10080 *J. Am. Chem. Soc.* **1994,** *116,* 10080–10088

Theoretical Study of the Structure and Reactivity of Ylides of N, P, As, Sb, and Bi

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Received August 23, 1993[®]

Abstract: The theoretical calculations at the MP2/DZ+d level have been carried out for the formation and the reaction of a series of ylides of group 15 elements, $H_3M{=}CH_2$, M = N, P, As, Sb, and Bi. First, the preparation of ylides by means of the salt method was evaluated: $MH_3 + CH_3Cl \rightarrow H_3M^+{-}CH_3 + Cl^-$, and $H_3M^+{-}CH_3 + OH^- \rightarrow H_3M{=}CH_2 + H_2O$. The ylide formation was most feasible for P, but it is highly endothermic for N and Bi. These ylides have in general larger ylide rather than ylene character, and the carbanion character increases in the order P < As < Sb < Bi. The N ylide is different from others in that it shows no double bond character at all; the N—C bond in $H_3N{-}CH_2$ is even longer than that in $H_2N{-}CH_3$. Two reaction routes of these ylides with formaldehyde were then investigated: $H_3M{=}CH_2 + H_2C{=}O \rightarrow$ ethylene + $H_3M{=}O$ (Wittig type) and $H_3M{=}CH_2 + H_2C{=}O \rightarrow$ ethylene oxide + MH_3 (Corey type). The Wittig reaction is favored both kinetically and thermodynamically for the P ylide. For the As, Sb, and Bi ylides, on the other hand, the Wittig-type reaction is favored kinetically but the Corey-type reaction is thermodynamically preferred. These differences are attributed to the relative oxygen affinity and the $H_3M{=}CH_2$ bond strength of these group 15 elements. The N ylide is very reactive in the Corey-type reaction due to the weak $H_3N{=}CH_2$ bond, but no intermediate nor transition state was found in the Wittig route. The different reaction pattern of the N ylide was primarily attributable to the larger electronegativity of N compared to P, As, Sb, Bi, and H.

Introduction

The Wittig reaction, the reaction of a phosphorus ylide with a carbonyl compound, is one of the most important organic transformations, and extensive investigation has been carried out from both the synthetic and the mechanistic points of view.[1,2] However, the study of analogous reactions by use of ylides of other group 15 elements has been limited.[3,4] An arsine ylide is known to undergo facile reactions with aldehyde but in different manners. It either gives alkene and arsine oxide, a Wittig-type reaction, or yields alkene oxide and trisubstituted arsine, a Corey-type reaction, depending on the structure of the ylide and the carbonyl compound. For example, the reaction of $Ph_3As{=}CHPh$ with PhCHO in THF gives stilbene oxide in 79% yield together with 7% stilbene, while the reaction with $Et_3As{=}CHPh$ affords 1% stilbene oxide and 87% stilbene.[5] On the other hand, only very few reports have been documented on the reaction of a carbonyl compound with analogous ylides of other elements, *i.e.*, Sb, Bi, and N.[6]

Several ab initio calculations have been carried out for the structures and the reactions of phosphorus ylides.[7-18] Calculations at the HF/4-31G* level for two possible reaction channels, the Wittig and the Corey pathways, showed that the Wittig route is favorable both kinetically and thermodynamically for the phosphorus ylide.[8] However, this study alone does not tell us why the Wittig reaction proceeds so smoothly for the phosphorus ylide. In the present study, we have carried out extensive ab initio calculations at a higher level of theory on the formation of ylides and their subsequent reactions with aldehyde in the two reaction routes and compared the results for ylides of five different group 15 elements. Several mechanistic questions were investigated, such as (1) why the P ylide favors Wittig reaction over the Corey reaction, (2) why the As ylide behaves differently from the P ylide, (3) what the stability and the reactivity of the Sb and Bi ylides are, and (4) why the N ylide does not undergo the Wittig-type reaction.

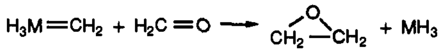
Theoretical Models and Computation

We have considered two phases of the ylide chemistry, the formation and the character as well as the reaction of ylides. First, calculations were carried out for two reactions (eqs 1 and 2), which are the most common sequence of reactions to synthesize ylides from alkyl halide. The relative feasibility of the ylide formation and the character and stability of the ylides are considered here. Then the two reactions of the ylides with formaldehyde were studied in detail (eqs 3 and 4).

$$MH_3 + CH_3Cl \longrightarrow H_3\overset{+}{M}{-}CH_3 + Cl^- \qquad (1)$$

$$H_3\overset{+}{M}{-}CH_3 + OH^- \longrightarrow H_3M{=}CH_2 + H_2O \qquad (2)$$

$$H_3M{=}CH_2 + H_2C{=}O \longrightarrow CH_2{=}CH_2 + H_3M{=}O \qquad (3)$$



$$H_3M{=}CH_2 + H_2C{=}O \longrightarrow CH_2(O)CH_2 + MH_3 \qquad (4)$$

M = N, P, As, Sb, and Bi

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[®] Abstract published in *Advance ACS Abstracts*, October 1, 1994.

(1) Maryanoff, B. E.; Raitz, A. B. *Chem. Rev.* **1989,** *89,* 863.

(2) Vedejs, E. *Top. Stereochem.*, in press.

(3) Johnson, A. W., Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993.

(4) Huang, Y. Z.; Shen, Y. *Adv. Organomet. Chem.* **1982,** *20,* 115.

