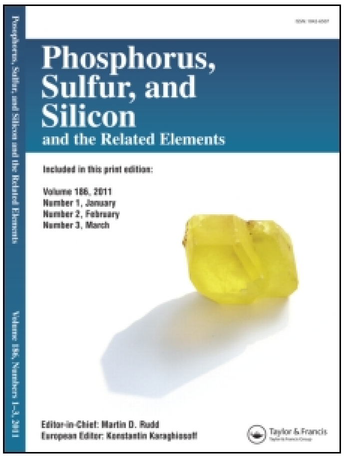

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STUDIES ON THE MECHANISM OF ACETOLYSIS OF DIPHENYLPHOSPHINYLPHENYLDIAZOMETHANE

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STUDIES ON THE MECHANISM OF ACETOLYSIS OF DIPHENYLPHOSPHINYLPHENYLDIAZOMETHANE

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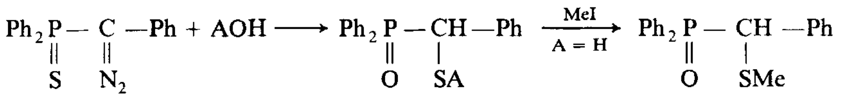
In an attempt to prove the existence of an oxaphosphorirane intermediate during the acetolysis reaction of diphenylphosphinylphenyldiazomethane (**1**), **1** was decomposed in ^{18}O-labeled acetic acid. However, the spectral analyses of the phosphinyl acetate (**7d**) thus obtained indicated that 1,2-oxygen migration caused by the formation of the anticipated oxaphosphorirane seemed not to occur.

The preparation of diazoalkanes containing heteroatom substituents and their decomposition to carbenes have been of current interest.[1] In particular, phosphinyldiazoalkanes have proved to be versatile reagents, undergoing the usual reactions of diazoalkanes and also showing carbenoid reactivity. They can be used to introduce a phosphoryl group into organic compounds, as in the phosphorylcyclopropanation of alkenes or arenes, and the phosphorylcyclopropenation of alkynes.[2] Phosphorylcarbenes also readily undergo rearrangements: hydride, alkyl, aryl, or acyl shifts leading to phosphorylated alkenes.[3]

Regitz has reported that carbenes derived from diphenylphosphinylphenyldiazomethane (**1**) insert into the O—H bonds of methanol and water to give α-methoxy- and α-hydroxybenzyldiphenylphosphine oxides, respectively.[4] On the other hand, we reported the synthesis of diphenylphosphinothioylphenyldiazomethane (**2**) and its thermolysis and photolysis which involve the following unusual 1,2 sulfur migration reaction (1).[5]



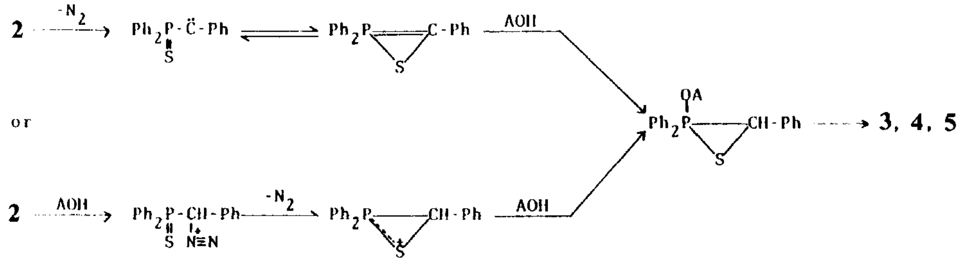
$$\underset{\underset{S}{\|}}{Ph_2P}-\underset{\underset{N_2}{\|}}{C}-Ph + AOH \longrightarrow \underset{\underset{O}{\|}}{Ph_2P}-\underset{\underset{SA}{|}}{CH}-Ph \xrightarrow[A = H]{MeI} \underset{\underset{O}{\|}}{Ph_2P}-\underset{\underset{SMe}{|}}{CH}-Ph \qquad (1)$$

2

3; A = MeCO
4; A = H

5

The formation of **3**, **4**, or **5** indicates a 1,2 sulfur migration during the reactions, and we have suggested a mechanism for these reactions involving a three-membered ring intermediate as shown in Scheme 1. On the basis of our results with the reaction of **2**, there is a possibility that insertion products from **1** might be formed through a similar 1,2 oxygen migration, giving a new phosphoryl oxygen atom from methanol or water. Therefore, we attempted the acetolysis reaction of ^{18}O-labeled diphenylphosphinylphenyldiazomethane (**1**) to determine whether such a 1,2 oxygen migration takes place.



