where k_{eff} is the experimentally determined effective rate constant; k_0 is the $[H^+]$ independent rate constant.

$$k_0 = k_{eff}\frac{K+[H^+]}{[H^+]},$$

K is the equilibrium constant of urea. The calculated value of k_0 in the whole investigated $[H^+]$ concentration range amounts to 0.45±0.04 L mol^{-1} s^{-1} (25.0±0.1 °C). Reaction (2) probably proceeds according to a scheme analogous to the mechanism of nitrosation of primary amines[6]:

$$CO(NH_2)_2 \xrightarrow{H^+} H_2NCONH_3^+ \xrightarrow[-H_2O]{HNO_2,\ H^+}$$

$$\longrightarrow [OHN{=}\overset{+}{N}HCONH_3^+] \xrightarrow[-H_2O]{} [N{=}\overset{+}{N}CONH_3^+] \longrightarrow$$

$$\xrightarrow[-N_2,\ H^+]{H_2O} [HOCONH_3^+] \longrightarrow CO_2 + NH_4^+.$$

The fact that NH_4^+ ions have not been detected previously[2,3] may be explained by low acidity of the reaction mixture and, correspondingly, low concentration of protonated urea. Our experiments revealed that an increase in the NH_4^+ and NO_3^- concentrations in the reaction solution *via* introducing $(NH_4)_2SO_4$ and $NaNO_3$ does not lead to a change in the reaction rate. Using the ionometry method we found that the hydrolysis of $CO(NH_2)_2$ yielding NH_4^+ under the conditions of our experiments does not occur. Similar data on the kinetics of interaction of $CO(NH_2)_2$ with HNO_2 were obtained by us in chloric acid solutions (0.02—1.0 *M* $HClO_4$).

Thus, it is necessary to account for the accumulation of ammonium ions in the solutions in the case of employing urea in removing traces of nitrous acid from solutions in analytical practice and during syntheses[4].

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Received April 29, 1999;
in revised form September 6, 1999

Reaction of diphenyl(trimethylsilyl)phosphine with α-oxo phosphonates

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We have previously reported[1] that diphenyl(trimethylsilyl)phosphine reacts with carbonyl compounds yielding diphenyl[alkyl(phenyl)trimethylsilyloxymethyl]phosphines. These compounds are of interest because of their potential use as ligands in complexes with transition metals.

In a continuation of these investigations, we studied the addition of diphenyl(trimethylsilyl)phosphine to α-oxo phosphonates. The reaction was completed in 10 min at 10 °C and resulted in the corresponding α-phosphino(α-silyloxy)phosphonates (**2**) in 45—95% yield depending on the structure of the starting oxo phosphonate (Scheme 1, Table 1).

The reaction can be conducted either without a solvent or in anhydrous diethyl ether or hexane. The addition of the solvent has practically no influence on the yield of the target product.

It should be noted that the addition of trimethylsilylphosphine to α-oxo phosphonates easily occurs without a catalyst, as opposed to trimethylsilylcyanide, which adds to carbonyl compounds[2] and oxo phosphonates[3] only in the presence of catalysts, *e.g.*, ZnI_2 or Bu_3SnCN.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2379—2380, December, 1999.

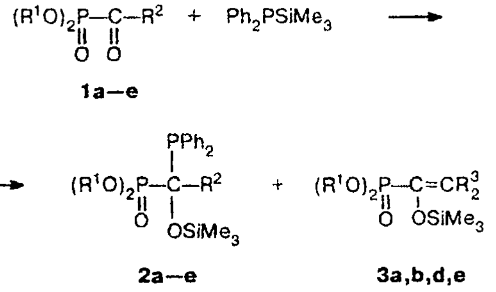
1066-5285/99/4812-2352 $22.00 © 2000 Kluwer Academic/Plenum Publishers

Table 1. The main physicochemical constants and ^{31}P NMR data for compounds **2**