(5) Gosney, I.; Lillie, T. J.; Lloyd, D. *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 487.

(6) Henry, M. C.; Wittig, G. *J. Am. Chem. Soc.* **1960,** *82,* 563.

(7) Lischka, H. *J. Am. Chem. Soc.* **1977,** *99,* 353.

(8) Höller, R.; Lischka, R. *J. Am. Chem. Soc.* **1980,** *102,* 4632.

(9) Eades, R. A.; Gassman, P. G.; Dixon, D. A. *J. Am. Chem. Soc.* **1981,** *103,* 1066.

(10) Vincent, M. A.; Schaefer, H. F., III; Schier, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1983,** *105,* 3806.

(11) Dixon, D. A.; Dunning, T., Jr.; Eades, R. A.; Gassman, P. G. *J. Am. Chem. Soc.* **1983,** *105,* 7011.

(12) Yates, B. F.; Bouma, W.; Radom, L. *J. Am. Chem. Soc.* **1984,** *106,* 5805.

(13) Dixon, D. A.; Smart, B. E. *J. Am. Chem. Soc.* **1986,** *108,* 7172.

(14) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987,** *109,* 1.

(15) Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1987,** 47.

(16) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987,** *109,* 2250.

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Table 1. Dependence of the Level of Computation on the Calculated Energy for the Reactions of $H_3P{=}CH_2$ with $H_2C{=}O$[a]

method	reactants	P_{1TS}	P_{10}	P_{20}	P_{2TS}	$CH_2CH_2 + H_3P{=}O$	P_{TS}	$CH_2CH_2O + PH_3$
HF/4-31G*	–494.753 86 (0.0)	–494.741 13 (8.0)	–494.811 54 (–36.2)	–494.806 52 (–33.0)	–494.761 03 (–4.5)	–494.833 09 (–49.7)	–494.714 64 (24.6)	–494.809 77 (–35.1)
HF/6-31G*	–495.258 67 (0.0)	–495.248 72 (6.2)	–495.310 29 (–32.4)	–495.305 48 (–29.4)	–495.261 56 (–1.8)	–495.338 53 (–50.1)	–495.216 24 (26.6)	–495.315 32 (–35.5)
HF/DZ+d	–160.906 73 (0.0)	–160.895 23 (7.2)	–160.956 87 (–31.5)	–160.950 98 (–27.8)	–160.908 16 (–0.9)	–160.986 09 (–49.8)	–160.863 48 (27.1)	–160.956 85 (–31.5)
MP2/DZ+d[b]	–161.450 32 (0.0)	–161.451 69 (–0.9)	–161.513 63 (–39.7)	–161.511 77 (–38.5)	–161.472 69 (–14.0)	–161.527 31 (–48.3)	–161.431 57 (11.8)	–161.498 00 (–29.9)

[a] In atomic units. Numbers in parentheses are the energies relative to the reactants (kcal/mol). [b] The energies and relative energies of M_{comp} and M_{1comp} are –161.456 32 (–3.8) and –161.459 59 (–5.8), respectively.

All calculations were carried out at the second-order Møller-Plesset perturbation (MP2) level[19] unless otherwise noted, with all electrons correlated by using the Gaussian 90[20] and 92[21] programs. For the first-row atoms the double-ζ (DZ) basis sets of Dunning and Hay[22] were used which were augmented with a set of six d-type polarization functions (d exponents 0.75 (C), 0.80 (N), and 0.85 (O)) while the 3-21G basis set was used for H.[23] For the heavier atoms the DZ basis sets and effective core potentials (ECP's) developed by Wadt and Hay[24] were employed; the relativistic ECP's were used for Sb and Bi. The DZ basis sets were augmented by a set of six d-type polarization functions (d exponents 0.550 (P), 0.293 (As), 0.211 (Sb), 0.185 (Bi), and 0.75 (Cl)). Optimizations were carried out by using gradient procedures. Vibrational frequencies were calculated at the HF level in order to characterize stationary points on the Wittig as well as the Corey reaction surface as minima or saddle points, and the geometries were further optimized at the MP2 level. Zero-point correction was made, after scaling by 0.9 for overestimation of the HF frequencies, when appropriate. The charge densities reported are based on the natural population analysis.[25,26] Geometrical parameters and vibrational frequencies are listed in the supplementary material.

Recent calculations by Bachrach indicated that improvement of the basis set beyond 6-31G* results in very little change in the calculated structures of P ylides.[18] The MP2 optimization was also noted to have little effect on the structures. In the present investigation, we have carried out preliminary calculations for the reactions of $H_3P{=}CH_2 + H_2C{=}O$ with various methods and compared the results. As Table 1 shows, the calculated energy of the transition state was found to highly depend on the level of optimization; for example, transition state P_{1TS} is higher in energy than the reactants at the HF level while it is lower at the MP2 level. Therefore, we report all the structures and energies obtained at the MP2/DZ+d level in this paper.