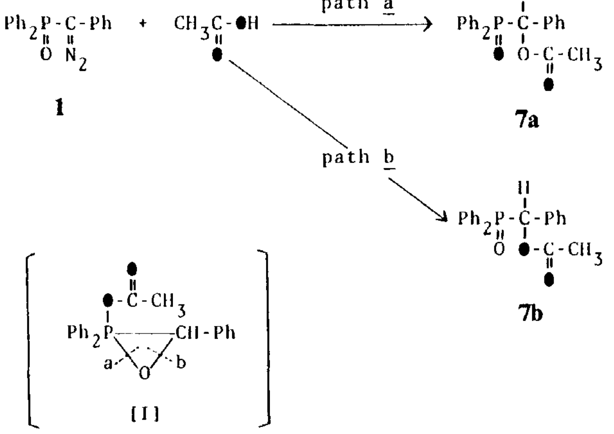
SCHEME 1

RESULTS AND DISCUSSION

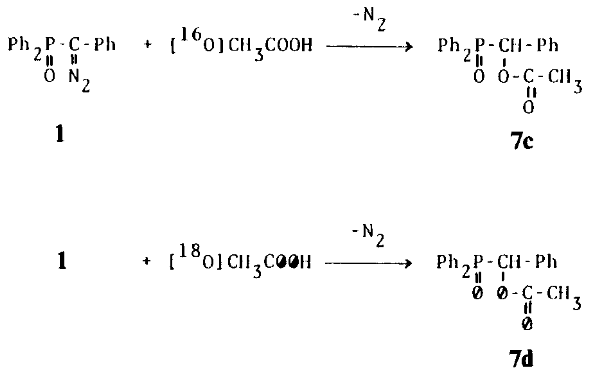
There are two possible methods for such mechanistic studies: use of ^{18}O-labeled phosphoryl compound or ^{18}O-labeled acetic acid. We chose use of the latter compound, because we were concerned with possible low ^{18}O-incorporation from ^{18}O-water.

If the reaction proceeds via an intermediate like [I] followed by fission *a*, the phosphoryl oxygen of the product might include heavy oxygen (path *a*), whereas if no rearrangement occurs the reaction might exclusively lead to **7b** (path *b*) as shown in Scheme 2. The notations O and ● symbolize ^{16}O- and ^{18}O-oxygens, respectively, and ◐ and Ø denote scrambled (a mixture of ^{16}O and ^{18}O) and unknown oxygens, respectively.

We carried out the acetolysis of **1** in ^{18}O-acetic acid, and the product (**7d**) of the acetolysis was analyzed by IR, ^{31}P NMR, ^{13}C NMR, and mass spectroscopy. Since 100% ^{18}O-enriched acetic acid was not available, we used scrambled acetic acid ($^{18}O_2 : {}^{18}O_1 : {}^{18}O_0 \simeq 1 : 2 : 1$) whose ^{18}O-enrichment was about 50%.



SCHEME 2



SCHEME 3

First, we carried out the reaction of benzyldiphenylphosphine oxide (**6**) with ^{18}O-acetic acid in order to confirm that phosphoryl oxygen suffers no oxygen exchange (2) under the conditions employed for the following reactions of **1**.

$$\mathrm{Ph_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{-CH_2-Ph} + [^{18}\mathrm{O}]\mathrm{CH_3C}\mathbf{O}\mathbf{O}\mathrm{H} \not\rightarrow \mathrm{Ph_2}\underset{\underset{\mathbf{O}}{\|}}{\mathrm{P}}\mathrm{-CH_2-Ph} \qquad (2)$$

6

Recently, ^{18}O isotope effects have been reported for ^{31}P NMR spectra,[6] and if the oxygen migration occurred, we should expect a heavy-oxygen isotope shift in the ^{31}P NMR signal, that is, an upfield shift caused by the ^{18}O nucleus directly bonded to ^{31}P nucleus. In a similar manner, an upfield shift has been shown to occur in ^{13}C NMR upon replacement of ^{16}O by ^{18}O.[7]

