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4-Phosphoranylidene-5(4*H*)-oxazolones II. Reactions with Alkylating Agents

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Summary. When treated with alkyl halides at 20–90°C without solvent or in acetonitrile, 4-phosphoranylidene-5(4*H*)-oxazolones (**1**) give 4-C-alkylation products **4** in good yields. Alkylation of **1** with alkyl triflates in CH_2Cl_2 at room temperature results in O-alkylation products **5**. No O-to 4-C-alkylation rearrangement can be observed. The spectroscopic properties of the alkylation products are reported and discussed.

Keywords. 4-Phosphoranylidene-5(4*H*)-oxazolones; Phosphorus ylides; 5(4*H*)-Oxazolone enolate ion equivalent; 4-C-alkylation; O-Alkylation; HSAB principle.

4-Phosphoranyliden-5(4*H*)-oxazolone, 2. Mitt. Reaktionen mit Alkylierungsreagentien

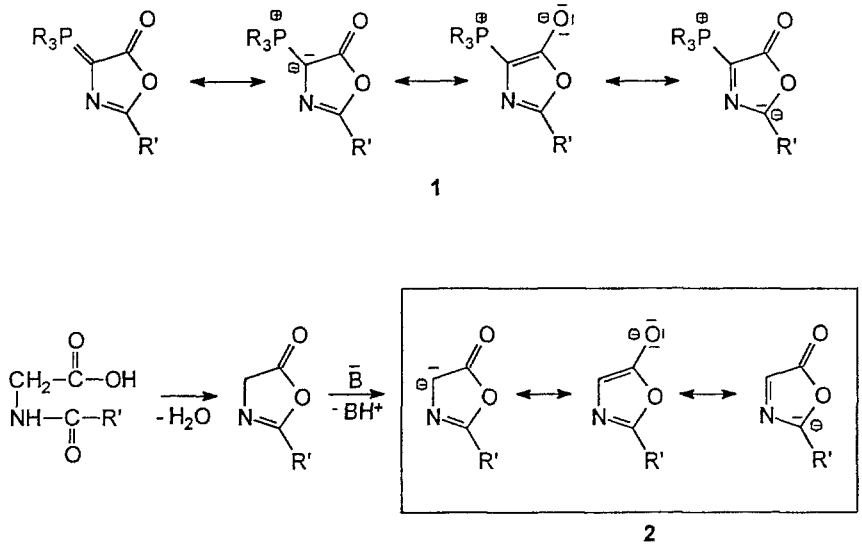
Zusammenfassung. Behandlung von 4-Phosphoranyliden-5(4*H*)-oxazolonen (**1**) mit Alkylhalogeniden bei 20–90°C ohne Lösungsmittel oder in Acetonitril liefert in guten Ausbeuten die 4-C-alkylierten Produkte **4**. Alkylierung von **1** mit Alkyltriflaten in CH_2Cl_2 bei Raumtemperatur ergibt O-alkylierte Produkte (**5**). E6 wurde keine Umlagerung von O-alkylierten zu C-alkylierten Verbindungen beobachtet. Die spektroskopischen Eigenschaften der Alkylierungsprodukte werden berichtet und diskutiert.

Introduction

Recently we have described the synthesis as well as both physical and spectroscopic properties of 4-phosphoranylidene-5(4*H*)-oxazolones (**1**), a hardly known class of phosphorus ylides derived from 5(4*H*)-oxazolones [1].

