(s-E)-diene conformation; e.g., **1h**, were found to participate readily in the LUMO$_{\text{diene}}$-controlled Diels–Alder reactions.[9] The stereochemistry of the [4 + 2] cycloaddition reaction products was established by spectroscopic techniques and was unambiguously confirmed with the single-crystal X-ray structure determination of adduct **9**.[13,14]

Studies of full scope of the inter- and intramolecular [4 + 2] cycloaddition reactions of α,β-unsaturated N-benzenesulfonyl imines as well as their applications are in progress and will be reported in due course.

Acknowledgment. This work was assisted through the financial support of the National Institutes of Health (CA 42056) and the Alfred P. Sloan Foundation. We thank Professor S. M. Weinreb for helpful discussions and Dr. P. Fanwick of the Purdue University X-ray Crystallography facility for the prompt experimental treatment of the X-ray structure determination of **9**.

Supplementary Material Available: General experimental procedures and full spectroscopic and physical characterization of **1a–j**, **2c–d**, **3–14** and full details of the X-ray structure determination of **9** are provided (30 pages). Ordering information is given on any current masthead page.

Oxaphosphetane Pseudorotation: Rates and Mechanistic Significance in the Wittig Reaction

Edwin Vedejs* and Charles F. Marth

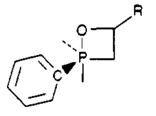
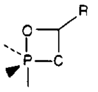
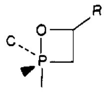
S. M. McElvain Laboratory of Organic Chemistry
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706

Received September 26, 1988

Theoretical investigations suggest a small energy advantage for the oxaphosphetane **1** vs **2** (hypothetical gas-phase species),[1] but the choice of **1** over **2** as the favored Wittig intermediate *in solution* has not been proved and is based on ^{1}H NMR chemical shifts and solid-state analogies.[2,3] The structures of unusually stable pseudorotamers **3,3′**, **4,4′**, and related compounds were likewise assigned by analogy.[4-6] We now report ^{13}C NMR evidence that **1** is indeed the favored solution species, together with the kinetics of pseudorotamer interconversion.

The NMR spectra of oxaphosphetanes **5,5′** (from Ph$_2$MeP=CH$_2$ + 3-pentanone; ^{1}H NMR, toluene-d_8: ring CH$_2$, δ 3.56, d, ^{1}J = 16.4 Hz; CH$_3$P, δ 1.91, d, ^{1}J = 13.7 Hz), **8a**,[7] or the analogous **8b** (^{13}C spectra; Table I) at −83 °C or above showed only one set of signals, indicating either a single pseudorotamer or rapid interconversion. However, the ^{1}H spectrum of dibenzophosphole (DBP) analogue **9,9′** (from (Me)DBP=CH$_2$ + 3-pentanone, −53 °C) contained two signals for the ring methylene protons (^{1}H NMR, CD$_2$Cl$_2$; ring CH$_2$, δ 3.92, d, ^{1}J = 16.5 Hz; δ 2.81, d, ^{1}J = 15.5 Hz; CH$_3$P, δ 1.72, d, ^{1}J = 14.1 Hz) and coalescence was observed near room temperature. Line shape analysis[8] (five points from −3 to +40 °C) gave the free energy $\Delta G^{\ddagger}_{\text{PSDRTN}}$ = 13.1 kcal/mol, but the fast exchange limit could not be reached due to competing Wittig decomposition to alkene and phosphine oxide, $\Delta G^{\ddagger}_{\text{DEC}}$ = 25 kcal/mol (43–55 °C, monitored by NMR).

Table I. ^{13}C NMR Data for Oxaphosphetanes **5**, **8**, and **9**

	chemical shifts (coupling)			
carbon	**8a**[a]	**8b**[a]	**9**[b]	**5**[c]
	obscured	133.8 ppm (125.0 Hz)	134.3 ppm (132.3 Hz)	148.8 ppm (70.5 Hz)
	54.3 ppm (87.4 Hz)	61.2 ppm (85.6 Hz)	54.5 ppm (82.2 Hz)	60.3 ppm (83.0 Hz)
	28.3 ppm (98.1 Hz)	29.6 ppm (99.0 Hz)	21.9 ppm (98.1 Hz)	24.4 ppm (96.4 Hz)

[a] Spectrum at −30 °C, deuterated toluene. [b] Spectrum at −53 °C, CD$_2$Cl$_2$. [c] Spectrum at −53 °C, deuterated toluene.