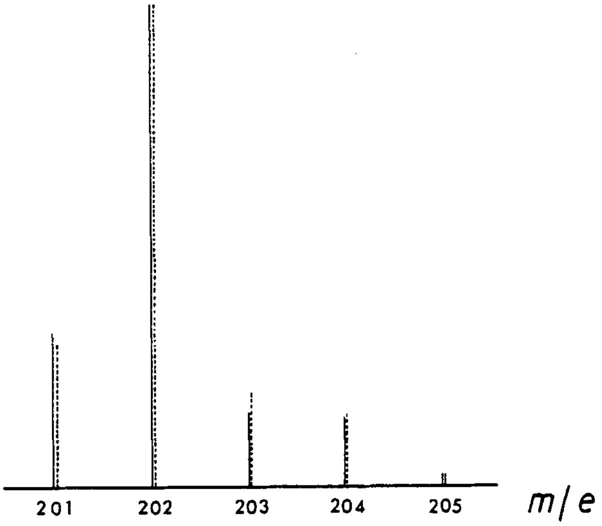
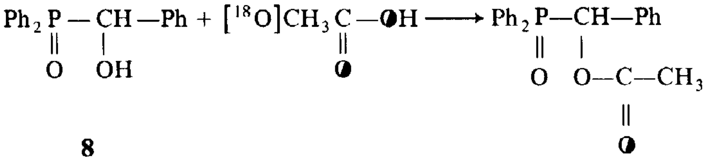


FIGURE 1 Observed and calculated peak intensities at *m/e* 201–205. —: Observed, ····: Calcd. for 27% migration.

Therefore, we attempted to detect the ^{18}O isotope shift by ^{31}P NMR and ^{13}C NMR, but failed to observe it in **7d**.

We observed a $\nu_{C=\bullet}$ (1715 cm^{-1}) in the IR spectrum of **7d**, whereas the $\nu_{C=O}$ of unlabeled **7c** was 1750 cm^{-1}. Moreover, we failed to observe a $\nu_{P=\bullet}$ in **7d**. Hence, we could not observe the 1,2 O-migration by IR. However, in the MS of **7d**, we noted the presence of fragment ions, $[\mathrm{Ph_2P\bullet}]^+$ and $[\mathrm{Ph_2P\bullet H}]^+$, which supported the possibility of the ^{18}O migration to the phosphorus atom. The ratio of $[\mathrm{Ph_2PO}]^+$ to $[\mathrm{Ph_2P\bullet}]^+$ was determined by comparing each peak (*m/e* 201–205) with the calculated intensities based on those observed for the unlabeled phosphinyl compound **7c**. The percentage of migration was thus calculated assuming that the reaction proceeds via either path *a* or path *b* in Scheme 2, and considering the known ^{18}O-contents of the ^{18}O-acetic acid used. Figure 1 shows the observed and the calculated fragmentation patterns for "27% migration," which was in conflict with the results by IR. In order to clarify the discrepancy, we prepared acetyl-labeled ester (**7e**) from α-hydroxybenzyldiphenylphosphine oxide (**8**) (3).



$$\mathrm{Ph_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OH}{|}}{CH}-Ph} + [^{18}\mathrm{O}]\mathrm{CH_3\underset{\underset{\bullet}{\|}}{C}-\bullet H} \longrightarrow \mathrm{Ph_2\underset{\underset{O}{\|}}{P}-\underset{\underset{O-\underset{\underset{\bullet}{\|}}{C}-CH_3}{|}}{CH}-Ph} \qquad (3)$$

8 **7e**

In a similar way, the ester (**7e**) was analyzed by MS and IR. In the IR spectrum no $\nu_{P=\bullet}$ was detected as expected, but by MS, **7e** showed 23% 1,2^{18}O-migration by comparison with the results for **7c**. Based on the mass spectral data, we came to the conclusion that the scrambling occurs in the MS.

From the above results, it is concluded that the acetolysis reaction of diphenylphosphinylphenyldiazomethane (**1**) does not proceed through 1,2 O-migration, but simply proceeds through a substitution reaction or an insertion of the resulting carbene to the O—H bond of acetic acid (path *b*) in Scheme 2. It is considered likely that the oxygen atom is too much smaller than sulfur to form the three-membered ring intermediate via path *a*.

EXPERIMENTAL

Mass spectra were measured on Hitachi RMU-6L and Jeol D-300 spectrometers (70 eV). IR spectra were measured with a Hitachi 260-30 spectrometer (KBr). ^{31}P NMR were run on a Jeol FX-90-Q spectrometer (36.28 MHz) using 85% H_3PO_4 as an external standard. ^{13}C NMR spectra were measured on a Jeol FX-90-Q spectrometer (22.53 MHz).

Benzyldiphenylphosphine oxide (**6**). To a solution of diphenylphosphine oxide (9.4 mMol) and butyllithium (10.4 mMol) in tetrahydrofuran (THF) (40 ml) was added benzyl chloride (16 mMol) in THF (15 ml) and the mixture was stirred for 20 hrs at room temperature. The reaction mixture was poured into cold aq. hydrochloric acid (4%), extracted with ether, and the extract was dried ($MgSO_4$). Evaporation of the extract gave **6** in 91% yield, m.p. 197–199°C (lit. 197–198°C^8), and ^{31}P NMR ($CHCl_3$) 29.35 ppm.