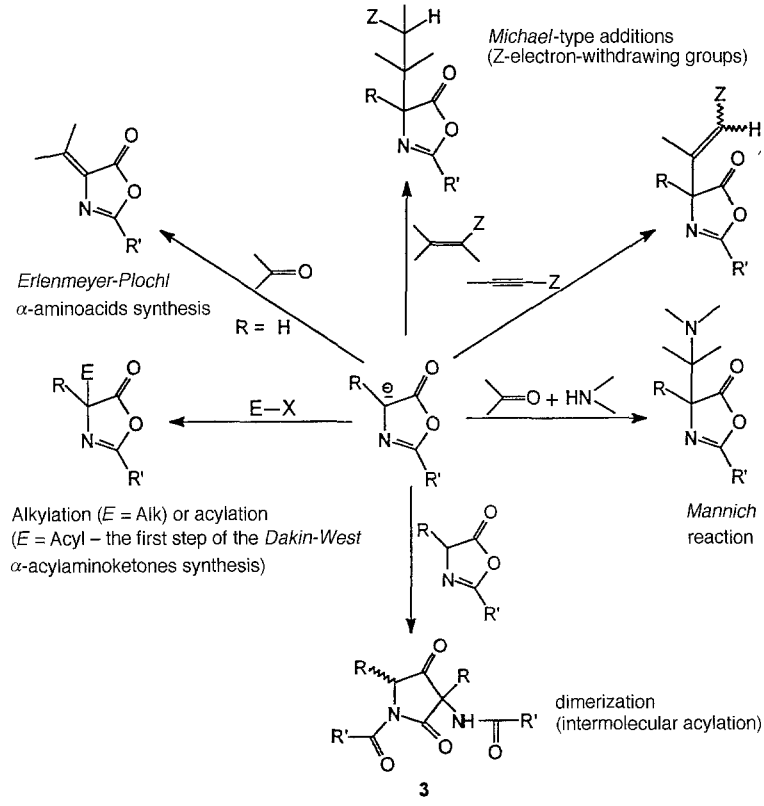
As the dipolar resonance structures of ylides **1** (Scheme 1) are isoelectronic with respect to the resonance structures of enolate ions derived from 5(4*H*)-oxazolones (**2**), one might expect that ylides **1** should display a reactivity pattern towards electrophilic agents similar to the reactivity of 5(4*H*)-oxazolone enolates.

Enolates **2** are intermediates of considerable importance in organic syntheses [2–4]. Their reactions with a variety of electrophilic reagents (*e.g.* alkylating [5–7] or acylating agents [8, 9], aldehydes or ketones [4, 10], *Michael* [2, 3, 11, 12] and *Mannich* [3, 13] reagents) are especially useful for the functionalization of the α-carbon atom in glycine and other α-amino acids (Scheme 2). In many cases, however, the synthetic utility of these reactions is strongly restricted due to the



Scheme 1

competitive acylation of the enolate ion by another oxazolone molecule, which eventually yields useless dimer **3** [5, 14–15]. Ylides **1** are entirely resistant to dimerization [1]; therefore, they may be considered to be promising synthetic equivalents of 5(4*H*)-oxazolone enolates [16–17].



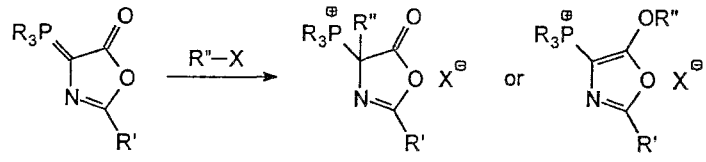
Scheme 2

In this contribution, we report the results of our successful attempts of alkylating ylides **1**. It is worth mentioning that an effective direct alkylation of 5(4*H*)-oxazolone enolates is possible only in the case of 5(4*H*)-oxazolones with a bulky substituent at position 4, as this variety of 5(4*H*)-oxazolones is relatively little susceptible to dimerization [5–6]. Further investigations on the removal of the phosphonium group from the alkylation products in order to transfom alkylated ylides into α-functionalized derivatives of glycine are in progress [17].

Results and Discussion

It might be expected from the resonance structures of ylides **1** (Scheme 1) that they should be ambident nucleophiles with nucleophilic centers on carbons at positions 4 and 2 of the oxazolone ring, on the oxygen of the carbonyl group, and on the nitrogen bearing a nonbonded electron pair.

When dissolved in methyl iodide and left at room temperature for a few days or a few weeks, ylides **1a** and **1c–e** undergo methylation at position 4 yielding phosphonium salts **4**. The alkylation product usually precipitates spontaneously from the reaction mixture (Table 1, procedure A). We have also developed a more efficient alkylation procedure which consists in heating the ylide with alkyl halide in acetonitrile in a sealed glass tube to 80 or 90°C for 1 to 24 hours (Table 1, procedure B). Methoxymethyl iodide reacts easily with ylide **1a** in acetonitrile even at room temperature. This method makes it possible to introduce not only simple alkyl groups in position 4 of the oxazolone ring, but also, *e.g.*, alkoxymethylene, alkoxycarbonylmethylene, or cyanomethylene groups, usually in good or even very good yields.



