig rearrangement product was recovered. In the case of the alkylation of **7** having a relatively acidic β-proton, (*E*)-1-alkenylphosphonates were obtained as the main products (**41**—**43**). These conditions and results are summarized in Table 3. The conversion of the α-alkylated products into carbonyl compounds is illustrated in the following scheme. Acid treatment of



the alkylated products gave quantitatively α-hydroxy phosphonates, which in turn were treated with dilute sodium hydroxide solution to give the carbonyl compounds. The alkylated α-silyloxy phosphonates were converted also directly to ketones by the alkaline treatment as reported in a previous communication.[4a] These results are summarized in Table 5. In the case of the preparation of β,γ-unsaturated ketones, Method A was found to be essential. When Method B was employed, considerable amounts of isomers of α,β-unsaturated ketones were formed. However, the conversion of **31** into aldehyde under the conditions of Method A or Method B led to the aldol condensation product as the main product. It is generally recognized that adducts of aldehydes with nucleophiles, such as alcohols, sodium sulfite, and hydrogen cyanide, are more stable than those of ketones under neutral or alkaline conditions.[16] The aldol condensation product seems to be formed predominantly owing to the relatively slow cleavage of P–C bond in the α-hydroxy phosphonates initially formed by alkali. In fact, when **31** was treated with 0.5 M NaOH–EtOH (1:1, v/v)

Table 5. Conversion of the α-alkylated α-trimethylsilyloxy phosphonates to carbonyl compounds

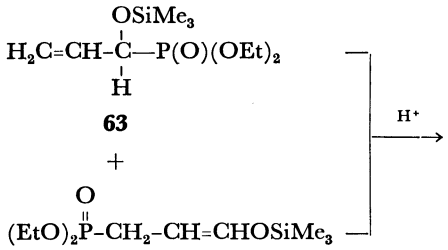
Phosphonate	Method	(time)	Product		Yield/%
18	A	{H+: 30 min, OH−: 20 min}		**44**	90
	B	20 min			86
19	A	{H+: 90 min, OH−: 5 min}		**45**	90
20	A	{H+: 3.5 h, OH−: 10 min}		**46**	81
	B	20 min			88
21	A	{H+: 40 min, OH−: 60 min}		**47**	94
20	B	2.5 h		**48**	83
23	B	30 min		**49**	95
24	A	{H+: 90 min, OH−: 10 min}		**50**	93
	B	30 min			94
25	A	{H+: 4 h, OH−: a)}		**1**	36
26	A	{H+: 5 h, OH−: 30 s}		**52**	96
27	A	{H+: 60 min, OH−: 30 s}		**53**	80
35	B	30 min		**54**	82
37	A	{H+: 30 min, OH−: 4 min}		**55**	75
38	B	30 min		**56**	85
28	B	15 min		**57**	69
29	B	30 min		**58**	90
30	B	45 min		**59**	91

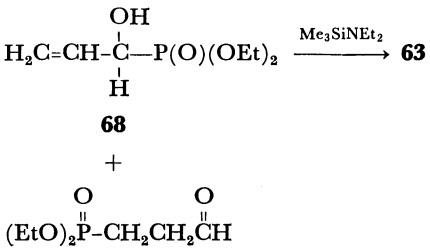
a) See Experimental.

and the reaction was quenched quickly after 1 min, diethyl 1-hydroxy-3-phenylpropylphosphonate (**60**) was isolated in quantitative yield. When **60** was further treated with the same alkali, the aldol condensation product was obtained as the main product. Therefore, our efforts were focussed on the P–C bond cleavage of **31** under milder conditions where the aldol condensation could be avoided. Thus, various conditions were tested in order to obtain aldehydes selectively. Finally, it was found that 3-phenylpropionaldehyde (**61**) could be obtained from **60** in 71% yield by employing the conditions of dilute sodium hydrogencarbonate in aqueous methanol under reflux for 2 h. In a similar manner, octanal (**62**) was obtained in 80% yield from **5**.

Synthesis of β-Alkylated Esters and Lactones. In order to extend the utility of 1:1 carbonyl adducts of DTMSP, we examined alkylation of 1,2-addition products obtained from DTMSP and α,β-unsaturated aldehydes.

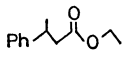
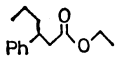
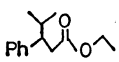
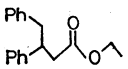
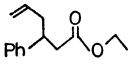
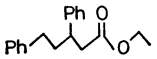
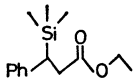
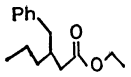
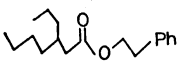
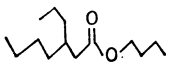
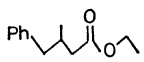
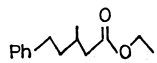
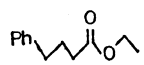
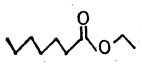
The reaction of DTMSP with α,β-unsaturated aldehydes provided predominantly 1,2-carbonyl addition compounds (**64**—**66**).[4a] In the case of acrylaldehyde, 1,4-addition product (**67**), however, was formed along with the 1,2-carbonyl adduct (**63**). These products could not be separated by distillation or column chromatography. In order to separate **63** from the mixture, it was first treated with acid for removal of the trimethylsilyl group and the resulting α-hydroxy phosphonate (**68**) was obtained by column chromatography. This material was further trimethylsilylated by treatment with *N*,*N*-diethyltrimethylsilylamine to afford **63**.





It was found that the alkylation of these 1,2-addition products occurred at the γ-position to give (*E*)-1-(trimethylsilyloxy)-1-alkenylphosphonates (**69**), while deuteration of the lithio derivatives gave α-deuterated 1-trimethylsilyloxy phosphonates exclusively. These results are of interest since Hünig[10e] reported that the 1,2-adducts of trimethylsilyl cyanide with unsaturated aldehydes were transformed to α-alkylated products exclusively on treatment with LDA followed by alkyl halides. Stork[11] also described that a similar alkylation of protected cyanohydrins of α,β-unsaturated aldehydes resulted in the exclusive for-

Table 6. Preparation of β-substituted esters (**71**—**84**)

