Table I. Data on Phosphate-Catalyzed Keto–Enol Tautomerism of Aldehydes and Compound I Reactions with Enols at 35 °C[a]

	equilibrium constant [enol]/[keto] K'_{enol}	rate constants, M^{-1} s^{-1} keto + phosphate k'_1	enol + phosphate k_{-1}
2-methylpropanal	1.2×10^{-4}	6.0×10^{-5}	0.5
propanal	8.0×10^{-6}	1.5×10^{-4}	19
butanal	5.5×10^{-6}	1.0×10^{-4}	19

[a] Ionic strength 0.67 M and pH 7.4; to correct for hydrate formation, multiply K'_{enol} and k'_1 by the factor $(1 + K_{hyd})$.

Table I. For 2-methylpropanal K_{enol} is 1.7×10^{-4} and k_1 8.6×10^{-5} M^{-1} s^{-1} with a correction for hydrate formation.[6] These results compare favorably with those obtained by other experimental and theoretical methods.[2]

Both propanal and butanal have cis–trans isomers in their enol forms. Our results can be fit with a single exponential curve for the burst phase which is followed by the linear zero-order phase. The burst results indicate either that there is no detectable difference in reactivity of the two geometric isomers with compound I, which would appear likely because of the known lack of selectivity in compound I reactions, or that one isomer is dominant. The observed linear behavior following the burst could be the sum of two zero-order reactions, one for each isomer.

Thus we have described a unique technique using peroxidase compound I for measuring rates and equilibria of keto–enol tautomerism which could readily be applied to a study of the influence of acid–base catalysts upon the rates.

(6) Pocker, Y.; Dickerson, D. G. *J. Phys. Chem.* **1969**, *73*, 4005-4012. Green, L. R.; Hine, J. *J. Org. Chem.* **1973**, *38*, 2801-2806.

Phosphinocarbene–Phosphaalkene Rearrangement and Intramolecular Wittig-like Reaction Involving a Phosphorus Vinyl Ylide

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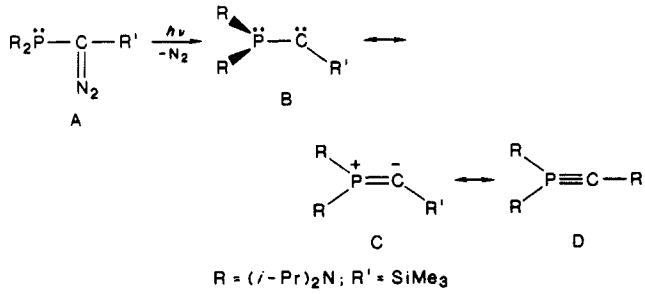
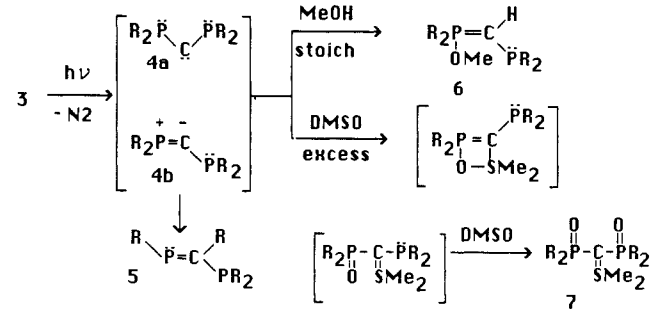
During the last decades, two of the most fascinating areas in chemistry have been the synthesis and reactivity of electron-deficient species and of p_π–p_π multiply bonded heavier main-group-element derivatives. We have recently prepared the first α-diazophosphines A and have shown by intermolecular trapping reactions that the corresponding α-phosphinocarbene B is a synthetic equivalent of phosphorus–carbon multiple-bonded species C or D.[1,2]



[†] Université Paul Sabatier.
[‡] Laboratoire de Chimie de Coordination du CNRS.