1 4 5

Scheme 3

4-C-Alkylation products of ylides derived from triphenylphosphine are crystalline compounds, stable at room temperature when protected from moisture, well soluble in CH_2Cl_2, $CHCl_3$, and CH_3CN, but insoluble in diethyl ether. They can be purified by dissolving in CH_2Cl_2 or CH_3CN and precipitating with diethyl ether. Ylide **1e**, derived from tributylphosphine, reacts smoothly with methyl iodide. The oily alkylation product **4ea**, however, seems to be unstable. The IR spectrum of the product revealed the expected strong $\nu_{C=O}$ and $\nu_{C=N}$ bands at 1819 and 1649 cm^{-1}, respectively; a satisfactory microanalysis has also been obtained (Table 1). However, our efforts to record clear ^1H and ^{13}C NMR spectra of **4ea** product failed.

Table 1. Alkylation of 4-phosphoranylidene-5(4*H*)-oxazolones

Ylide **1**			Alkylating agent	Procedure	Solvent	Temperature °C	Reaction time	Product	Yield (%)	M.p. °C	IR (cm^{-1})	Elemental analyses (%)							
												calcd.				found			
No.	R	R′	$R''-X$									C	H	N	P	C	H	N	P
1a	Ph	Ph	CH_3–I	A	none	20	40 d	**4aa**	64	161.5–162.5[a]	1822s,1640s[b]	59.70	4.11	2.49	5.50	59.47	4.26	2.40	5.43
1a	Ph	Ph	CH_3–I	A	none	20	80 d	**4aa**	78										
1a	Ph	Ph	CH_3–I	B	MeCN	80	12 h	**4aa**	55										
1a	Ph	Ph	CH_3OCH_2–I	B	MeCN	20	1h	**4ab**	72	152–153.5	1819s,1636s	58.70	4.25	2.36	5.22	58.57	4.55	2.26	5.41
1b	Ph	Me	CH_3–I	A	none	20	7 d	–[c]	79	124–128 (dec.)	1821m,1768s,1671m	55.11	4.22	2.79	6.18[d]	54.93	4.39	3.00	5.98
1c	Ph	*i*-Pr	CH_3–I	A	none	20	13 d	**4ca**	68	123–124.5	1816s,1654s	50.84	4.43	2.28	5.04[e]	51.14	4.39	2.60	4.72
1d	Ph	*t*-Bu	CH_3–I	A	none	20	19 d	**4da**	85	177.5–178	1822s,1808s,1649s	57.47	5.01	2.58	5.70	57.17	5.00	2.76	5.55
1d	Ph	*t*-Bu	CH_3–I	B	MeCN	80	12 h	**4da**	99										
1d	Ph	*t*-Bu	C_2H_5–I	B	MeCN	90	24 h	**4dc**	40	170–171	1810s,1649s	58.18	5.24	2.51	5.56	58.06	5.42	2.76	5.79
1d	Ph	*t*-Bu	CH_2 =$CHCH_2$–I	B	MeCN	80	4 h	**4dd**	75	184.5–185	1819s,1651s	59.06	5.13	2.46	5.44	59.36	4.76	2.74	5.14
1d	Ph	*t*-Bu	$C_6H_5CH_2$–Br	B	MeCN	80	6 h	**4de**	98	110–111.5[f]	1820s,1808m,1650s	60.29	5.06	2.13	4.71[g]	59.88	5.27	2.29	4.89
1d	Ph	*t*-Bu	$C_2H_5OOCCH_2$–I	B	MeCN	80	12 h	**4df**	96	118.5–120	1811s,1735s,1642s	56.60	5.08	2.28	5.03	56.28	5.08	2.18	4.78
1d	Ph	*t*-Bu	N≡CCH_2–I	B	MeCN	80	18 h	**4dg**	85	142.5–143.5	2254w,1823s,1643s	57.05	4.61	4.93	5.45	56.80	4.91	5.15	5.19
1e	Bu	*t*-Bu	CH_3–I	A	none	20	3 d	**4ea**	47	viscous oil	1819s,1649s	49.69	8.13	2.90	6.41	49.33	8.10	2.92	6.46
1a	Ph	Ph	CH_3–OSO_2CF_3	C	CH_2Cl_2	20	0.25 h	**5ah**	81	184.5–186	1620s,1603s,1270s[h]	59.49	3.96	2.39	5.29	59.69	3.81	2.40	5.47
1a	Ph	Ph	C_2H_5–OSO_2CF_3	C	CH_2Cl_2	20	1 h	**5ai**	40	179–181.5	1616s,1602s,1272s[h]	60.10	4.20	2.34	5.17	59.88	3.94	2.55	5.36
1d	Ph	*t*-Bu	CH_3–OSO_2CF_3	C	CH_2Cl_2	20	0.25 h	**5dh**	83	157–158	1620s,1269s[h]	57.34	4.81	2.48	5.48	57.09	5.18	2.17	5.35