Phosphonate	Conditions for alkylation R′X(eqiuv.)[a]	Conditions for esterification R″OH	Product	Compd No.	Yield/%
66	MeI (1.15) −78 °C, 1 h	EtOH 78 °C, 1 h		**71**	63
	MeI (5.5) −78 °C→r.t. 3 h	EtOH 78 °C, 1 h			76
	n-PrI (1.15) −78 °C, 30 min	EtOH 78 °C, 2 h		**72**	76
	i-PrI (1.1) −78 °C→r.t. 3 h	EtOH 78 °C, 2.5 h		**73**	84
	$PhCH_2Br$ (1.15) −78 °C, 30 min	EtOH 78 °C, 2.5 h		**74**	89
	allyl-Br (1.1) −78 °C→r.t. 40 min	EtOH 78 °C, 2.5 h		**75**	81
	$PhCH_2CH_2Br$ (1.1) −78 °C→r.t. 4.5 h	EtOH 78 °C, 2.5 h		**76**	69
	Me_3SiCl (1.15) −78 °C→r.t. 5 h	EtOH 78 °C, 2 h		**77**	49
	Me_3SiBr (1.1) −78 °C→r.t. 2 h	EtOH 78 °C, 4 h			52
65	$PhCH_2Br$ (1.2) −78 °C, 40 min	EtOH 78 °C, 2.5 h		**78**	51
	n-BuI (1.15) −78 °C, 30 min	$PhCH_2CH_2OH$(5 ml) 80 °C, 3 h		**79**	45
	n-BuI (1.1) −78 °C, 30 min	*n*-BuOH 80 °C, 3 h		**80**	52
64	$PhCH_2Br$ (1.1) −78 °C, 1 h	EtOH 78 °C, 6 h		**81**	75
	$PhCH_2CH_2Br$ (1.05) −78 °C, 1 h	EtOH 78 °C, 6 h		**82**	44
63	$PhCH_2Br$ (1.1) −78 °C, 1 h	EtOH 78 °C, 6 h		**83**	11
	n-BuI (1.2) −78 °C, 1 h	EtOH 78 °C, 6 h		**84**	5

a) The amount of LDA employed was almost the same as that of alkyl halide in each experiment.

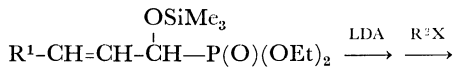
TABLE 7. ELEMENTAL ANALYSES AND ^{1}H-NMR DATA OF β-SUBSTITUTED ESTERS (**71**—**84**)

Compound	Molecular formula	Found (%)	Calcd (%)	^{1}H-NMR(CCl_4) δ
71	$C_{12}H_{16}O_2$[28]			1.10(3H, t, J=7 Hz, CH_3), 1.27(3H, d, J=8 Hz, CH_3CPh), 2.45 (2H, d, J=8 Hz, CH_2(C=O)), 2.91—3.53(1H, m, CH), 3.97(2H, q, J=7 Hz, CH_2-O), 7.12(5H, s, ArH)
72	$C_{14}H_{20}O_2$	C: 76.75 H: 9.21	76.33 9.15	0.87(3H, t, CH_3), 1.10(3H, t, J=7 Hz, CH_3), 1.00—1.85(4H, m, CH_2CH_2), 2.50(2H, d, J=7.5 Hz, CH_2(C=O)), 2.82—3.35(1H, m, CH), 3.95(2H, q, CH_2-O), 7.10(5H, s, ArH)
73	$C_{14}H_{20}O_2$	C: 76.18 H: 9.09	76.33 9.15	0.73 and 0.93(3H and 3H, dd, J=6.5 Hz, $(CH_3)_2C$), 1.00(3H, t, J=7 Hz, CH_3), 1.40—2.20(1H, m, CH), 2.33—3.04(3H, m, CH-CH_2(C=O)), 3.87(2H, q, J=7 Hz, CH_2-O), 7.10(5H, s, ArH)
74	$C_{18}H_{20}O_2$	C: 80.52 H: 7.60	80.56 7.51	1.00(3H, t, J=7 Hz, CH_3), 2.50(2H, d, J=6.5 Hz, CH_2(C=O)), 2.83(2H, d, J=7.5 Hz, CH_2Ph), 3.10—3.60(1H, m, CH), 3.88 (2H, q, CH_2-O), 7.00(5H, s, ArH), 7.05(5H, s, ArH)
75	$C_{14}H_{18}O_2$	C: 77.19 H: 8.31	77.03 8.31	1.07(3H, *t*, J=7 Hz, CH_3), 2.50(2H, t, J=7 Hz, C=C-CH_2), 2.50 (2H, d, J=6 Hz, CH_2(C=O)), 2.80—3.40(1H, m, CH), 3.93(2H, q, J=7 Hz, CH_2-O), 4.70—5.10(2H, m, CH_2=C)
76	$C_{19}H_{22}O_2$[29]			1.04(3H, t, J=7 Hz, CH_3), 1.65—2.10(2H, m, $PhCCH_2$), 2.23—2.58(4H, m, $PhCH_2$ and CH_2(C=O)), 2.80—3.40(1H, m, CH), 3.90(2H, q, J=7 Hz, CH_2-O), 7.03(5H, s, ArH), 7.13(5H, s, ArH)
77	$C_{14}H_{22}O_2Si$[30]			0.09(9H, s, Me_3Si), 1.16(3H, t, J=7 Hz, CH_3), 2.76(2H, s, CH_2-(C=O)), 2.79(1H, b, CH), 4.25(2H, q, J=7 Hz, CH_2-O), 7.09 (5H, m, ArH)
78	$C_{15}H_{22}O_2$	C: 76.58 H: 9.43	76.88 9.46	0.87(3H, t, J=5.5 Hz, CH_3), 1.21(3H, t, J=7 Hz, CH_3C-O), 1.30(4H, b, CH_2CH_2), 2.20(2H, s, CH_2(C=O)), 2.21(1H, m, CH), 2.57(2H, m, $PhCH_2$), 4.03(2H, q, J=7 Hz, CH_2-O), 7.11(5H, s, ArH)[a]
79	$C_{18}H_{28}O_2$	C: 78.50 H: 10.07	78.21 10.21	0.88(6H, m, CH_3), 1.25(10H, m, $(CH_2)_3$ and CH_2CH_2), 1.50—1.10(1H, m, CH), 2.12(2H, d, J=5 Hz, CH_2(C=O)), 2.85(2H, t, CH_2Ph), 4.20(2H, t, CH_2-O), 7.15(5H, s, ArH)
80	$C_{14}H_{28}O_2$	C: 73.09 H: 12.14	73.62 12.36	2.15(1H, d, J=5 Hz, one of CH_2(C=O)), 2.17(1H, d, J=7 Hz, one of CH_2Ph), 4.03(2H, t, J=6 Hz, CH_2-O)
81	$C_{13}H_{18}O_2$[31]			0.80—1.00(3H, m, CH_3), 1.28(3H, *t*, J=7 Hz, CH_3), 1.87—2.90 (5H, m, $PhCH_2$ and CH_2(C=O) and CH), 4.03(2H, q, J=7 Hz, CH_2-O), 7.10(5H, s, ArH)
82	$C_{14}H_{20}O_2$[32]			0.97(3H, d, J=6 Hz, CH_3), 1.18(3H, t, J=7 Hz, CH_3), 1.36—1.83(2H, m, $PhCCH_2$), 1.83—2.28(3H, m, CH_2(C=O) and CH), 2.56(2H, t, J=7.5 Hz, $PhCH_2$)
83	$C_{12}H_{16}O_2$[33]			1.25(3H, t, J=7 Hz, CH_3), 1.70—2.43(4H, m, CH_2CH_2(C=O)), 2.65(2H, m, $PhCH_2$, J=7 Hz), 4.07(2H, q, CH_2-O), 7.15(5H, s, ArH)
84	$C_9H_{18}O_2$[34]			0.53—1.43(14H, m, pentyl and CH_3), 2.20(2H, dd, J=9.4 Hz, J=8 Hz, CH_2(CO)), 4.06(2H, q, CH_2-O)

a) In this case, $CDCl_3$ was used as the solvent.