Results and Discussion

Ylide Formation. Phosphorus ylides are usually prepared by the reaction of phosphine and alkyl halide, followed by proton abstraction from the resultant phosphonium salt by an appropriate base. Arsine ylides may be synthesized in a similar manner,[3,4] but the ylides of Sb, Bi, and N are not easily accessible by this salt method due to the lower nucleophilicity of MR_3 as well as the lower stability of the ylides.[6] Thus, a nitrogen ylide can be prepared by the salt method using a strong base such as PhLi, but is only stable as the Li salt complex.[27,28] A stibonium salt could not be prepared from the reaction of $SbPh_3$ with methyl halides, but a more reactive methylating agent, $[(CH_3)_3O^+][BF_4^-]$, should be used; the salt thus prepared was treated with PhLi to give the Sb ylide.[6] A bismuth ylide is most difficult to obtain, and only a stabilized ylide has been prepared by the reaction of a diazo compound with $BiPh_3$.[29] A stabilized Sb ylide was also synthesized by the same method.[30] In the present investigation, we have first of all considered how large a difference exists in the ylide preparation process for $H_3M{=}CH_2$, M = N, P, As, Sb, and Bi.

The reaction energy of the onium salt formation from MH_3 and CH_3Cl (eq 1) was calculated at the MP2/DZ+d level. The absolute values will not be discussed because the absence of solvation effect makes the reaction highly endothermic (132.4, 134.7, 146.7, 151.5, and 165.0 kcal/mol for M = N, P, As, Sb, and Bi, respectively) and also because the basis set used here is not adequate for anionic species.[31,32] In spite of the known deficiency of the basis set used here for calculations of energies of anion species, the calculated reaction energies are not very much different from the gas-phase experimental values for M = N (122.3 kcal/mol) and P (122.0 kcal/mol).[33] Furthermore, Cl^- is common for the series of elements, and thus the calculated reaction energy should reflect the relative intrinsic nucleophilicity of a series of MH_3. Clearly NH_3 and PH_3 are much more nucleophilic than AsH_3 and SbH_3, and BiH_3 is least nucleophilic. The reaction energies of the proton abstraction from the salt yielding the ylides (eq 2) were found to be –124.2 (N), –154.9 (P), –149.9 (As), –147.3 (Sb), and –145.3 (Bi) kcal/mol. Here again, the absolute numbers are exaggerated, but the calculated trend is cnsistent with the results of deuterium exchange experiments of tetramethylonium salts (Me_4M^+, I^-, M = N, P,

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(17) Streitwieser, A.; Rajca, A.; McDowell, R. S.; Glaser, R. *J. Am. Chem. Soc.* **1987**, *109*, 4184.

(18) Bachrach, S. M. *J. Org. Chem.* **1992**, *57*, 4367.

(19) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.

(20) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, I. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *GAUSSIAN 90*; Gaussian Inc.: Pittsburgh, PA, 1990.

(21) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andress, J. L.; Rachavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(22) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 3, pp 1–27.

(23) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(24) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(25) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(26) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(27) Wittig, G.; Wetterling. *Liebigs Ann. Chem* . **1947**, *557*, 193.

(28) Wittig, G.; Polster, R. *Liebigs Ann. Chem.* **1956**, *599*, 1.

(29) Loyd, D.; Singer, M. I. C. *Chem. Ind. (London)* **1967**, 787.

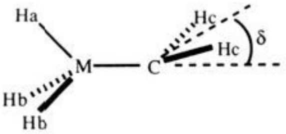
(30) Loyd, D.; Singer, M. I. C. *J. Chem. Soc., Chem. Commun.* **1971**, 2941.

(31) It is known that there are difficulties in calculating energies of anions such as Cl^- and OH^-; these cannot be adequately treated by the basis set used here. However, the computation of the exact reaction energies is not the purpose of the present study; the purpose is to see the difference in the reaction energies for different M elements. We have calculated $E(Cl^-) - E(CH_3Cl)$ at MP4SDTQ with and without the diffuse function, and found that the energy is 7.5 kcal/mol smaller with the diffuse function. Thus, the reaction energies reported in the paper are overestimated by about 7.5 kcal/mol for all M elements, but the relative reaction energies are not affected by the error associated with Cl^- or OH^-.

(32) One of the reviewers suggested that the MP2 level of theory can be too low for estimating the effect of M on the energetics of reaction 1. In order to test the influence of the level of theory on the effect of M, higher level calculations were carried out with the diffuse function for reactions 1, 2, 5, and 6. Shown in Table 8 are the reaction energies calculated at the MP4SDTQ as well as QCISD(T) level on the MP2-optimized geometry, together with those of some similar calculations with the 6-311+G(2d,p) basis set. The results indicate that the influence of the calculation method on the relative reaction energies for different M elements is small (~2 kcal/mol), and therefore the use of MP2 is justified. Furthermore, the use of a larger basis set, 6-311+G-(2d,p), at the MP4SDTQ and QCISD(T) levels resulted in only a slight difference in the reaction energies.

(33) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*, 1.

Table 2. Calculated Parameters of $H_3M{=}CH_2$, M = N, P, As, Sb, and Bi[a]



M	M=C	M—H_a	M—H_b	C—H_c	δ	q_M[b]	q_C[c]
N	1.561	1.039	1.026	1.104	67.6	−0.795	−0.741
P	1.681	1.433	1.401	1.090	29.2	0.955	−1.207
As	1.819	1.555	1.510	1.095	46.1	1.016	−1.184
Sb	2.014	1.745	1.695	1.100	50.4	1.357	−1.235
Bi	2.117	1.807	1.749	1.106	61.4	1.222	−1.110

[a] At MP2/DZ+d. All distances in angstroms and all angles in degrees. [b] Natural charges on M. [c] Natural charges on C.