[a] Ref. [18]: m.p.: 162–164°C (dec.); [b] Ref. [18]: 1820 and 1640 cm^{-1} (KBr); [c] probably a mixture of alkylation products, mainly N-alkylation product; [d] for the formula $C_{23}H_{21}NO_2PI$; [e] for the formula $C_{25}H_{25}NO_2PI{\cdot}CH_2Cl_2$; [f] after recrystallization from MeCN/Et_2O: m.p.: 164.5 – 166°C; [g] for the formula $C_{32}H_{31}NO_2PBr{\cdot}CH_2Cl_2$; [h] in MeCN

The reaction of methyl iodide with ylide **1b** possessing a small methyl group at position 2 leads probably to an unstable mixture of 4-C- and N-methylation products. The IR spectrum of the product contains a strong absorption band at 1768 cm^{-1} which might be assigned to the $\nu_{C=O}$ absorption of the N-methylation product, and lower intensity bands at 1821 and 1671 cm^{-1} which probably correspond to the $\nu_{C=O}$ and $\nu_{C=N}$ absorption of the 4-C-alkylation product. We were not able to get clear ^1H and ^{13}C NMR spectra of the obtained substance; however, we have achieved a satisfactory microanalysis for the formula of isomeric methylation products (Table 1).

Lobanov et al. [18] have described a similar alkylation of ylide **1a** with methyl iodide yielding a product whose m.p., IR, and ^1H NMR spectra are in reasonable agreement with our data concerning compound **4aa**. Our results differ, however, substantially from *Lobanov's* results in one point: the Russian authors purified the alkylation product by dissolving it in methyl alcohol and precipitating it with diethyl ether, whereas we have found that methyl alkohol at room temperature easily opens the oxazolone ring, affording the N-benzoyl-α-(triphenylphosphonio)alanine methyl ester iodide [17].

The structure of 4-C alkylation products has been confirmed by their spectroscopic properties (IR, ^1H, ^{13}C, and ^{31}P NMR) as well as by satisfactory results of elemental analyses (see Tables 1 and 2). In spite of prolonged drying *in vacuo* (0.1–0.2 mm Hg, 45°C), some phosphonium salts **4** precipitated from methylene chloride retain one molecule of solvent per one molecule of salt.

As it has been reported in our previous paper [1], the transformation of 5(4*H*)-oxazolones into corresponding ylides **1** causes a shift of the carbonyl absorption band towards lower frequencies by at least 120 cm^{-1} (from 1825–1810 to 1690–1655 cm^{-1}). The shift is a result of the strong coupling between the free electron pair of the ylide and the carbonyl group. 4-C-Alkylation products **4** again display the absorption pattern typical for 5(4*H*)-oxazolones, with two strong, very diagnostic bands at 1823–1810 cm^{-1} ($\nu_{C=O}$) and 1654–1636 cm^{-1} ($\nu_{C=N}$), which is a consequence of the lack of a free electron pair on the α-carbon of the oxazolone ring.

The ^1H and ^{13}C NMR spectroscopic data presented in Table 2 confirm the proposed structure of phosphonium salts **4**; the values of the ^{31}P chemical shifts (30.2–28.4 ppm) agree quite well with the range of 27.0–19.1 ppm reported in the literature for some similar phosphonium salts [19].