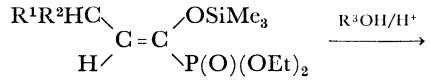
mation of α-alkylated products. Our results are in contrast to their two reports. The results of the highly regioselective γ-alkylation in the present reaction might be due to steric hindrance of the neighboring phosphoryl group. The (*E*)-1-(trimethylsilyloxy)-1-alkenylphosphonate **69** were sensitive toward moisture during work-up and tend to decompose gradually into acylphosphonates (**70**). Acylphosphonates are known to be labile toward moisture and decompose into carboxylic acids and dialkyl phosphonates.[17] It has been reported that reactions of acylphosphonates with nucleophiles such as alcohols,[18] amines,[18c,19] and carbanions[20] gave acylated products. Because of the instability of the alkylated products, the reaction mixture was further treated with alcohols in the presence of *p*-toluenesulfonic acid, whereupon the alkylated products were successfully converted *via* acylphosphonates to β-alkyl-substituted esters (**71**—**84**). These results

were summarized in Table 6.

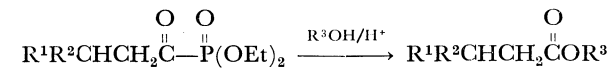


63—66

63: $R^1=H$ **65**: $R^1=n$-Pr
64: $R^1=Me$ **66**: $R^1=Ph$

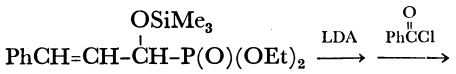


69a: $R^1=Ph$, $R^2=Me$
69b: $R^1=Ph$, $R^2=CH_2Ph$
69c: $R^1=n$-Pr, $R^2=CH_2Ph$

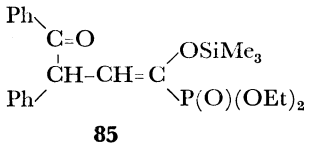


70 **71—84**

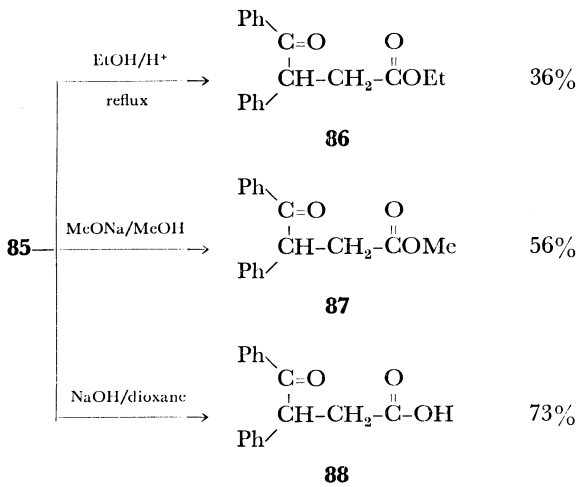
In a similar manner, benzoylation of the lithio derivative of **66** followed by treatment with alcohols under alkaline or acidic conditions or with aqueous sodium hydroxide solution gave the products depicted in the following scheme.



66

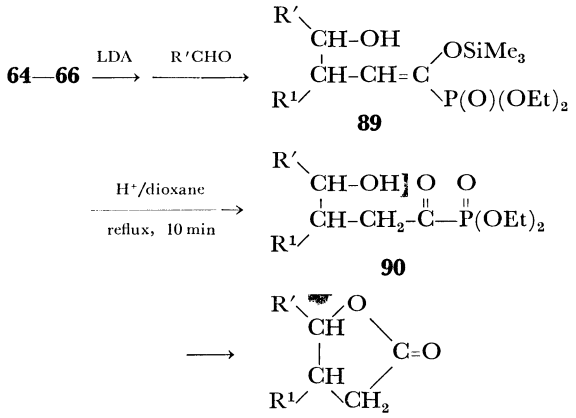


85



86 **87** **88**

Next, we examined the lactonization in term of intramolecular acylation utilizing the promising feature of acylphosphonate intermediates as acylating species. By treatment of the lithiated derivatives of **64—66** with aldehydes, 4-hydroxy-1-trimethylsilyloxy-1-alkenylphosphonates (**89**) could be expected to be formed. These phosphonates were also expected to be converted by acid treatment into 4-hydroxy-1-oxoalkylphosphonates (**90**), which would be cyclized under such acidic conditions to give lactones. Thus, several lactones (**91—95**) were obtained by one-pot reaction in good yields. These results are summarized in Table 8. Evans has recently reported a similar type of lactonization utilizing 1:1 carbonyl addition products of triethylsilyl *N,N,N',N'*-tetramethylphosphorodiamidite with α,β-unsaturated aldehydes in which tetrabutylammonium fluoride was used for the removal of the trimethylsilyl group and for the cyclization.[21]



89 **90** **91—95**

In conclusion, it is noted that 1:1 carbonyl adducts of aldehydes with DTMSP could be used widely as the precursors of acyl anion equivalents and homoenolates.

Experimental

NMR spectra were measured at 60 MHz on a Hitachi R 24-B spectrometer. IR spectra were recorded on a Hitachi Model EPI-G3 spectrophotometer.

Materials. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled over potassium hydroxide after reflux for 6 h, redistilled over sodium wire after reflux for 6 h, and finally purified by distillation from benzophenone ketyl. Alkyl halides, acyl halides, carbonyl compounds, and other reagents were purified by distillation or recrystallization before use. Diethyl trimethylsilyl phosphite (DTMSP) was prepared according to the method previously reported.[1] Butyllithium (2—3 M) in hexane, kindly gifted from Sankyo Kasei Co., was used after titration.

All lithiation, alkylation, and acylation reactions were carried out under argon atmosphere.

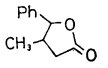
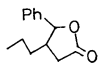
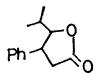
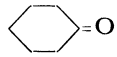
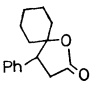
Diethyl α-(Trimethylsilyloxy)benzylphosphonate (1).
Method A: To a solution of DTMSP (6.18 g, 29.4 mmol) in dry benzene (5 ml) was added dropwise benzaldehyde (3.21 g, 30.2 mmol) with continuous stirring. The mixture was stirred at room temperature for 6 h. After removal of the benzene *in vacuo*, distillation gave **1** (8.49 g, 91%): Bp 118—123 °C/0.08 mmHg† (lit,[22] 124—125 °C/1.0—1.5 mmHg); NMR($CDCl_3$) δ 0.25(9H, s, Me_3Si), 1.37(6H, t, J=7 Hz, CH_3), 4.18(4H, m, CH_2), 5.15(1H, d, J=14 Hz, CHP), 7.50(5H, m, ArH). Found: C, 53.38; H, 8.07%. Calcd for $C_{14}H_{25}O_4PSi$: C, 53.14; H, 7.96%.

Method B: Diethyl phosphonate (6.61 g, 47.9 mmol) was added dropwise to sodium (1.18 g, 51.3 mmol) in dry ether (50 ml). Exothermic reaction took place with evolution of hydrogen gas and a white precipitate was formed gradually. After 3 h benzaldehyde (4.82 g, 45.4 mmol) was added. The precipitate was dissolved at once and the solution turned bright brown. Then, chlorotrimethylsilane (5.11 g, 47.0 mmol) was added, and a precipitate appeared. After removal of the ether, distillation without separation of the precipitate gave **1** (9.64 g, 67%).