The detailed structure of oxaphosphetane **9,9′** (−53 °C, slow exchange) is defined by the ^{13}C spectrum. Three quaternary aromatic (DBP) carbons (δ 152.7, d, J = 12 Hz; 143.1, d, J = 18 Hz; 135.9, d, J = 14 Hz) cannot be assigned with certainty, but a fourth signal at δ 134.3 ppm is unique because of the large ^{13}C–^{31}P coupling (^{1}J = 132 Hz), characteristic of an equatorial sp^2 carbon in the trigonal bipyramid.[9] Equally informative is the ^{13}C–^{31}P coupling constant of $^{1}J_{\text{P–C}}$ = 82 Hz for the ring C-3 signal (δ 54.5). The J value is consistent with **9** or **9′**, but not with the equatorial oxygen isomer **10** where apical C-3 should have $^{1}J_{\text{P–C}} < 20$ Hz.[9]

The characteristic ^{13}C–^{31}P coupling constants **9,9′** can be used to evaluate the geometry of unconstrained oxaphosphetanes. For example, the averaged ^{13}C NMR spectrum of pseudorotamers **5,5′** has nearly the same $^{1}J_{\text{P–C}}$ = 83 Hz for C$_3$ as in **9,9′** (82 Hz), indicating that the population of **7** is negligible.[10] The quaternary aryl C–P coupling of 70.5 Hz is close to the mean estimated if **5**/**5′** are dominant relative to **6** at equilibrium (0.5[$^{1}J_{\text{equat}}$ = ca. 132 Hz + $^{1}J_{\text{apical}}$ = ca. 15 Hz] = 74 Hz). Similarly, the ^{13}C NMR spectra of **8a** and **8b** (Table I) correspond to dominant pseudorotamers having apical oxygen and the DBP unit spanning apical–equatorial sites. These results confirm the conventional oxaphosphetane representations **1**, **5**, **9**, etc. as orginally assumed for typical Wittig intermediates.[2]

Pseudorotation rates (k_{PSDRTN} = 5.6 × 10^3 sec^{-1})[11] and decomposition rates k_{DEC} = 7.3 × 10^{-5} s^{-1}) for **9** at 43 °C differ by a factor of ca. 10^8 and the corresponding free energies of activation differ by 11.5 kcal/mol. Only the minimum pseudorotation rate of **5** can be estimated ($k_{\text{PSDRTN}} \geq 3 \times 10^3$ s^{-1} at −83 °C) since the coalescence temperature could not be reached, but the activation barrier for alkene formation $\Delta G^{\ddagger}_{\text{DEC}}$ is again greater than ca. 10 kcal/mol above the pseudorotation barrier. Therefore, pseudorotation does not control the rate of the Wittig decomposition step.

---

(1) (a) Höller, R.; Lischka, H. *J. Am. Chem. Soc.* **1980**, *102*, 4632. (b) Bestmann, H. J.; Chandrasekhar, J.; Downey, W. G.; Schleyer, P. von R. *J. Chem. Soc., Chem. Commun.* **1980**, 978. (c) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987**, *109*, 1.

(2) (a) Vedejs, E.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1973**, *95*, 5778. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823.

(3) (a) Ul-Haque, M.; Caughlan, C. N.; Ramirez, F.; Pilot, J. F.; Smith, C. P. *J. Am. Chem. Soc.* **1971**, *93*, 5229. (b) Bestmann, H. J.; Roth, K.; Wilhelm, E.; Bohme, R.; Burzlaff, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 876.

(4) Ramirez, F.; Pfohl, S.; Tsolis, E. A.; Pilot, J. F.; Smith, C. P.; Ugi, I.; Marquarding, D.; Gillespie, P.; Hoffmann, P. *Phosphorus* **1971**, *1*, 1.

(5) (a) Gibson, J. A.; Röschenthaler, G. *Z. Naturforsch. B* **1977**, *32*, 599. Allwörden, U.; Tseggai, I.; Röschenthaler, G.-V. *Phos. Sulfur* **1984**, *21*, 177. (b) Kolodyazhnyi, O. I. *J. Gen. Chem. USSR* **1986**, *56*, 246.