The alkylation of ylides **1** with alkyl triflates gave completely different results. The reactions, which were carried out in CH_2Cl_2 at room temperature (Table 1, procedure C), yielded O-alkylation products **5** in times up to 1 h. In a separate alkylation experiment with ylide **1a** using methyl triflate we didn't observe (IR) any signs of a consecutive O- to 4-C-alkylation product rearrangement for several days. Phosphonium salts **5** were precipitated from the reaction mixtures with diethyl ether and identified as described above for the 4-C-alkylation products.

There is no absorption of any carbonyl group in the range of 1850–1650 cm^{-1} in the IR spectra of phosphonium salts **5**; the strong absorption bands in the range of 1620–1600 cm^{-1} can be assigned to the stretching vibrations of the conjugated C=N and C=C bonds. Another characteristic strong absorption near 1270 cm^{-1} should be attributed to the stretching vibration of the exocyclic C–O bonds. ^1H,

Table 2. ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data 4-phosphoranylidene-5(4*H*)-oxazolone alkylation products **4** and **5**

^{1}H NMR ($CDCl_3$/*TMS*) δ(ppm)	^{13}C NMR								^{31}P NMR
	Oxazolone ring δ(ppm) /J_{C-P} (Hz)			$(C_6H_5)_3P=$ δ(ppm) /J_{C-P} (Hz)				Other carbons δ(ppm) /J_{C-P} (Hz)	δ (ppm)
	C_2	C_4	C_5	C_1	C_2	C_3	C_4		
4aa 8.08–7.39 (m, $20H_{arom}$), 2.23 (d, 3H, Me, $J = 16.7$ Hz)[a]	164.8 / 11.2	70.7 / 60.0	173.4 / 3.8	113.6 / 84.7	134.7 / 9.8	131.2 / 12.8	136.8 / 3.0	135.0, 129.4, 128.5, 122.9 (other arom.), 22.4 (Me)	29.8
4ab 8.05–7.50 (m, $20H_{arom}$), 4.31 (dd, 1H, CH_2^b, J_{H-H}=9.8 Hz, J_{H-P}=9.5 Hz), 4.26 (dd, 1H, CH_2^b, J_{H-H} = 10.0 Hz, J_{H-P} = 5.6 Hz), 3.29 (s, 3H, MeO)	165.8 / 11.6	75.9 / 60.3	171.4 / 3.4	114.0 / 85.0	134.7 / 10.1	131.0 / 13.1	136.6 / 3.7	135.0, 129.4, 128.5, 122.9 (other arom.), 72.3 (CH_2), 60.3 (MeO)	
4ca 8.13–7.65 (m, $15H_{arom}$), 2.67 (dqq, 1H, C*H*Me_2, J_{H-P} = 2.7 Hz, J_1 = 6.9 Hz, J_2 = 6.9 Hz), 2.14 (d, 3H, Me, J_{H-P} = 16.2 Hz), 1.03 (d, 3H, CH*Me*$^c_2$, J_1 = 6.9 Hz), 0.91 (d, 3H, CH*Me*$^c_2$, J_2 = 6.9 Hz)	173.8 / 10.7	69.3 / 59.8	173.7 / 4.6	113.4 / 84.2	134.7 / 9.8	131.2 / 12.8	136.8 / 3.0	29.3 (*C*HMe$_2$), 22.0 (Me), 18.3 (CH*Me*$_2^c$),18.1 (CH*Me*$^c_2$),	30.2
4da 8.10–7.64 (m, $15H_{arom}$), 2.16 (d, 3H, Me, J_{H-P} = 16.0 Hz), 1.11 (s, 9H, CMe_3)	175.9 / 11.4	69.4 / 59.6	173.8 / 4.5	113.4 / 84.0	134.8 / 10.5	131.3 / 12.8	136.8 / 3.5	34.6 (*C*Me$_3$), 26.4 (C*Me*$_3$), 22.4(Me)	30.2