Diethyl Trimethylsilyloxymethylphosphonate (2). Diethyl

† 1 mmHg≈133.322 Pa.

Table 8. Preparation of lactones (**91**—**95**) from **64**—**66**

Adduct	Aldehyde or ketone[a)]	Time/min	Product	Compd No.	Yield/% (*trans*/*cis*)[b)]
64	PhCHO	40		**91**	51 (75/25)
65	PhCHO	60		**92**	54 (75/25)
66	PhCHO	40		**93**	78 (85/15) (59%, TBAF)
66	*i*-C_3H_7CHO	40		**94**	80 (60/40)
66		40		**95**	33

a) In these reactions 1.2 equiv. of aldehyde or ketone was employed. b) The ratio of *trans*/*cis* was calculated on the base of the NMR spectra of **91**—**94** (see Table 9).

Table 9. ^1H NMR data of lactones (**91**—**95**)

Compound	^1H NMR($CDCl_3$) δ
91	0.60(3H, d, J=7 Hz, *trans* CH_3), 1.03(3H, m *cis* CH_3), 1.90—2.97(3H, m, CH_2 and CHC-O), 4.80(1H, d, J=8 Hz, *cis* CH-O), 5.46(1H, d, *trans* CH-O), 7.20(5H, m, Ph)
92	1.43—0.53(7H, m, $CH_3(CH_2)_2$), 2.50(3H, m, CH_2 and CH-O), 4.93(d, J=7 Hz, *cis* CH-O), 5.53 (1H, d, J=7 Hz, *trans* CH-O), 7.23(5H, m, Ph).
93	2.90(2H, m, CH_2), 3.50(1H, m, CHC-O), 5.35(1H, d, J=8 Hz, *trans* CH-O), 5.73(1H, d, J= 7 Hz, *cis* CH-O), 7.17(10H, s, Ph)
94	0.93(6H, m, CH_3), 1.87(1H, m, $CH(CH_2)_2$), 2.70(2H, d, J=7 Hz, *cis* CH_2), 2.85(2H, d, J=7 Hz, *trans* CH_2), 3.43(1H, m, CHC-O), 4.27(1H, d, J=7 Hz, *trans* CH-O), 4.37(1H, d, J=7 Hz, *cis* CH-O), 7.27(5H, s, Ph)
95	0.50—2.33(10H, m, $(CH_2)_5$), 2.89(2H, m, $CH_2C(O)$), 3.43(1H, m, CH), 7.13(5H, s, Ph)

phosphonate (6.02 g, 43.6 mmol) was added to sodium (1.2 g, 52.2 mmol) in dry ether (20 ml). After stirring for 2 h, paraformaldehyde (1.50 g, 50.0 mmol) in dry ether (10 ml) was added. A white precipitate appeared at once but it was dissolved on addition of chlorotrimethylsilane (5.85 g, 53.8 mmol). The mixture was stirred at room temperature for 6 h. After removal of the solvent distillation gave **2** (7.20 g, 69%): Bp 72—75 °C/0.6 mmHg (lit,[23] 113 °C/9 mmHg); NMR ($CDCl_3$) δ 0.13(9H, s, Me_3Si), 1.30(6H, t, J=7 Hz, CH_3), 3.75(2H, d, J=9 Hz, CH_2P), 3.80—4.32(4H, m, CH_2O). Found: C, 40.04; H, 8.66%. Calcd for $C_8H_{21}O_4PSi$: C, 39.98; H, 8.81%.

*Diethyl 1-(Trimethylsilyloxy)ethylphosphonate (**3**).* To a solution of DTMSP (11.0 g, 52.3 mmol) in dry benzene (20 ml) was introduced acetaldehyde (90 mmol) which was generated from paraaldehyde by heating with a catalytic amount of *p*-toluenesulfonic acid (TsOH). After standing for 4 h, the solvent was removed *in vacuo* and distillation afforded **3** (11.7 g, 88%): Bp 62—63 °C/0.4 mmHg (lit,[22] 82 °C/1 mmHg); NMR(CCl_4) δ 0.15(9H, s, Me_3Si), 1.29 (6H, t, J=7 Hz, CH_3C-O), 1.33(3H, dd, J=7 Hz, J=16.5 Hz, CH_3CP), 3.78—4.22(5H, m, CH_2O and CHP).

*Diethyl 1-(Trimethylsilyloxy)propylphosphonate (**4**).* To a solution of DTMSP (5.66 g, 26.9 mmol) in dry benzene (10 ml) was added dropwise propionaldehyde (1.74 g, 30.0 mmol) at room temperature. After being stirred for 6 h, the solution was concentrated *in vacuo* and the residual oil was distilled to give **4** (5.30 g, 72%): Bp 80—82 °C/1 mmHg; IR(NaCl) 968, 1030, 1060, 1117, 1170, 1230, 1255 (νP=O), 1394, 1448, 1460, 2970 cm^{-1}; NMR(CCl_4) δ 0.15 (9H, s, Me_3Si), 0.99 (3H, t, J=7 Hz, CH_3CC), 1.34(6H, t, J=7 Hz, CH_3C-O), 1.10—1.85(2H, m, CCH_2C), 3.51—3.80(1H, m, CHP), 3.80—4.35(4H, m, CH_2O). Found: C, 44.44; H, 9.81%. Calcd for $C_{10}H_{25}O_4PSi$: C, 44.76; H, 9.39%.

*Diethyl 1-Trimethylsilyloxy-2-methylpropylphosphonate (**5**).* To a solution of DTMSP (7.58 g, 36.0 mmol) in dry benzene (15 ml) was added isobutyraldehyde (2.80 g, 38.8 mmol) dropwise at room temperature. The mixture was stirred for 6 h. The usual work-up as described before gave **5** (8.65 g, 83%): Bp 69—72 °C/0.35 mmHg; NMR(CCl_4) δ 0.14 (9H, s, Me_3Si), 0.97(6H, d, J=7.3 Hz, $(CH_3)_2C$), 1.31

(6H, t, J=7 Hz, CH_3C–O), 1.62—2.40(1H, m, CHCP), 3.59(1H, dd, J=7.5 Hz, J=4.5 Hz, CHP), 3.78—4.31(4H, m, CH_2O). Found: C, 46.75; H, 9.64%. Calcd for $C_{11}H_{27}O_4PSi$: C, 46.78; H, 9.64%.

*Diethyl 1-(Trimethylsilyloxy)octylphosphonate (**6**).* To a solution of DTMSP (18.3 g, 87.1 mmol) in dry benzene (10 ml) was added dropwise octanal (9.67 g, 75.4 mmol) at room temperature. After stirring for 3 h, the solvent was removed and distillation of the residual oil gave **6** (23.1 g, 91%): Bp 104—105 °C/0.04 mmHg: NMR(CCl_4) δ 0.15 (9H, s, Me_3Si), 0.92(3H, t, J=4.5 Hz, terminal CH_3), 1.32(6H, t, J=7 Hz, CH_3C–O), 1.31(12H, m, $(CH_2)_6$), 3.73(1H, m, CHP), 3.75—4.35(4H, m, CH_2O). Found: C, 52.85; H, 10.55%. Calcd for $C_{15}H_{35}O_4PSi$: C, 53.22; H, 10.42%.