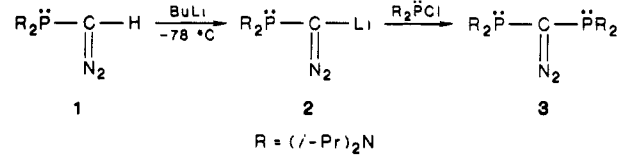
(1) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781.

Scheme I



Here we wish to report that, although phosphinocarbenes always possess a multiple-bond character, intramolecular rearrangements typical of either carbene or ylide behavior may occur, depending on the nature of the diazo–carbon substituent.

Bis(phosphino)diazomethane **3**[3] was prepared by a two-step, one-pot reaction from the [bis(diisopropylamino)phosphine]diazomethane (**1**)[1] via the corresponding lithium salt **2**.



From an acetonitrile–benzene solution, **3** recrystallized at room temperature as air-stable orange crystals in 85% yield and was fully characterized including by X-ray analysis.[4] Of particular interest, the N–N bond length (1.15 Å) is slightly longer, and the C–N bond distance (1.28 Å) is slightly shorter, than those observed in diazoalkanes.[5] The lower multiplicity of the nitrogen–nitrogen bond is confirmed by a low IR frequency (2010 cm^{-1}).

Photolysis in benzene solution at 300 nm or attempted distillation of **3** at 100 °C (10^{-2} mmHg) led to phosphaalkene **3**[3] in nearly quantitative yield. This rearrangement could either result from a concerted migration–nitrogen-loss mechanism or involve a phosphinocarbene intermediate **4**. In fact, products **6** and **7**,[3] obtained by irradiation of **3** in the presence of methanol and dimethyl sulfoxide, respectively, clearly demonstrate the intermediacy of a phosphinocarbene **4** possessing phosphorus–carbon multiple-bond character (Scheme I). Note that the trapping agents do not react with **3** in the absence of UV light.

Addition of the lithium salt **2** to acyl chlorides led after workup to a mixture of acetylenic derivatives **10**[3] and 1,3,4-oxadiazoles **9**[3] that were fully characterized, including an X-ray analysis for **9b**.[4] However, when trimethylacetyl chloride was used, phosphino diazo ketone **8a** was observed in solution at 0 °C by NMR (δ ^{31}P +70.6) and IR ($\nu(CN_2)$ 2045, $\nu(CO)$ 1640 cm^{-1}) spectroscopy. Products **10** can also be obtained in one step by heating the silylated diazophosphine **11**[1] with acyl chlorides (Scheme II).

In contrast with **3**, no 1-2 shift, which would have led to phosphaalkenes **13** or phosphinoketenes **14**, was observed. It seems quite reasonable to postulate that **10** results from an intramolecular Wittig-like reaction involving a phosphorus vinyl ylide **12b** (Scheme III).

These results, as a whole, support theoretical calculations that predict, for the parent compound H_2PCH, a phosphinocarbene phosphorus vinyl ylide separation of only 4 kcal/mol[6] and a small energy barrier for the rearrangement to the more thermodynamically favored phosphaalkene structure. Moreover, it is clear that although α-dicarbenoid species of the first-row elements always behave as triple-bonded compounds;[7] in contrast, when a second

(2) Other unstable α-diazophosphines have recently been prepared: Keller, H.; Maas, G.; Regitz, M. *Tetrahedron Lett.* **1986**, *27*, 1903.
(3) Microanalytical, mass spectral, IR, and NMR data for each new compound isolated are given in the supplementary material.
(4) Full details of X-ray crystal structures will be published elsewhere.
(5) Patai, S. *The Chemistry of Diazonium and Diazo Groups*; Wiley: New York, 1978.
(6) Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F. *Inorg. Chem.* **1986**, *25*, 2185.