Table 3. M—C Bond Lengths and Bond Orders of $H_3M{=}CH_2$, $HM{=}CH_2$, and $H_2M{-}CH_3$[a]

M	$H_3M{=}CH_2$	$HM{=}CH_2$	$H_2M{-}CH_3$
N	1.561	1.290	1.473
	(0.773)	(1.928)	(0.928)
P	1.681	1.679	1.861
	(1.360)	(1.748)	(0.896)
As	1.819	1.799	1.987
	(1.286)	(1.754)	(0.906)
Sb	2.014	1.993	2.178
	(1.275)	(1.682)	(0.869)
Bi	2.117	2.058	2.251
	(1.061)	(1.644)	(0.843)

[a] At MP2/DZ+d. Numbers in parentheses are bond orders.

As, and Sb).[34] The proton abstraction is most favorable for the phosphonium ion and least favorable for the ammonium ion. The overall feasibility of the ylide formation can be evaluated by eq 5, the combination of the onium salt formation from MH_3 and

$$MH_3 + CH_3OH \rightarrow H_3M^+{-}CH_3 + OH^- \rightarrow H_3M{=}CH_2 + H_2O \quad (5)$$

$$\Delta E \text{ (kcal/mol)} = 66.2 \text{ (N)}, 37.7 \text{ (P)}, 54.7 \text{ (As)}, 62.1 \text{ (Sb)}, 77.6 \text{ (Bi)}$$

CH_3OH, and the ylide formation from the onium salt and hydroxide anion. Clearly the P ylide is most easily formed among the five group 15 ylides. The N ylide and the Bi ylide are very high in energy thermochemically.

One way to estimate the relative stability of the ylides is to compare the internal proton transfer energies (eq 6).[11,12,16] It

$$H_3M{=}CH_2 \rightarrow MH_2{-}CH_3 \quad (6)$$

$$\Delta E \text{ (kcal/mol)} = -68.2 \text{ (N)}, -52.3 \text{ (P)}, -68.2 \text{ (As)}, -77.3 \text{ (Sb)}, -93.0 \text{ (Bi)}$$

was reported that the N ylide is 73.5 and 66.3 kcal/mol higher in energy than methylamine while the values are 57.9 and 52.5 for the P analog at the MP3/6-31G**//HF/6-31G*[16] and POL-CI[12] levels, respectively; thus, the P ylide is more stable than the N ylide. The present calculations at MP2/DZ+d gave the same trend for the N and P ylides and further indicate that the ylide of a heavier element becomes progressively unstable, consistent with the results shown above.

Character of Ylides. In Tables 2 and 3 are listed the calculated parameters of the ylides, together with some of the geometrical parameters of $HM{=}CH_2$ and $H_2M{-}CH_3$. The P—C bond length for $H_3P{=}CH_2$ was found to be 1.681 Å, similar to that (1.679 Å) calculated for $HP{=}CH_2$ but much shorter than that (1.861 Å) for $H_2P{-}CH_3$. The $H_3M{=}CH_2$ bond length for the heavier elements becomes progressively longer from 1.681 Å for P to 2.117 Å for Bi, and that for the Bi ylide is halfway in between $HBi{=}CH_2$ and $H_2Bi{-}CH_3$. From these, one might consider that the P ylide has a large contribution from the ylene structure. Contrary to these geometrical features, however, the ab initio bond order[35,36] at the MP2 level was calculated to be 1.360 for $H_3P{=}CH_2$; thus, this species has higher ylide rather than ylene character. This is consistent with the extensive calculations on phosphorus ylides by Radom[12,16] and Bachrach.[18] The bond order becomes smaller for a heavier element, and is nearly unity for the Bi ylide. The out-of-plane bending angle (δ) of the P ylide was calculated as 29.2°, in agreement with the observed value (28°) by X-ray analysis for $Ph_3P{=}CH_2$,[37] and found to increase in the

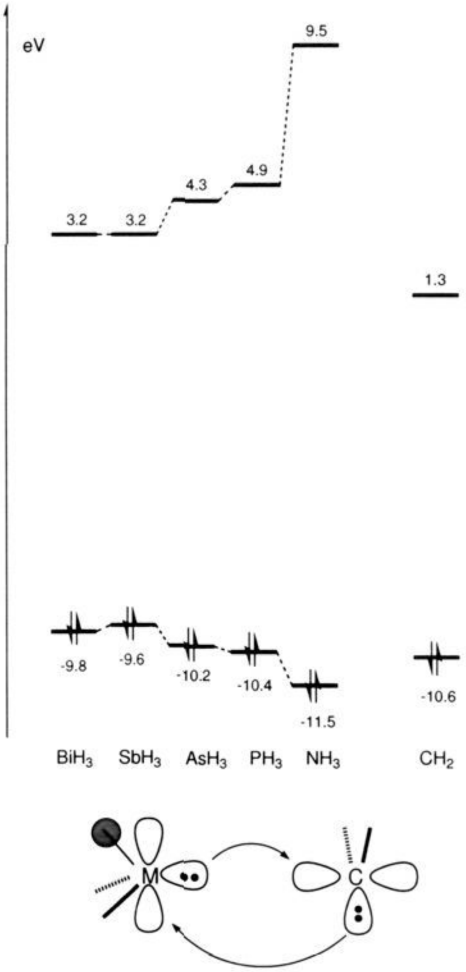


Figure 1. Bonding model of $H_3M{=}CH_2$ and the frontier molecular orbital levels of MH_3 and CH_2 ($^1A_1$).