(6) **3** and **3′** decompose at 120 °C without interconversion. **4** and **4′** pseudorotate rapidly at 20 °C because one oxygen can always occupy an apical site; see: Ramirez, F.; Ugi, I. *Adv. Phys. Org. Chem.* **1971**, *9*, 25; and ref 5a.

(7) Vedejs, E.; Marth, C. F. *J. Am. Chem. Soc.* **1988**, *110*, 3948.

(8) (a) Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1978**, *32*, 145. (b) DNMR5 program: Stephenson, D. S.; Binsch, G. *Quantum Chemistry Program Exchange* **1978**, *11*, 365.

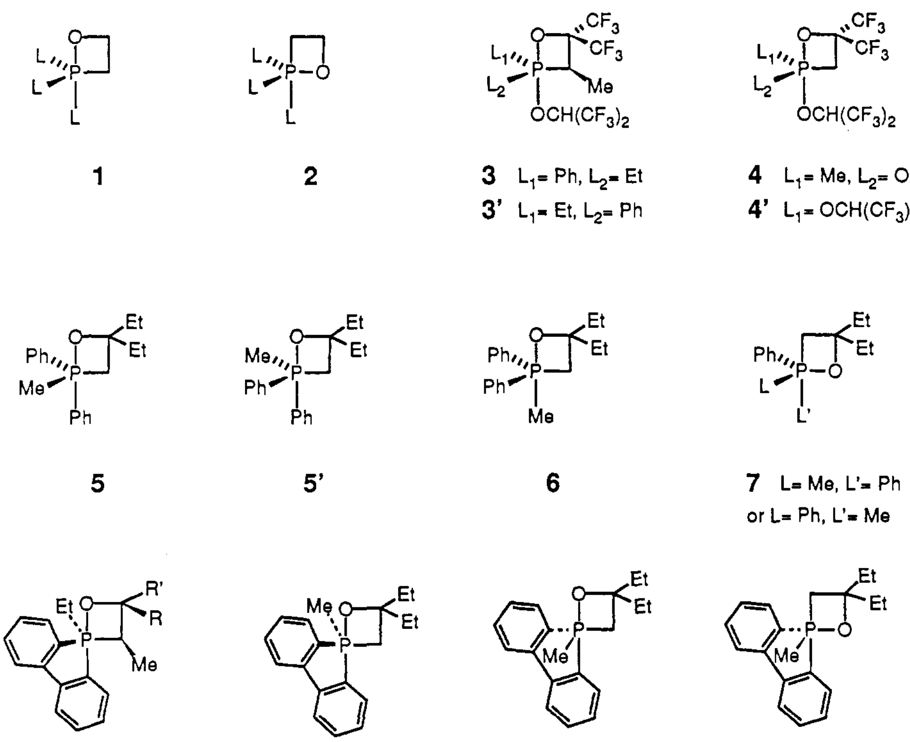
(9) Kay, P. B.; Trippett, S. *J. Chem. Research (S)* **1986**, 62.

(10) $J_{\text{P–C}}$ = 84–85 Hz is reported for adducts of Ph$_3$P=^{13}CHC$_3$H$_7$ + PhCHO: Maryanoff, B. E.; Reitz, A. B.; Mutter, M. S.; Inners, R. R.; Almond, H. R., Jr.; Whittle, R. R.; Olofson, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 7664.

(11) Similar pseudorotation rates are observed for other DBP-containing phosphoranes, precedents that guided our selection of **8** and **9** for study: Hellwinkel, D.; Lindner, W.; Schmidt, W. *Chem. Ber.* **1979**, *112*, 281, and earlier references therein. Whitesides, G. M.; Eisenhut, M.; Bunting, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5398.