Diphenylphosphinylphenyldiazomethane (**1**). This compound was prepared by Regitz' method,^{9} m.p. 155–156°C (lit. 160°C), ^{31}P NMR ($CHCl_3$) 26.59 ppm, IR (KBr) $\nu_{P=O}$ 1188 and 1202, $\nu_{C=N_2}$ 2075 cm^{-1}.

α-Hydroxybenzyldiphenylphosphine oxide (**8**). The oxide was prepared by the literature method,[10] m.p. 168–170°C (lit. 172–174°C), and ^{31}P NMR ($CHCl_3$) 31.23 ppm.

^{18}O-Acetic acid. Acetyl chloride (13 mMol) was added dropwise to $H_2O—^{18}O$ (12 mMol) [Water-^{18}O (Normalized), 97 atom %^{18}O, Merck Sharp & Dohme Canada] with stirring at room temperature and the mixture was stirred for 2 hrs. Evolved HCl was removed at −20°C in vacuo and distillation gave ^{18}O-acetic acid in 68% yield (48.58% ^{18}O-enriched), b.p. 118°C. By mass spectral analyses, the isotopic contents of oxygen were $^{18}O_2 : {}^{18}O_1 : {}^{18}O_0 = 0.92 : 1.99 : 1.09$ on the basis of the intensities of the parent peaks (m/e 64, 62, and 60). No ^{18}O isotope effect was observed within the resolution of 0.06 Hz in ^{13}C NMR.

Reaction of **1** *with ^{18}O-acetic acid.* A mixture of **1** (0.135 mMol) and ^{18}O-acetic acid (0.22 mMol) was stirred at room temperature under argon for 1.5 days. The product (**7d**), after washing with water, was dried over anhydrous magnesium sulfate and recrystallized from benzene, m.p. 177–179°C. The yield was 83%, ^{31}P NMR ($CHCl_3$) 28.74 ppm, and IR (KBr) $\nu_{C=O}$ 1750, $\nu_{C=\bullet}$ 1715 cm^{-1}. There was no peak separation observed within the resolution of 0.24 Hz.

α-Acetoxybenzyldiphenylphosphine oxide (**7e**) *from alcohol* (**8**). A solution of ^{18}O-acetic acid (0.849 mMol), *N,N′*-dicyclohexylcarbodiimide (0.97 mMol),[11] **8** (0.958 mMol), and 4-pyrrolidinopyridine (0.09 mMol) in dichloromethane (8 ml) was allowed to stand at room temperature for 8 hrs. The resulting *N,N′*-dicyclohexylurea was filtered and the filtrate was successively washed with water (3 × 15 ml), 2% aq. hydrochloric acid (3 × 15 ml), and water (3 × 15 ml), dried ($MgSO_4$), and the solvent was evaporated in vacuo. **7e**; m.p. 177–179°C (72% yield), IR (KBr) $\nu_{C=O}$ 1750, $\nu_{C=\bullet}$ 1715, and $\nu_{P=O}$ 1200 cm^{-1}.

Mass spectral analyses. The observed MS results on **7d** and **7e** are shown in Table I, along with the calculated results for 27% and 23% migration, respectively. The intensity of the fragment ion, $[Ph_2POH]^+$, at m/e 202 (base peak) was normalized. The identification of each fragment ion (m/e 202 and 204) was confirmed by high-resolution mass spectral data (see Table II).

TABLE I

Calculated and Observed peak intensities of **7d** and **7e**

		7d		**7e**	
m/e	Fragment Ions	Obd.	Calcd.[a]	Obd.	Calcd.[b]
201	$[Ph_2PO]^+$	32.2	29.5	21.4	21.8
202	$[Ph_2POH]^+$	100	100	100	100
203	c	15.2	19.3	12.1	16.0
204	$[Ph_2P\bullet H]^+$	14.2	15.1	10.6	10.5
205	d	2.2	2.2	1.68	1.71

[a] Calcd. for 27% migration.
[b] Calcd. for 23% migration.
[c] $[Ph_2POH—^{13}C]^+ + [Ph_2POH_2]^+ + [Ph_2P\bullet]^+$.
[d] $[Ph_2P\bullet H—^{13}C]^+ + [Ph_2P\bullet H_2]^+$.

TABLE II

High-resolution mass spectral data of $[Ph_2POH]^+$ and $[Ph_2POH]^+$

	m/e	
Fragment Ions	Obd.	Calcd.
$[Ph_2POH]^+$	202.0583	202.0548
$[Ph_2P\bullet H]^+$	204.0546	204.0589

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