Compound	R^1	R^2	M.p. /°C	^{31}P NMR, δ (d)	$^2J_{PCP}$ /Hz	Yield according to ^{31}P NMR (%)[a]	Found/Calculated (%) C	Found/Calculated (%) P	Molecular formula
2a	Et	Me	92	11.0, 23.5	20	98 (95)	56.85 57.53	14.20 14.15	$C_{21}H_{32}P_2O_4Si$
2b	Et	Pr^i	—[b]	9.3, 21.0	22	55	59.00 59.22	13.25 13.3	$C_{23}H_{36}P_2O_4Si$
2c	Et	Ph	102	9.0, 24.0	26	45 (40)	61.89 62.40	12.36 12.40	$C_{26}H_{34}P_2O_4Si$
2d	Me$_3$Si	Me	81	7.0, 9.0	19	100 (95)	50.71 50.70	11.26 11.78	$C_{23}H_{40}P_2O_4Si_3$
2e	Me$_3$Si	Pr^i	—[b]	6.2, 9.4	18	70	—	—	—

[a] The yield of the reaction products after isolation and purification is given in parentheses. [b] Oil.

Scheme 1



R	a	b	c	d	e
R^1	Et	Et	Et	Me$_3$Si	Me$_3$Si
R^2	Me	Pr^i	Ph	Me	Pr^i
R^3	H	Me	—	H	Me

The reaction was monitored by IR spectroscopy by following the disappearance of the absorption band (ν 1675 cm^{-1}) corresponding to the carbonyl group vibration of the starting α-oxo phosphonates and also by ^{31}P NMR spectroscopy. The addition of silylphosphine to oxo phosphonates (R^2 = Me or Pr^i) resulting in the formation of product **2** is accompanied by a side process, *viz.*, silylation of the enol form of the oxo phosphonate yielding 2—5% of α-silyloxyvinylphosphonates **3** (δ(^{31}P) 14—19; IR, ν 1625 cm^{-1}).

In the ^{31}P NMR spectra, the signals of the two phosphorus nuclei in compounds **2** are manifested as doublets with $^2J_{PCP}$ = 18—26 Hz.

The ^{1}H NMR spectrum of compound **2a** contains signals for the trimethylsilyl group (δ(^{1}H) −0.4), the phenyl groups at P^{III} (δ(^{1}H) 7.4, multiplet), the ethoxy groups at P^{IV} (δ(^{1}H) 4, multiplet, and 1.2, triplet), and the methyl group (δ(^{1}H) 1.5, broad doublet). The characteristic high-field signal of the silyloxy groups at P^{IV} (δ(^{1}H) −0.7) corresponds to compound **2d**. Other signals coincide in chemical shifts with those for compound **2a**.

^{1}H NMR spectra were recorded on a Tesla BS-497 (60 MHz) spectrometer in $CDCl_3$ at a working frequency of 60 MHz with Me_4Si as the internal standard. ^{31}P NMR spectra were taken on a Varian FT-80A (32.4 MHz) instrument with 85% H_3PO_4 as the external standard. IR spectra were recorded on an IKS-22 instrument (NaCl). Reactions with diphenyl(trimethylsilyl)phosphine were conducted until the signal (δ(^{31}P) −57) in the ^{31}P NMR spectrum of the reaction mixture disappears. The reactions were carried out under dry argon in anhydrous solvents. The starting α-oxo phosphonates **1** were obtained by the reported method.[4]

The reaction of diphenyl(trimethylsilyl)phosphine with oxo phosphonates (general procedure). Diphenyl(trimethylsilyl)phosphine (5 mmol) was placed in a Schlenk vessel supplied with a dropping funnel, and α-oxo phosphonate (5 mmol) was added with stirring at 10 °C. The reaction mixture was kept for 30 min, and in the case of compounds **2a,c,d** the mixture solidified. The reaction mixture was warmed to −20 °C, and the crystals were washed with anhydrous diethyl ether (3×5 mL). Compounds **2a,c,d** were recrystallized from CH_2Cl_2. Compounds **2b,e** were isolated as oils after washing with anhydrous diethyl ether (3×5 mL). The yields of the reaction products, their melting points, and the spectral data are given in Table 1.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 98-03-33061a; the Leading Scientific Schools Program, Project No. 96-15-97484) and the Integration of Higher Schools and the Academy of Sciences Program (Grant No. 234).

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Received May 18, 1999;
in revised form June 22, 1999