0002-7863/89/1511-1519$01.50/0

Chart I



1 2 3 L_1= Ph, L_2= Et

3' L_1= Et, L_2= Ph

4 L_1= Me, L_2= $OCH(CF_3)_2$

4' L_1= $OCH(CF_3)_2$, L_2= Me

5 5' 6 7 L= Me, L'= Ph or L= Ph, L'= Me

8a R= H, R'= CMe_2CH_2Ph

8b R= R'= Et

9 9' 10

Even though $\Delta G^{\ddagger}_{DEC}$ is of much higher energy than $\Delta G^{\ddagger}_{PSDRTN}$, there can still be an *apparent* correlation between slow decomposition rates and slow pseudorotation in certain oxaphosphetanes such as **3** and **4** compared to **5**. Consider the relevant transition-state geometries; TS_{PSDRTN} lies between **1** and **2**, and will increasingly resemble **2** as the stability of **2** vs **1** decreases (Hammond postulate). Since **2** has equatorial oxygen, the partly rehybridized P–C_3 bond in TS_{PSDRTN} will be longer than in **1**. TS_{DEC} should also have an elongated P–C_3 bond because advanced P–C vs C–O bond breaking is predicted according to bond strength comparisons as well as calculations.[1] Both TS_{DEC} and TS_{PSDRTN} in **3** or **4** will therefore be destabilized by the electronegative CF_3 groups, substituents that favor trigonal-bipyramidal structures, apical oxygen geometries, and shorter (equatorial) P–C_3 bonds.[12] The result will be a decrease in k_{DEC} and a *coincidental* decrease in k_{PSDRTN}. In more typical Wittig intermediates, the geometry of TS_{DEC} leading to alkene could be increasingly different from the geometry of **2** or of TS_{PSDRTN}. However, the geometric options are severely restricted for any cyclic 4-membered structure that contains phosphorus, and TS_{DEC} will have certain geometric features in common with **2** regardless of mechanistic details.

The conclusion that both TS_{DEC} and TS_{PSDRTN} have an elongated P–C_3 bond does not mean that **2** is a required intermediate[13] or that any specific pseudorotamer is necessary before decomposition can occur. A preequilibrium of **1** with **2** affects decomposition rates only if (1) TS_{PSDRTN} is greater than or comparable to TS_{DEC} in free energy, or (2) if **2** is more stable than **1**. Otherwise, the relative populations of pseudorotamers or the path to the transition state can have no kinetic significance (Curtin–Hammett principle).[14] Advanced P–C_3 bond breaking in the decomposition step is likely in any event, and this interpretation would apply to a diradical cleavage as well as to an asynchronous cycloreversion. We prefer the latter description for the decomposition of typical Wittig intermediates to alkenes and phosphine oxide pending further evidence.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8603163).

---

[12] Holmes, R. R. *Pentacoordinate Phosphorus*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol I and II.

[13] (a) Bestmann, H. J.; Vostrowsky, O. *Top. Curr. Chem.* **1983**, *109*, 85. (b) Bestmann, H. J. *Pure Appl. Chem.* **1980**, *52*, 771. (c) Bestmann, H. J. *Pure Appl. Chem.* **1979**, *51*, 515.

[14] For a discussion of fundamentals, see: Eliel, E. L. *Stereochemistry of Carbon Compounds*, McGraw-Hill: New York, 1962; pp 151–152 and 237–239.

A Novel Example of a Di-μ-chloro-Stabilized Octahedral Coordination of Aluminum by Cyclam. Synthesis and Molecular Structure of $[(CH_3)_2AlCl]_2[Al{\cdot}C_{10}H_{20}N_4][Al(CH_3)_2]$

Gregory H. Robinson,* Mark F. Self, Samuel A. Sangokoya, and William T. Pennington

Department of Chemistry, Clemson University
Clemson, South Carolina 29634-1905

Received October 31, 1988

For some time now this laboratory has had an interest in the organoaluminum chemistry of multidentate amines. Interactions of organoaluminum species with multidentate amines containing N–H fragments have proven to be quite interesting in that such systems, characteristically involving Al–R/N–H bond cleavage, result in novel organoaluminum products possessing extensive aluminum–nitrogen networks. We have recently reported several such unusual organoaluminum compounds.[1-6] To assess the

---

[1] Robinson, G. H.; Sangokoya, S. A.; Moise, F.; Pennington, W. T. *Organometallics* **1988**, *7*, 1887.

[2] Robinson, G. H.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 1453.

[3] Robinson, G. H.; Appel, E. S.; Sangokoya, S. A.; Zhang, H.; Atwood, J. L. *J. Coord. Chem.* **1988**, *17*, 373.

[4] Robinson, G. H.; Moise, F.; Pennington, W. T.; Sangokoya, S. A. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 387.

[5] Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852.

[6] Robinson, G. H.; Rae, A. D.; Campana, C. F.; Byram, S. K. *Organometallics* **1987**, *6*, 1227.

0002-7863/89/1511-1520$01.50/0