*General Procedure for the Synthesis of Diethyl 1-Hydroxy-1-(trimethylsilyl)alkylphosphonates (**8—10**). The Wittig Rearrangement of Diethyl 1-(Trimethylsilyloxy)alkylphosphonates (**2—4**).* To a cold solution (−78 °C) of diisopropylamine (0.5 ml, 3.58 mmol) in dry THF (10 ml) or DME (10 ml) was added butyllithium (3.58 mmol) in hexane. After 0.5 h, an appropriate 1-trimethylsilyloxyphosphonate (**2—5**) was added. The mixture was stirred at −78 °C for the time given in Table 1, and then or after warming to room temperature the resulting solution was poured into a vigorously stirred mixture of 1 M NH_4Cl (20 ml) and CH_2Cl_2 (20 ml). The CH_2Cl_2 layer was collected and the aqueous layer was further extracted with CH_2Cl_2 (3×10 ml). The organic extracts were combined, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on silica gel (hexane–ether) to give a 1-hydroxy-1-(trimethylsilyl)alkylphosphonate (**8**, **9**, or **10**) and the starting phosphonate. The physical properties of the new compounds **8—10** are listed in Table 2.

*Trimethylsilyl Diphenylphosphinite (**16**).*[15] A mixture of diphenylphosphine oxide (10.5 g, 52 mmol) and *N,N*-diethyltrimethylsilylamine (9.08 g, 62.5 mmol) was stirred at room temperature for 4 h under slightly reduced pressure. Distillation gave **16** (12.8 g, 89%): Bp 110 °C/0.8 mmHg. This compound was identified with an authentic sample reported by Issleib by comparison with its physical data.[15]

*[1-(Trimethylsilyloxy)propyl]diphenylphosphine Oxide (**17**).* To a solution of propionaldehyde (1.17 g, 20.2 mmol) in dry benzene (10 ml) was added **16** (5.41 g, 19.7 mmol). The exothermic reaction took place. After the mixture was stirred at room temperature for 3 h, the solvent was removed *in vacuo*. The residue was chromatographed on silica gel (hexane–ether) to give **17** (2.5 g, 38%) as a crude material and (1-hydroxypropyl)diphenylphosphine oxide (1.98 g, 39%). While the former was too sensitive toward moisture to be purified, the latter was well characterized by its NMR spectrum and elemental analysis: NMR($CDCl_3$) δ 0.99(3H, t, J=7 Hz, CH_3), 1.65(2H, m, CH_2), 4.21(1H, m, CHP), 5.14(1H, s, OH), 7.32(6H, s, ArH), 7.70(4H, m, ArH). Found: C, 68.90; H, 6.80%. Calcd for $C_{15}H_{17}O_2P$: C, 69.22; H, 6.59%.

*General Procedure for Alkylation of α-Lithiated 1-(Trimethylsilyloxy)alkylphosphonates (**1—7**).* To a cooled solution (−78 °C) of diisopropylamine in dry THF was added an equimolar amount of butyllithium in hexane. After 0.5 h an appropriate phosphonate was added. The lithiation time was listed in Table 3. Then an alkyl halide or a disulfide was added to the mixture. The reaction time was also shown in Table 3. The mixture was poured into a vigorously stirred mixture of 1 M NH_4Cl and CH_2Cl_2. The organic layer was collected and the aqueous layer was further extracted with CH_2Cl_2 three times. The organic extracts were combined, dried over Na_2SO_4, evaporated *in vacuo* to dryness, and chromatographed on silica gel (hexane–ether) to give an α-alkylated phosphonate as listed in Table 3. The amounts of the reagents used are listed in Table 3. All new compounds were characterized by their NMR spectra and elemental analyses. The previously known compounds were identified by comparison with their NMR spectra. These data are listed in Table 4.

General Procedure for Transformation of 1-(Trimethylsilyloxy)-alkylphosphonates into Carbonyl Compounds. Method A: An appropriate alkylated phosphonate (2 mmol) was dissolved in a mixture of methanol (10 ml) and water (1 ml) and then a catalytic amount (30 mg) of *p*-toluenesulfonic acid was added. The mixture was refluxed for the time given in Table 5. The mixture was first treated with a mixture of CH_2Cl_2 (25 ml) and water (25 ml). The organic layer was collected and the aqueous layer was further extracted with CH_2Cl_2 (3×10 ml). The organic extracts were combined, dried over Na_2SO_4, and evaporated *in vacuo* to afford a crude 1-hydroxyalkylphosphonate derivative. It was further treated with a mixture of EtOH (30 ml) and 1 M NaOH (30 ml). After the time given in Table 5, the mixture was extracted with CH_2Cl_2 (3×10 ml). The extracts were combined, dried over Na_2SO_4, evaporated *in uacuo*, and chromatographed on silica gel to give a pure carbonyl compound.

In the following cases, special conditions were employed: 1) Diethyl 1-trimethylsilyloxy-1-phenylbutylphosphonate (**20**) was treated with 2 M HCl (2.5 ml) in MeOH instead of TsOH and the reaction was carried out at room temperature. 2) Allyl phenyl ketone was obtained by treatment of the detrimethylsilylated intermediate with a large excess amount of Na_2CO_3 (1 g) in a mixture of CH_2Cl_2 (20 ml) and EtOH (10 ml) at room temperature for 3 d or by treatment with a catalytic amount of tetrabutylammonium hydroxide for 1 min in a heterogeneous mixture of ether (20 ml) and 1 M NaOH (20 ml). According to the former treatment allyl phenyl ketone was obtained in 36% yield along with (*E*)-1-phenyl-2-buten-1-one (10%) and the latter gave the ketone in 36% yield.

Diethyl 1-Hydroxy-1-phenyl-3-butenylphosphonate(Purified Intermediate). Mp 71—73 °C; NMR($CDCl_3$) δ 1.15 and 1.19 (3H and 3H, t and t, J=7 Hz, CH_3C–O), 2.96(2H, dd, J=J=7 Hz, C=CCH_2), 3.63—4.30(4H, m, CH_2O), 4.53 (1H, s, OH), 4.80—5.17(2H, m, CH_2=C), 5.26—5.90(1H, m, C=CH), 7.13(3H, m, ArH), 7.45(2H, m, ArH). Found: C, 59.34; H, 7.33%. Calcd for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.45%.

Method B: To a solution of an alkylated phosphonate (2—3 mmol) in ethanol (30 ml) was added 1 M NaOH (30 ml). The solution was stirred for the period as shown in Table 5. The mixture was poured into a mixture of CH_2Cl_2 (20 ml) and 1 M NH_4Cl (20 ml). The organic layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (3×50 ml). The CH_2Cl_2 extracts were combined, dried over Na_2SO_4, concentrated, and chromatographed on silica gel (hexane–ether) to give a carbonyl compound.