Table 4. Reaction Energy for the Wittig and Corey Reactions[a]

M	ΔE_3[b]	ΔE_4[c]	$\delta\Delta E$[d]
N	−1.5 (0.0)	−58.3 (−52.6)	56.8 (−52.6)
P	−48.3 (−46.0)	−29.9 (−27.8)	−18.4 (−18.2)
As	−34.8 (−32.7)	−46.9 (−44.0)	12.1 (11.3)
Sb	−31.1 (−29.1)	−54.3 (−50.9)	23.2 (21.8)
Bi	−22.8 (−20.5)	−69.7 (−65.7)	46.9 (45.2)

[a] MP2/DZ+d energies (kcal/mol). Numbers in parentheses are energies with zero-point correction based on the HF frequencies. [b] Reaction energies of eq 3. [c] Reaction energy of eq 4. [d] Relative reaction energy, $\Delta E_3 - \Delta E_4$.

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(34) Doering, W. von E.; Hoffmann, K. *J. Am. Chem. Soc.* **1955**, *77*, 521.

(35) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 73; **1986**, *29*, 477.

(36) Villar, H. O.; Dupuis, M. *Chem. Phys. Lett.* **1987**, *142*, 59.

(37) Schmidbaur, H.; Jeong, J.; Achier, A.; Graf, W.; Wilkinson, D. L.; Muller, G. *New J. Chem.* **1989**, *13*, 341.

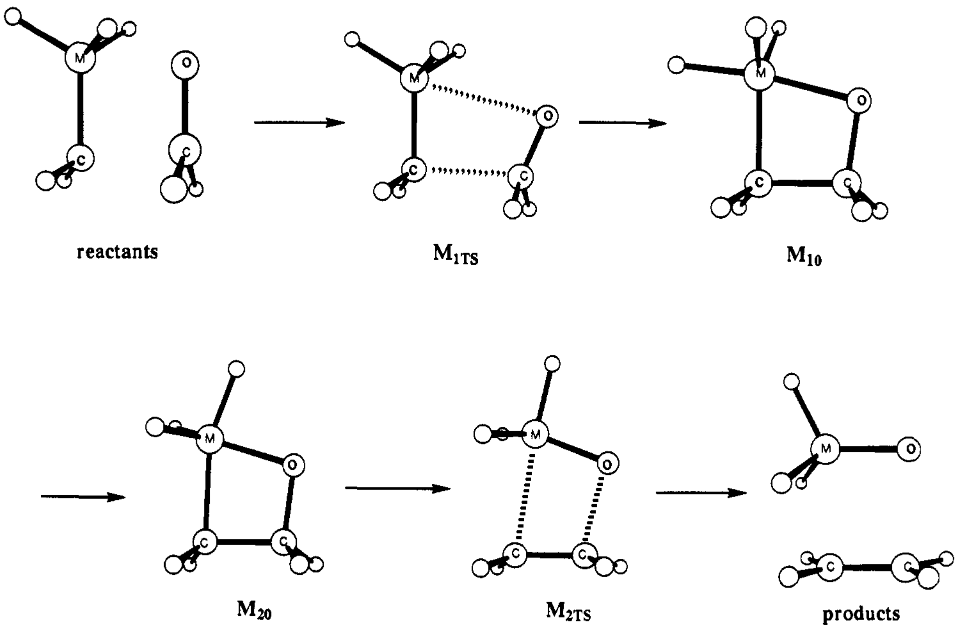

Figure 2. Reaction route of the Wittig-type reaction.

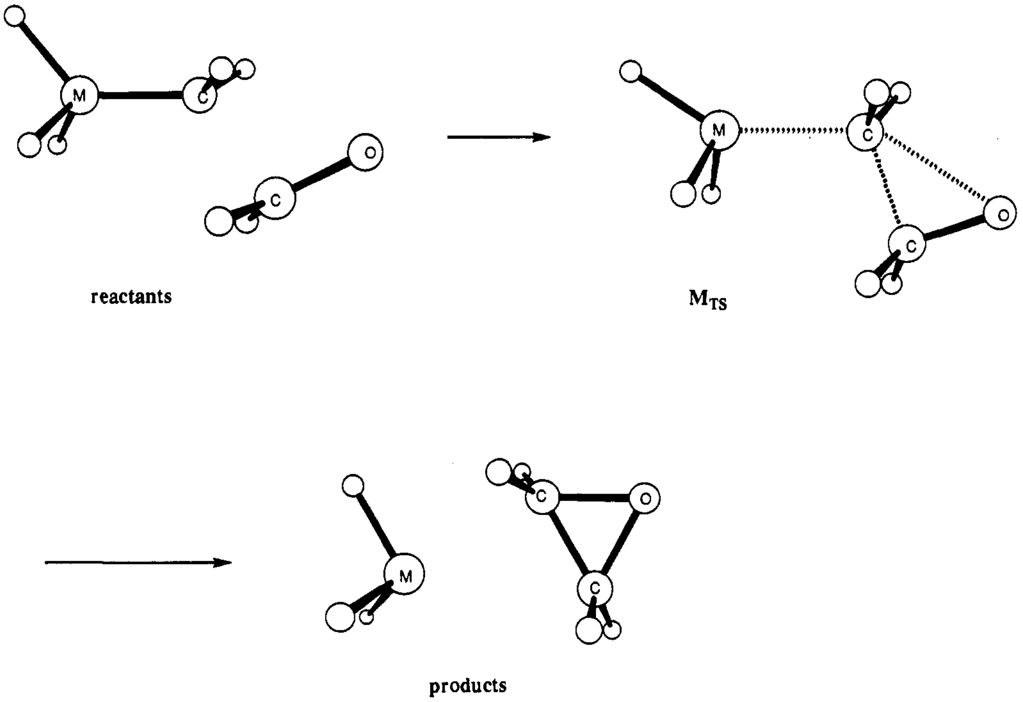

Figure 3. Reaction route of the Corey-type reaction.