4dc 8.05–7.70 (m, $15H_{arom}$), 2.66–2.41 (m, 2H, CH_2), 1.04 (s, 9H, CMe_3), 0.93 (t, 3H, Me, J = 7.1 Hz)	176.4 / 10.8	73.9 /60.0	173.4 / 4.4	113.6 / 84.5	134.8 / 9.8	131.2 / 12.8	136.8 / 3.0	34.8 (*C*Me$_3$), 27.7(CH_2), 26.5 (C*Me*$_3$), 8.0/10.5 (CH_2*Me*)	28.9
4dd 8.15–7.70 (m, $15H_{arom}$), 5.57–5.38 (m, 1H, C*H* =CH_2), 5.35–5.26 (m, 2H, CH=C*H*$_2$), 3.23–3.07 (m, 2H, C*H*$_2$CH=CH_2), 1.02 (s, 9H, CMe_3)	176.4 / 10.9	73.2 / 58.8	172.9 / 4.6	113.5 / 84.4	134.9 / 9.8	131.4 / 12.9	136.9 / 3.1	126.1/11.4 (*C*H=CH_2), 124.8 (CH= *C*H$_2$), 37.7 *C*H$_2$CH=CH_2), 34.7 (*C*Me$_3$), 26.5 (C*Me*$_3$)	28.4
4de 8.18–7.78 (m, 15H, Ph_3P), 7.40–7.02 (m, 5H, *Ph*CH_2), 3.77 (dd, 1H, CH_2^b, J_{H-H} = 13.0 Hz, J_{H-P} = 2.7 Hz), 3.62 (dd, 1H, CH_2^b, J_{H-H} = 13.0 Hz, J_{H-P} = 8.9 Hz), 0.72 (s, 9H, CMe_3)	175.7 / 10.9	73.6 / 58.1	173.3 / 4.6	113.6 / 84.3	134.8 / 9.8	131.3 / 12.8	137.0 / 3.0	130.5, 129.8 / 11.7, 128.84, 128.78 (other arom.), 39.9 (CH_2), 34.2 (*C*Me$_3$), 25.8 (C*Me*$_3$)	28.5
4df 8.09–7.80 (m, $15H_{arom}$), 4.15 (q, 2H, CH_2Me, J = 7.2 Hz), 3.61 (dd, 1H, CH_2CO^b, J_{H-H} = 16.8 Hz, J_{H-P} = 4.5 Hz), 3.41 (dd, 1H, CH_2CO^b, J_{H-H} = 16.9 Hz, J_{H-P} = 6.8 Hz), 1.26 (t, 3H, Me, J = 7.1 Hz), 0.99 (s, 9H, CMe_3)	178.3 / 10.0	70.5 / 57.5	172.9 / 3.5	112.9 / 84.2	135.1 / 9.8	131.4 / 13.0	137.1 / 3.1	166.5 / 17.6 (CH_2*C*O), 62.9 (CH_2CO), 38.2 (OCH_2), 34.7 (*C*Me$_3$), 26.2 (C*Me*$_3$), 14.0 (CH_2*Me*),	29.5
4dg 8.15–7.60 (m, $15H_{arom}$), 4.06, (dd, 1H, CH_2^b, J_{H-H} = 17.0 Hz, J_{H-P} = 3.7 Hz), 3.97 (dd, 1H, CH_2^b, J_{H-H} = 17.1 Hz, J_{H-P} = 7.5 Hz), 1.03 (s, 9H, CMe_3)	178.5 / 9.9	70.2 / 61.2	171.4 / 3.6	112.2 / 84.7	135.2 / 10.1	131.6 / 13.1	137.3 / 3.0	112.1 / 6.7 (CN), 35.0 (*C*Me$_3$), 26.8 (CH_2), 26.4 (C*Me*$_3$)	29.5
5ah 8.05–7.65 (m, 15H, Ph_3P), 7.50–7.35 (m, 5H, Ph), 4.12 (s, 3H, Me)	155.1 / 19.3	91.5 /146.8	167.1 / 28.0	117.8 / 94.0	134.2 / 11.0	130.3 / 13.4	135.5 / 3.0	131.5, 129.0, 126.3, 125.3 (other arom.), 61.0 (Me)	9.7
5ai 8.00–7.69 (m, 15H, Ph_3P), 7.51–7.42 (m, 5H, Ph), 4.50 (q, 2H, CH_2, J = 7.1 Hz), 1.11 (t, 3H, Me, J = 7.1 Hz)	155.2 / 19.0	91.5 / 146.8	166.7 / 26.7	117.9 / 94.0	134.2 / 11.0	130.3 / 13.3	135.5 / 3.0	131.5, 129.0, 126.3, 125.4 (other arom.), 71.1 (CH_2), 14.3 (Me)	9.4
5dh 7.89–7.61 (m, $15H_{arom}$), 3.99 (s, 3H, Me), 1.40 (s, 9H, CMe_3)	164.6 / 18.0	89.1 / 147.3	167.1 / 26.9	118.1 / 94.1	134.1 / 10.9	130.2 / 13.4	135.3 / 3.1	60.4 (Me), 34.4 (*C*Me$_3$), 28.0 (C*Me*$_3$)	9.3