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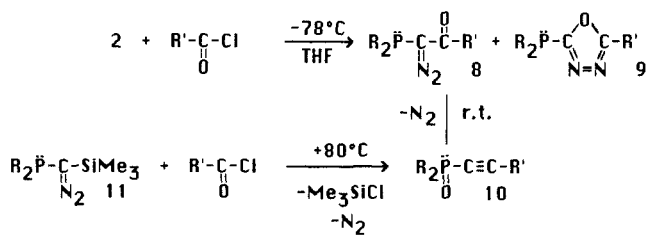
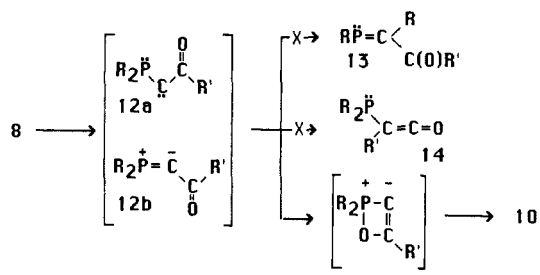
Scheme II



Scheme III



row element is involved, the carbenoid character is competitive, as recently shown for –S–N,[8] –C–SF_3,[9] and even –Si–Si–[10] derivatives.

Acknowledgment. We thank the CNRS (GRECO Basses Coordinences) for support of this research.

Supplementary Material Available: Microanalytical, mass spectral, IR, and NMR (^1H, ^{13}C, ^{31}P, ^{15}N) data (3 pages). Ordering information is given on any current masthead page.

(7) Curtis, T. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 2161.
(8) Glemser, O.; Mews, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 883 and references cited therein. Atkinson, R. S.; Judkins, B. D. *J. Chem. Soc., Perkin Trans.* **1981**, 2615.
(9) Pötter, B.; Seppelt, K.; Simon, A.; Peters, E. M.; Hettich, B. *J. Am. Chem. Soc.* **1985**, *107*, 980.
(10) Sekiguchi, A.; Zigler, S. S.; West, R., unpublished results.

Thiophosphoryl-Transfer Reactions: A General Synthesis and Configurational Analysis of O-Substituted [^{16}O,^{18}O]Thiophosphates

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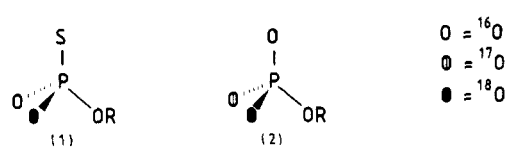
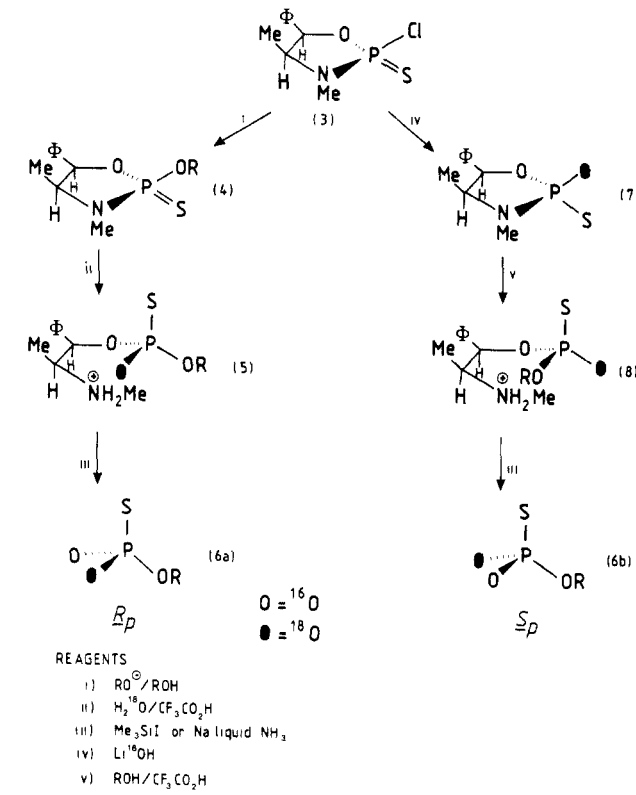
Received May 28, 1986