order As (46.1°) < Sb (50.4°) < Bi (61.4°). Thus, the ylide has larger carbanion character in this order.[38]

The N ylide showed quite different character from the ylides of other group 15 elements as reported previously by Radom[16] and by Dixon and Gassman.[9,11] The N—C bond length is not in between those of $HN{=}CH_2$ and $H_2N{-}CH_3$, but is longer than the single bond of $H_2N{-}CH_3$. The out-of-plane angle is as large as 67.6°. The angle is within the region expected for simple carbanions such as $^-CH_3$ and $CH_3{}^-CHCH_3$; the angles for these species are 71.2° and 61.3°, respectively, at HF/6-31G*.[18] The N—C bond order of $H_3N{=}CH_2$ was calculated to be 0.773, showing that the bond is weaker than a single bond. The HOMO of the N ylide has little π-bond character as exhibited by the overlap population (−0.022 for the N ylide compared to 0.303 for the P ylide), consistent with these structural characteristics. Therefore, it is concluded from the calculations that the ylide carbon of the N ylide should have strong nucleophilic character, which was indeed observed experimentally.[39]

The differences in the ylide structure can be rationalized by regarding that the ylide results from an interaction between MH_3 and CH_2 ($^1A_1$) (Figure 1). Radom compared the binding energies of the $H_3M{-}CH_2$ ($^1A_1$) bond as a measure of the stability of a series of ylides ($HX{=}CH_2$, X = NH_2, OH, F, PH_2, SH, Cl) and found that the binding energy is much smaller for the first-row system than the second-row system.[16] On the basis of the frontier molecular orbital argument the N—C bond is expected to be very weak because (1) the interaction between the LUMO of CH_2 and the HOMO of NH_3 is unfavorable due to the low HOMO level of NH_3 and (2) the interaction of the HOMO of CH_2 with the LUMO of NH_3 is unlikely due to the high LUMO level of

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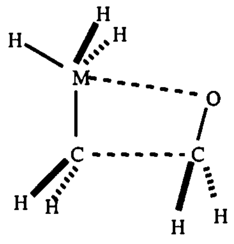
[38] Yamamoto, Y.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1975**, 668.

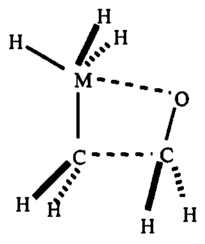
[39] Doering, W. von E.; Hoffmann, A. K. *J. Chem. Soc., Chem. Commun.* **1975**, 668.

Table 5. Geometrial Parameters of M_{1comp}, M_{1TS}, M_{10}, M_{20}, M_{2TS}, M_{comp}, and M_{TS}, M = P, As, Sb, and Bi[a]



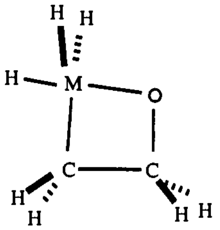
M_{1comp}

M	C–C	M–O	M–C	C–O	C–C–O	C–M–O	M–C–C
P	2.933 (0.032)	3.296 (0.005)	1.694 (1.281)	1.231 (1.912)	108.7	83.3	87.5
As	2.901 (0.037)	3.303 (0.006)	1.830 (1.209)	1.232 (1.905)	109.0	80.5	88.0
Sb	2.896 (0.030)	3.415 (0.010)	2.025 (1.193)	1.232 (1.906)	109.4	75.4	90.0
Bi	2.805 (0.031)	3.352 (0.015)	2.128 (0.987)	1.233 (1.895)	108.0	72.7	90.7



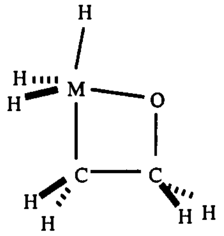
M_{1TS}

M	C–C	M–O	M–C	C–O	C–C–O	C–M–O	M–C–C
P	2.081 (0.319)	2.691 (0.049)	1.737 (1.014)	1.273 (1.643)	110.3	74.8	93.8
As	2.204 (0.254)	2.763 (0.041)	1.860 (1.023)	1.262 (1.690)	109.3	74.2	91.9
Sb	2.367 (0.173)	2.889 (0.046)	2.049 (1.053)	1.252 (1.746)	107.6	72.4	90.4
Bi	2.429 (0.135)	2.956 (0.044)	2.145 (0.910)	1.246 (1.783)	106.5	70.8	90.5



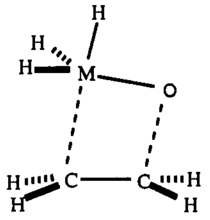
M_{10}

M	C–C	M–O	M–C	C–O	C–C–O	C–M–O	M–C–C
P	1.539 (0.852)	1.790 (0.580)	1.852 (0.836)	1.430 (1.023)	98.4	76.3	89.6
As	1.544 (0.835)	1.941 (0.615)	1.972 (0.843)	1.427 (1.049)	102.1	72.4	90.3
Sb	1.546 (0.817)	2.075 (0.590)	2.166 (0.822)	1.431 (1.033)	105.4	67.9	89.8
Bi	1.546 (0.818)	2.167 (0.500)	2.238 (0.740)	1.422 (1.071)	107.4	65.8	90.2