*Diethyl 1-Trimethylsilyloxy-2-propenylphosphonate (**63**).* To a solution of acrylaldehyde(1.17 g, 20.8 mmol) in dry benzene (5 ml) was added DTMSP (4.46 g, 21.2 mmol) with stirring on an ice bath. After stirring at room temperature for 6 h the solvent was removed, and distillation gave a mixture (4.90 g, Bp 105 °C/1.25 mmHg) of **63** and **67**. The mixture (32 g) was treated with TsOH·H_2O (1 g) in MeOH (500 ml) and H_2O (20 ml) under reflux for 3 h. After extraction with CH_2Cl_2 (4×100 ml) and drying

over Na_2SO_4, and removal of the solvent, the residue was chromatographed on silica gel (hexane–ether) to give a detrimethylsilylated phosphonate of **63** (14.3 g, 38%). The α-hydroxy phosphonate (14 g) was further treated with *N,N*-diethyltrimethylsilylamine (16.5 ml) at 50 °C under slightly reduced pressure for 3 h. Then, the mixture was evaporated *in vacuo* and chromatographed on silica gel (hexane–ether) to give **63**: NMR(CCl_4) δ 0.15(9H, s, Me_3Si), 1.29(6H, t, J=7 Hz, CH_3C–O), 4.05(4H, m, CH_2O), 4.33(1H, m, CHP), 4.98—5.50(2H, m, CH_2=C), 5.69—6.27(1H, m, C=CH). This product was used further for alkylation without purification.

*Diethyl 1-Trimethylsilyloxy-2-butenylphosphonate (**64**).* To a solution of *trans*-2-butenal (1.54 g, 21.9 mmol) in dry benzene (5 ml) was added DTMSP (4.71 g, 22.4 mmol). The reaction mixture was stirred at room temperature for 6 h. After removal of the benzene *in vacuo*, distillation gave **64** (4.45 g, 72%): Bp 110—113 °C/1.8 mmHg; NMR($CDCl_3$) δ 0.15(9H, s, Me_3Si), 1.30(6H, t, J=7 Hz, CH_3C–O), 1.57—1.81(3H, m, CH_3C=C), 3.80—4.53(5H, m, CH_2–O and CHP), 5.62(2H, m, CH=CH). Found: C, 46.87; H, 9.49%. Calcd for $C_{11}H_{25}O_4PSi$: C, 47.12; H, 8.99%.

*Diethyl 1-Trimethylsilyloxy-2-hexenylphosphonate (**65**).* To a solution of *trans*-hexenal (9.95 g, 101 mmol) in dry benzene (10 ml) was added DTMSP (19.52 g, 92.8 mmol) with stirring on an ice bath. Then the mixture was stirred at room temperature for 8 h. After removal of the solvent *in vacuo*, distillation gave **65** (21.6 g, 73%): Bp 90—100 °C/0.15—0.20 mmHg; NMR(CCl_4) δ 0.20(9H, s, Me_3Si), 0.95(3H, t, terminal CH_3), 1.33(6H, t, J=7 Hz, O–C–CH_3), 1.40(2H, m, CH_2CC=C), 1.80—2.30(2H, b, CH_2C=C), 3.80—4.33(4H, m, CH_2–O), 4.25—4.50(1H, m, CHP), 5.50—5.77(2H, m, CH=CH). Found: C, 50.48; H, 9.95%. Calcd for $C_{13}H_{29}O_4PSi$: C, 50.63; H, 9.48%.

*Diethyl 1-Trimethylsilyloxy-3-phenyl-2-propenylphosphonate (**66**).* To a solution of cinnamaldehyde (3.82 g, 28.9 mmol) in dry benzene (5 ml) was added dropwise DTMSP (6.27 g, 29.8 mmol) with stirring at room temperature. The mixture was further stirred at room temperature for 6 h. After removal of the solvent, distillation of the residual oil gave **66** (6.94 g, 70%): Bp 134—137 °C/0.10 mmHg; NMR(CCl_4) δ 0.19(9H, s, Me_3Si), 1.29(6H, t, J=7 Hz, CH_3C–O), 3.78—4.33(4H, m, CH_2O), 4.50(1H, dd, J=16, J=5.5 Hz, CHP), 5.97—6.80(2H, m, CH=CH), 7.23(5H, m, Ph). Found: C, 55.97; H, 8.18%. Calcd for $C_{16}H_{27}O_4PSi$: C, 56.12; H, 7.95%.

*Lithiation and Deuteration of **63**.* To a cooled (−78 °C) solution of LDA(3.58 mmol) in dry THF (10 ml) was added 805 mg (3.02 mmol) of **66**, whereupon the solution turned orange yellow. After 0.5 h, CD_3OD (0.2 ml) was added and the solution was treated with 1 M ammonium chloride (20 ml). The mixture was extracted with CH_2Cl_2 (4× 20 ml). The organic extracts were combined, concentrated to dryness, and chromatographed on silica gel (hexane–ether) to give deuterated diethyl 1-hydroxy-2-propenylphosphonate (169 mg, 29%) and deuterated **63** (68 mg, 8%).

*Lithiation and Deuteration of **64**.* Deuterated diethyl 1-hydroxy-2-butenylphosphonate (557 mg, 78%) and deuterated **64** (110 mg, 12%) were obtained from **64** (952 mg, 3.40 mmol), LDA (3.58 mmol) in dry THF (10 ml), and CH_3OD (0.5 ml).

*Lithiation and Deuteration of **65**.* The deuterated **65** (587 mg, 84%) was similarly obtained from **65** (905 mg, 2.94 mmol), LDA (3.58 mmol) in dry THF (10 ml), and CH_3OD (0.5 ml).

*Lithiation and Deuteration of **66**.* Deuterated 1-hydroxy-3-phenyl-2-propenylphosphonate (169 mg, 29%) and deuterated **66** (68 mg, 8%) were similarly obtained from **66** (970 mg, 2.83 mmol), LDA (3.19 mmol) in dry THF (10 ml), and CD_3OD (0.2 ml).

*Preparation of **85**.* To a solution of 4 mmol of LDA in THF (15 ml) at −78°C was added **66** (1.23 g, 3.6 mmol) and the solution was stirred for 30 min. Benzoyl chloride (607 mg, 4.32 mmol) was added and the mixture was warmed gradually to room temperature. After being stirred at room temperature for 30 min, the solution was poured into a stirred heterogeneous mixture of 1 M NH_4Cl (10 ml) and CH_2Cl_2 (10 ml). The CH_2Cl_2 layer was collected and the aqueous solution was further extracted with CH_2Cl_2 (3× 10 ml). The organic extracts were combined, dried over Na_2SO_4, and evaporated to give the crude **85**, which was used without purification for further transformations into **86**—**88**.

*Esterification of **85**. Under Acidic Conditions*: The crude **85** was dissolved in dry ethanol (20 ml) and TsOH·H_2O (5 mg) was added. After being refluxed for 2 h, the mixture was poured into a stirred mixture of 1 M NaOH (20 ml) and CH_2Cl_2 (20 ml). The organic layer was collected, combined with further CH_2Cl_2 extracts (3×10 ml), dried over Na_2SO_4, evaporated, and chromatographed on silica gel (hexane–ether) to give **86** (362 mg, 36%): NMR($CDCl_3$) δ 7.90 and 7.17(10H, m, ArH), 5.07(1H, dd, J=9 Hz, J=6 Hz, CHPh), 4.00(2H, m, CH_2O), 3.36(1H, dd, J=16 Hz, J=9 Hz, $CH^aC(=O)O$), 2.63(1H, dd, J=16 Hz, J=6 Hz, $CH^bC(=O)O$), 1.10(3H, t, CH_3).