[^{16}O,^{18}O]Thiophosphate (**1**) and [^{16}O,^{17}O,^{18}O]phosphate (**2**) esters have been utilized extensively to determine the stereochemical course of many enzyme-catalyzed thiophosphoryl-[1] and



phosphoryl-transfer[2] reactions. Although the stereochemical

Scheme I



courses of some simple chemical phosphoryl-transfer reactions have recently been determined,[3,4] hitherto *simple thiophosphoryl*-transfer reactions have not been studied. With existing methods these would in fact be difficult to determine. Such studies would be of interest since (i) the stereochemical course of enzyme-catalyzed thiophosphoryl-transfer reactions has frequently been assumed to be the same as for the natural phosphoryl-transfer reaction and it would be pertinent to determine whether these reactions are indeed stereochemically equivalent[5] and (ii) thiophosphate monoesters have been reported to react more rapidly via a dissociative reaction than the corresponding phosphate esters.[6] We report here the first simple chemical configurational analysis of structures such as **1** (R = alkyl or aryl)[7] together with general synthetic routes to simple [^{16}O,^{18}O]thiophosphate monoesters (**1**).[8]

Our two general routes to isotopically chiral [^{16}O,^{18}O(or ^{17}O)]thiophosphate monoesters of either the R_P or S_P absolute configuration are shown in Scheme I. By analogy with the previously published route(s) to [^{16}O,^{17}O,^{18}O]phosphate esters,[9]

(1) Eckstein, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 423. Frey, P. A. *Tetrahedron* **1982**, *38*, 1541.
(2) Knowles, J. R. *Annu. Rev. Biochem.* **1980**, *49*, 877. Lowe, G. *Acc. Chem. Res.* **1983**, *16*, 244. Gerlt, J. A.; Coderre, J. A.; Mehdi, S. *Adv. Enzymol.* **1983**, *55*, 291.
(3) Buchwald, S. L.; Knowles, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1438. Buchwald, S. L.; Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4911. Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6126.
(4) Cullis, P. M.; Rous, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 6721. Cullis, P. M.; Rous, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 1298.
(5) The demonstration for a number of enzymes that phosphoryl and thiophosphoryl transfer proceed with the same stereochemical course (see ref 1 and 2) would suggest that within the constraints of the enzyme active site these two reactions are equivalent.
(6) Breslow, R.; Katz, I. *J. Am. Chem. Soc.* **1968**, *90*, 7376.
(7) Two configurational analyses have been reported for AMPS ^{18}O and other nucleoside [^{18}O]thiophosphates: the first relies on the stereospecific enzyme-catalyzed phosphorylation of the *pro-R/S* oxygen as the key step (Sheu, K.-F. R.; Frey, P. A. *J. Biol. Chem.* **1977**, *252*, 4445); the second method has assigned the absolute configurations of the *O,S*-dimethyl nucleoside triesters by relating these to the *O*-methyl nucleoside diesters which have been assigned on the basis of the known stereoselectivity of snake venom phosphodiesterase (Cummins, J. H.; Potter, B. V. L. *J. Chem. Soc., Chem. Commun.* **1985**, 851). Neither method was suitable for our proposed study.
(8) Previous syntheses of isotopically chiral thiophosphate monoesters based on the *meso*-hydrobenzoin route (Cullis, P. M.; Lowe, G. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2317. Jarvest, R. L.; Lowe, G. *J. Chem. Soc., Chem. Commun.* **1979**, 364) have been reported but not extensively applied. Similarly [γ-^{16}O,^{18}O,S]ATP and [^{18}O]AMPS have been synthesized by routes that would not easily be extendible to simple thiophosphate esters.

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