[a] Ref. [18]: 7.90–7.40 (m, Ph_3P and Ph), 2.17 (d, Me, J = 16 Hz); [b]one of two diastereotopic protons of the methylene group; [c]one of two diastereotopic methyl groups of the isopropyl group

^{13}C, and ^{31}P NMR spectroscopic data (Table 2) also confirm the proposed structure of phosphonium salts **5**; the ^{31}P chemical shift values (9.7–9.3 ppm) are close to the value 13.9 ppm quoted by *Nesmeyanov et al.* [20] for a similar phosphonium salt (*cis*-$Ph_3P^+CH{=}CHOH\ Cl^-$).

The different course of alkylation of 4-phosphoranylidene-5(4*H*)-oxazolones by alkyl halides and alkyl triflates is readily explainable in terms of the hard and soft acids and bases principle (HSAB) [21]. Alkyl halides, being softer alkylating agents, attack the ylide at position 4, as the less electronegative C-4 atom is a softer nucleophilic center of the ambident ylide than the more electronegative oxygen of the carbonyl group. Alkyl triflates, as harder electrophiles, tend to react preferentially with the oxygen atom of the carbonyl group as the hardest nucleophilic center of the ylide.

Experimental

Melting points, determined in capillary tubes, are uncorrected. IR spectra were recorded on a Zeiss Specord M 80 spectrophotometer; the measurements were carried out, unless otherwise noted, in CH_2Cl_2 (0.2 *M*) using cells of 0.075 mm. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian VXR-300 spectrometer at operating frequencies of 300, 75.5, and 121.4 MHz, respectively, in the FT mode. In the case of ^1H and ^{13}C NMR spectra, *TMS* was used as an internal standard; ^{31}P NMR spectra were referenced to external 85% phosphoric acid. Alkyl halides, acetonitrile, benzene, and diethyl ether were purified by distillation and dried over molecular sieves (4 Å). The purification of CH_2Cl_2 has been described previously [22].

Alkylation of 4-phosphoranylidene-5(4H)-oxazolones **1** *(general procedures)*

Procedure A

A mixture of 4-phosphoranylidene-5(4*H*)-oxazolone (4 mmol) and methyl iodide (0.16 mol, 10 ml) was refluxed for 15 min. The reaction mixture was left standing at room temperature for the time given in Table 1. The precipitated crystals were filtered, washed with benzene and dried *in vacuo*. For further purification, the crude phosphonium salt was dissolved in CH_2Cl_2 or acetonitrile, the pure product was precipitated with a twice as large volume of diethyl ether, filtered, washed with a mixture of CH_2Cl_2 or acetonitrile with diethyl ether in a ratio of 1:2 (*v/v*), and dried *in vacuo* (0.01–0.02 mmHg) at 45°C for 1–2 h.

Procedure B

A mixture of 4-phosphoranylidene-5(4*H*)-oxazolone (2.5 mmol), alkyl halide (3.75 mmol), and acetonitrile (2 ml), placed in a sealed glass tube, was heated in an oil bath at 80–90°C for 4–24 hours; in the case of phosphonium salt **4ab**, the reaction was carried out at 20°C. The reaction mixture was evaporataed to dryness *in vacuo*. The residue was extracted three times with boiling benzene (5 ml) to remove unreacted ylide. The crude phosphonium salt was dried *in vacuo* and purified as described above (Procedure A).

Procedure C

To a stirred solution of 4-phosphoranylidene-5(4*H*)-oxazolone (1 mmol) in CH_2Cl_2 (5 ml), alkyl triflate (3 mmol) was added at room temperature. After 0.25–1 h, the pure O-alkylated product was

precipitated with diethyl ether (6 ml). The precipitated white crystals were filtered, washed with a mixture of CH_2Cl_2 and diethyl ether in a ratio of 1:2 (*v/v*), and dried *in vacuo* (0.01–0.02 mmHg) at 45°C for 1–2 h.

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