M_{20}

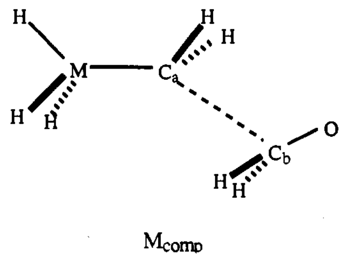
M	C–C	M–O	M–C	C–O	C–C–O	C–M–O	M–C–C
P	1.521 (0.873)	1.699 (0.791)	1.934 (0.732)	1.466 (0.918)	97.6	76.1	87.5
As	1.527 (0.865)	1.869 (0.755)	2.046 (0.747)	1.454 (0.957)	101.6	72.2	88.4
Sb	1.534 (0.848)	2.030 (0.683)	2.214 (0.739)	1.451 (0.973)	105.0	67.7	88.7
Bi	1.534 (0.846)	2.127 (0.569)	2.285 (0.661)	1.438 (1.022)	107.2	65.6	89.1



M_{2TS}

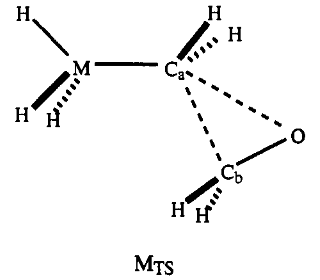
M	C–C	M–O	M–C	C–O	C–C–O	C–M–O	M–C–C
P	1.406 (1.281)	1.565 (1.159)	2.394 (0.311)	1.863 (0.413)	104.0	78.7	80.5
As	1.402 (1.312)	1.701 (1.192)	2.510 (0.280)	1.914 (0.403)	106.6	76.2	81.4
Sb	1.394 (1.362)	1.865 (1.144)	2.667 (0.232)	2.012 (0.369)	108.8	73.7	82.9
Bi	1.393 (1.395)	1.933 (1.015)	2.765 (0.197)	2.007 (0.380)	109.9	70.8	82.9

Table 5 (Continued)



M_{comp}

M	$M–C_a$	$C_a–C_b$	$C_b–O$	$C_a–O$	$M–C_a–C_b$	$C_a–C_b–O$	$M–C_a–O$
N	1.540 (0.665)	1.562 (0.807)	1.312 (1.554)	2.365 (0.058)	107.7	110.5	139.0
P	1.691 (1.307)	2.963 (0.009)	1.227 (1.948)	3.540 (0.006)	134.4	108.0	153.6
As	1.828 (1.222)	2.897 (0.014)	1.228 (1.943)	3.461 (0.007)	141.7	107.0	161.5
Sb	2.022 (1.227)	2.852 (0.015)	1.228 (1.940)	3.394 (0.008)	139.3	105.5	159.6
Bi	2.124 (1.015)	2.741 (0.024)	1.229 (1.927)	3.277 (0.012)	143.1	101.9	164.9



M_{TS}

M	$M–C_a$	$C_a–C_b$	$C_b–O$	$C_a–O$	$M–C_a–C_b$	$C_a–C_b–O$	$M–C_a–O$
N	1.725 (0.397)	1.514 (0.867)	1.348 (1.312)	2.112 (0.307)	115.6	95.0	155.1
P	1.968 (0.559)	1.586 (0.708)	1.322 (1.338)	2.120 (0.242)	112.2	93.1	150.7
As	1.928 (0.835)	1.795 (0.486)	1.279 (1.587)	2.395 (0.098)	120.3	101.1	151.9
Sb	2.107 (0.901)	1.951 (0.340)	1.263 (1.667)	2.486 (0.085)	126.7	99.1	156.8
Bi	2.188 (0.803)	2.101 (0.235)	1.251 (1.738)	2.566 (0.080)	136.0	96.6	165.0

[a] At MP2/DZ+d. All distances in angstroms and all angles in degrees. Numbers in parentheses are bond orders.

NH_3. The absence of the latter interaction is responsible for the lack of π-bond character of the N ylide. Among the series of the P, As, Sb, and Bi ylides, the difference in the energy level of the frontier MOs is small. The interaction between MH_3 and CH_2 would be most favorable for the P ylide due to the shortest M—C bond length as well as the most effective orbital overlap among the series, and therefore the P—C bond should have the largest double bond character. The increasing out-of-plane angle, P < As < Sb < Bi < N, reflects the decreasing double bond character in this order.

Another way of looking at the factor that makes the N—C bond of the N ylide longer than the single bond of $H_2N—CH_3$ is the electronic properties of the molecules. At the MP2 level, the natural charges on M in MH_3 were calculated to be -1.13, 0.12, 0.20, 0.47, and 0.50 for M = N, P, As, Sb, and Bi, respectively, consistent with the electronegativity order (N > H > P > As > Sb > Bi). Since the charge on C in CH_2 ($^1A_1$) is negative (-0.15), an attractive interaction arises when MH_3 and CH_2 approach each other for M = P, As, Sb, and Bi. This electrostatic effect between MH_3 and CH_2 is reflected in the charge distribution in $H_3M{=}CH_2$; as listed in Table 2, the ylide carbon bears a negative charge for all the ylides, and this negative charge is counterbalanced by the adjacent positive charge on M for P, As, Sb, and Bi. For M = N, however, the electrostatic interaction cannot be attractive due to the large electronegativity of N. This electronic effect on the M—C bond length can be supported by comparing the bond lengths of $H_3M{=}CH_2$ and $H_3M^+—CH_3$. For M = P, $H_3P^+—CH_3$ has a longer P—C bond length (1.803 Å) than $H_3P{=}CH_2$ simply because the protonated ylide has no π-bond character any more. In contrast, $H_3N^+—CH_3$ has a shorter N—C bond length (1.516 Å) than $H_3N{=}CH_2$, consistent with the reduced electrostatic repulsion upon protonation.