Under Alkaline Conditions. The crude **85** was prepared from **66** (1.86 g, 5.38 mmol) and was treated with sodium methoxide prepared from sodium (143 mg, 6.2 mmol) in dry methanol (20 ml). The solution turned reddish brown. After being stirred for 30 min, the mixture was poured into a mixture of 1 M NH_4Cl (20 ml) and CH_2Cl_2 (20 ml). The usual work-up gave **87** (813 mg, 56%).

*Synthesis of **88**.* The crude **85** was prepared from **66** (1.48 g, 4.32 mmol), dissolved in dioxane (30 ml), treated with 1 M NaOH (30 ml). After being stirred for 15 min, the solution was treated with a mixture of 1 M NH_4Cl (20 ml) and CH_2Cl_2 (20 ml). Dilute hydrochloric acid was added until the aqueous layer had been acidified to pH 1. The aqueous layer was extracted with CH_2Cl_2 (4× 20 ml). The usual work-up gave **88** (802 mg, 73%). The products **86**—**88** were identified with the authentic samples by comparison with their spectral data.

General Procedure for the Synthesis of Lactones. To a THF solution of 3.3 mmol of LDA at −78 °C was added 3 mmol of an appropriate phosphonate (**64**—**66**). The mixture was stirred at −78 °C for the time given in Table 8 and warmed gradually to room temperature. The mixture was poured into a stirred mixture of 1 M NH_4Cl (20 ml) and CH_2Cl_2 (20 ml). The CH_2Cl_2 layer was collected and the aqueous layer was extracted with CH_2Cl_2 (3×20 ml). The combined CH_2Cl_2 extracts were dried over Na_2SO_4, evaporated, and dissolved in dioxane (10 ml). To the solution was added 571 mg (3 mmol) of TsOH·H_2O, and the mixture was refluxed in the presence of molecular sieves 3A for 10 min. After cooling to room temperature, the solution was diluted with water (20 ml) and extracted with CH_2Cl_2 (3×20 ml). The combined extracts were dried over Na_2SO_4, evaporated, and chromatographed on silica gel (hexane–ether) to give a lactone given in Table 8. All of the products were identified by comparison with their spectral data with authentic samples previously reported.[21,24–26]

*Diethyl 1-Trimethylsilyloxy-3-phenyl-1-butenylphosphonate (**69a**).* To a cooled (−78 °C) solution of LDA (3.31 mmol) in dry THF (10 ml) was added **66** (1048 mg, 3.06 mmol),

the solution turned bright brown. After 0.5 h methyl iodide (515 mg, 3.63 mmol) was added. The solution turned yellow. Then the mixture was gradually warmed to room temperature. After 3 h, the solution was quenched with 1 M NH_4Cl, extracted with CH_2Cl_2 (3×25 ml) and dried over Na_2SO_4. After removal of the solvent, chromatography on silica gel afforded **69a** (473 mg, 43%) as a crude material: NMR(CCl_4) δ 0.18(9H, s, Me_3Si), 1.25 and 1.28(3H and 3H, t and t, J=7 Hz, CH_3C–O), 2.35—3.33(1H, m, CH), 3.98 (4H, m, CH_2O), 5.92(1H, dd, J=J=10 Hz, CH=C–P), 7.13(5H, s, Ph).

*Diethyl 1-Trimethylsilyloxy-3,4-diphenyl-1-butenylphosphonate (**69b**).* To a cooled (−78 °C) mixture of **66** (1594 mg, 4.66 mmol) and LDA (5.45 mmol) in dry THF (10 ml) was added benzyl bromide (984 mg, 5.75 mmol). After stirring at −78 °C for 0.5 h, the usual work-up gave **69b** (1305 mg, 69%) as a crude material: NMR(CCl_4) δ 0.07 (9H, s, Me_3Si), 1.19(6H, t, J=7 Hz, CH_3C–O), 2.90(1H, d, J=8.1 Hz, one of CH_2Ph), 2.91(1H, d, J=6.6 Hz, one of CH_2Ph), 2.40—3.20(1H, m, CH), 5.97(1H, dd, J=J= 10 Hz, CH=C), 7.00(5H, s, Ph), 7.07(5H, s, Ph).

*Diethyl 1-Trimethylsilyloxy-3-benzyl-1-hexenylphosphonate (**69c**).* To a cooled (−78 °C) solution of **65** (1051 mg, 3.29 mmol) and LDA (3.58 mmol) in 10 ml of dry THF was added benzyl bromide (0.420 ml, 3.54 mmol). After stirring at −78 °C for 0.5 h, the usual work-up gave **69c** (755 mg, 58%) as a crude material: IR(NaCl): 1045, 1260(P=O), 1370, 1394, 1606, 1635, 1696, 1728, 2920, 2955, 3015 cm^{-1}; NMR(CCl_4) δ 0.13 (9H, s, Me_3Si), 0.90(3H, t, J=6 Hz, CH_3CC), 1.30(10H, m, CH_2CH_2 and CH_3C–O), 2.75(3H, m, $PhCH_2$ and CH), 3.98(4H, m, CH_2O), 5.50(1H, dd, J=J=9.5 Hz, CH=C), 7.15(5H, s, Ph).

General Procedure for the Synthesis of β-Substituted Carboxylates. To a cooled solution of diisopropylamine (1.12±0.09 equiv.) in dry THF was added an equimolar amount of butyllithium in hexane. After 0.5 h an appropriate phosphonate (3.0 mmol) was added. After stirring at −78 °C for 0.5 h, alkyl halide (1.12±0.09 equiv.) was added. The reaction time and the temperature were given in Table 6. The mixture was poured into a mixture of CH_2Cl_2 (20 ml) and 1 M NH_4Cl (20 ml) with vigorous stirring. The CH_2Cl_2 layer was collected and the aqueous layer was further extracted with CH_2Cl_2 (3×20 ml). The organic extracts were combined, dried over Na_2SO_4, and concentrated *in vacuo*. The residual oil was dissolved into ethanol (30 ml) without further purification and a catalytic amount of TsOH was added. The reaction time and the temperature were given in Table 6. The resulted solution was diluted with water and extracted with CH_2Cl_2 (3×20 ml). The combined organic layers were dried over Na_2SO_4, concentrated to dryness, and chromatographed on silica gel (hexane–ether) gave a β-substituted carboxylate. The data of the NMR spectra and elemental analyses for all new compounds are summarized in Table 7. The previously known products are characterized by their NMR spectra.

References

1) Part XVII: M. Sekine, M. Nakajima, T. Hata, *Bull. Chem. Soc. Jpn.*, **55**, 218 (1982); Part XVI: M. Sekine, M. Nakajima, and T. Hata, *J. Org. Chem.*, **46**, 4030 (1981); Part XV: M. Sekine, K. Okimoto, K. Yamada, and T. Hata, *ibid.*, **46**, 2097 (1981).

2) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965).

3) a) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969); b) D. Seebach, *Synthesis*, **1**, 17 (1969); c) D. Seebach and M. Kolb, *Chem. & Ind.*, **1974**, 687; d) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974); e) S. S. Washburne, *J. Organomet. Chem.*, **83**, 155 (1974); f) D. Seebach and D. Enders, *Angew. Chem., Int. Ed. Engl.*, **14**, 15 (1975); g) O. W. Lever, Jr., *Tetrahedron*, **32**, 1943 (1976); h) S. S. Washburne, *J. Organomet. Chem.*, **123**, 1 (1976); i) D. Seebach, K. Geiss, M. Kold, and A. K. Beck, "Modern Synthetic Methods," Chemiker-Verband, Zürich (1976), p. 173; j) P. F. Hudrlik, "New Applications of Organometallic Reactions in Organic Synthesis," ed by D. Seyferth, Elsevier, Amsterdam (1976), pp. 127—160; k) B. Gröbel and D. Seebach, *Synthesis*, **1977**, 357; l) D. Seebach, E. W. Colvin, F. Lehr, and T. Weller, *Chimia*, **33**, 1 (1979); m) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **18**, 239 (1979).

4) Our preliminary communications have already been reported: a) T. Hata, A. Hashizume, M. Nakajima, and M. Sekine, *Tetrahedron Lett.*, **1977**, 363; b) T. Hata, M. Nakajima, and M. Sekine, *ibid.*, **1979**, 2047; c) M. Sekine, M. Nakajima, A. Kume, and T. Hata, *ibid.*, **1979**, 4479.

5) a) P. Savignac, A. Breque, and F. Mathey, *Synth. Commun.*, **9**, 287, 487 (1979); b) R. E. Koenigkramer and H. Zimmer, *Tetrahedron Lett.*, **1980**, 1017; c) R. E. Koenigkramer and H. Zimmer, *J. Org. Chem.*, **45**, 3994 (1980).

6) a) V. S. Abramov, L. P. Semenova, and L. G. Semenova, *Dokl. Alad. Nauk SSSR*, **84**, 281 (1952); *Chem. Abstr.*, **47**, 3227 (1953); b) L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 479 (1957); c) I. Shahak and E. D. Bergmann, *Isr. J. Chem.*, **4**, 225 (1966); d) L. H. Horner and H. Roder, *Chem. Ber.*, **103**, 2984 (1970); e) G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds," Wiley, New York (1976), Vol. 7, p. 30.

7) a) G. Wittig and L. Löhmann, *Justus Liebigs Ann. Chem.*, **550**, 260 (1942); b) D. L. Dalvymple, T. L. Kruger, and W. N. White, "The Chemistry of the Ether Linkage," ed by S. Patai, Interscience, New York (1967), p. 617; c) U. Schöllkopf, *Angew. Chem. Int. Ed. Engl*, **9**, 763 (1970).

8) A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974) and references cited therein.

9) a) R. West, R. Lose, H. F. Stewart, and A. Wright, *J. Am. Chem. Soc.*, **93**, 282 (1971); b) A. Wright, D. Ling, P. Boudjouk, and R. West, *ibid.*, **94**, 4784 (1972).

10) a) K. Deuchert, U. Hertenstein, and S. Hünig, *Synthesis*, **1973**, 777; b) S. Hünig and G. Wehner, *ibid.*, **1975**, 180; c) G. Wehner and S. Hünig, *ibid.*, **1975**, 391; d) U. Hertenstein and S. Hünig, *Angew. Chem. Int. Ed. Engl.*, **14**, 179 (1975). e) U. Hertenstein, S. Hünig, and M. Öller, *Synthesis*, **1976**, 416.

11) a) G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **93**, 5286 (1971); b) G. Stork and L. Maldonado, *ibid.*, **96**, 5272 (1974).

12) A. Kalir and D. Balderman, *Synthesis*, **1973**, 358.

13) M. Hamana, T. Endo, and S. Saeki, *Tetrahedron Lett.*, **1975**, 903.

14) R. M. Jacobson, G. P. Lahm, and J. W. Clader, *J. Org. Chem.*, **45**, 395 (1980).

15) K. Issleib and B. Walther, *Angew. Chem. Int. Ed. Engl.*, **6**, 88 (1967).

16) Y. Ogata and A. Kawasaki, "The Chemistry of the Carbonyl Group," ed by S. Patai, Interscience, New York (1970), Vol. 2, pp. 1—69.

17) a) B. Ackerman, T. A. Jordan, C. R. Eddy, and D. Swern, *J. Am. Chem. Soc.*, **78**, 4444 (1956); b) K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.*, **86**, 3862 (1964); c) W. Jugelt, S. Andreae, and G. Schubert, *J. Prakt. Chem.*, **1971**, 83; d) R. Kluger and J. Chin, *J. Am. Chem. Soc.*, **100**, 7382 (1978); e) R. Kluger, D. C. Pike, and J. Chin, *Can.*

J. Chem., **56**, 1792 (1978); f) K. S. Narayanan and K. D. Berlin, *J. Am. Chem. Soc.*, **101**, 109 (1979).

18) a) M. I. Kabachnik and P. A. Rossiiskaya, *Izu. Akad. Nauk SSSR, Ser. Khim.*, **1945**, 597; *Chem. Abstr.*, **41**, 88 (1945); b) K. Terauchi and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **43**, 883 (1970); c) A. P. Pashinkin, T. K. Gazizov, and A. N. Pudovik, *Zh. Obshch. Khim.*, **40**, 28 (1970); *Chem. Abstr.*, **72**, 100827 (1970).

19) M. Soroka and P. Mastalerz, *Zh. Obshch. Khim.*, **44**, 463 (1974); *Chem. Abstr.*, **80**, 121058 (1974).

20) a) I. Shahak and E. D. Bergmann, *Isr. J. Chem.*, **4**, 225 (1966); b) I. Shahak, *Tetrahedron Lett.*, **1966**, 2201; c) G. M. Baranov, V. V. Perekalin, M. V. Ponamarenko, and I. A. Orlovskii, *Khim. Primen. Forsfororg. Soedin., Tr. Konf.*, 4th, **1969**, 228; d) O. G. Plantema, H. de Konig, and H. O. Huisman, *Tetrahedron Lett.*, **1975**, 2945; e) M. Sekine, M. Satoh, H. Yamagata, and T. Hata, *J. Org. Chem.*, **45**, 4162 (1980).

21) D. A. Evans, J. M. Takacs, and K. M. Hurst, *J. Am. Chem. Soc.*, **101**, 371 (1979).

22) Z. S. Novikova, S. N. Mashoshina, T. Sapozhnikova, and I. F. Lupsenko, *Zh. Obshch. Khim.*, **41**, 2622 (1971).

23) N. F. Orlov, V. P. Nileshkevich, and E. S. Andronov, *Zh. Obshch. Khim.*, **35**, 2193 (1965).

24) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 5905 (1968).

25) J. B. Bush, Jr., and H. Finkbeiner, *J. Am. Chem. Soc.*, **90**, 5903 (1968).

26) M. Tokuda, Y. Yokoyama, T. Taguchi, A. Suzuki, and M. Itoh, *J. Org. Chem.*, **37**, 1859 (1972).