Reactions of Ylides. Ylides can react with aldehydes in either of two possible modes, the Wittig-type reaction (eq 3) and the Corey-type reaction (eq 4). The reaction energies for these processes calculated at the MP2/DZ+d level are listed in Table 4. The Wittig reaction is favored for the P ylide by 18.2 kcal/mol as expected, while all other ylides prefer the Corey-type reaction. The energetic preference for the latter reaction is substantial for the N ylide (52.6 kcal/mol) and Bi ylide (45.2 kcal/mol) but not so large for the As ylide (11.3 kcal/mol).

The extensive studies in the literature from both experimental and theoretical viewpoints have shown that the Wittig reaction proceeds through the oxaphosphetane intermediates (Figure 2, M = P).[1,2,8,14] The current view is as follows. The first intermediate (P_{1O}), in which the new P–C bond lies in the apical position of the pentacoordinated P atom, forms via [2s + 2s] cycloaddition with the planar cyclic transition state (P_{1TS}) in the gas phase.[7,8] This process is formally symmetry-forbidden but was calculated to be feasible because of the highly polar character of both the ylide and aldehyde.[8] The second intermediate (P_{2O}), which has the P–O bond in the apical position, is slightly higher in energy than the first one, and gives the final product through P_{2TS}. The Corey-type reaction, on the other hand, goes through the transition state P_{TS}, in which the aldehyde oxygen attacks the ylide carbon, displacing PH_3 (Figure 3).

P, As, Sb, and Bi Ylides. The fact that the first Wittig transition state (M_{1TS}) is lower in energy than the reactants indicates the presence of a complex between the two states. Indeed, we could find complexes, M_{1comp}, for four ylides (M = P, As, Sb, and Bi), whose geometrical parameters are listed in Table 5.[40] In Table 6 are summarized the relative energies with respect to the reactants of all the extrema on the Wittig reaction surface. It can be seen that the complexation induces little geometrical change in both the ylide and aldehyde, although it lowers the energy by about 6 kcal/mol. The C–C bond lengths are very large, indicating that the interaction between the ylides and the aldehyde is basically electrostatic. The geometrical parameters of M_{1TS} are shown in Table 5. All the M_{1TS}'s have planar geometries as observed previously for P_{1TS}.[8] The reaction barrier is lower and the C–C bond length is longer in the order P < As < Sb < Bi; thus, the complex is more reactive and the transition state is earlier for M_{1comp} of the heavier element. The C–C bond order (0.319–0.135) is much larger than the M–O bond order (0.049–0.041) for each M_{1TS}, and thus the cyclization is highly asynchronous.

General features of the geometries of M_{1O} and M_{2O} are basically the same for the four elements (Table 5). M_{1O} is slightly more

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(40) In order to assure that the complex formation is not due to the basis set superposition error (BSSE) in the MP2/DZ+d level, calculations with a larger basis set were carried out at the MP2/6-311+G(2df,p) level. The results clearly indicate that BSSE is not important in the present case; for example, P_{1comp} was calculated to be -5.9 kcal/mol more stable than the reactants at MP2/6-311+G(2df,p), which is very close to -5.8 kcal/mol at MP2/ZD+d.

Table 6. Relative Energies with Respect to the Reactants of the Extrema in the Wittig- and Corey-Type Reactions[a]

M	M_{1comp}	M_{1TS}	M_{10}	M_{20}	M_{2TS}	M_{comp}	M_{TS}
N						−19.1	−17.2 (−14.2)
P	−5.8	−0.9 (1.8)	−39.7 (−33.9)	−38.5 (−32.6)	−14.0 (−9.7)	−3.8	11.8 (14.2)
As	−6.3	−3.6 (−1.2)	−41.4 (−35.7)	−38.3 (−32.9)	−10.5 (−6.5)	−4.2	4.0 (6.3)
Sb	−6.1	−4.7 (−2.5)	−50.8 (−45.3)	−49.4 (−44.1)	−16.8 (−12.9)	−4.3	0.9 (3.2)
Bi	−6.6	−6.1 (−3.6)	−45.1 (−39.3)	−43.8 (−38.3)	−10.2 (−6.2)	−4.7	−2.7 (−2.6)

[a] MP2/DZ+d energies (kcal/mol). Numbers in parentheses are energies with zero-point correction based on the HF frequencies.

Table 7. Dipole Moment of All the Extrema on the Potential Energy Surface[a]

M	M_{1comp}	M_{1TS}	M_{10}	M_{20}	M_{2TS}	M_{comp}	M_{TS}
P	1.95	5.14	2.47	2.00	2.14	5.45	7.26
As	2.28	4.41	2.83	2.38	2.70	5.58	8.74
Sb	2.35	3.39	2.82	2.58	3.05	5.39	7.12
Bi	2.51	3.07	3.10	2.94	3.46	5.11	5.95

[a] MP2/DZ+d, in debyes.

Table 8. Reaction Energies at the MP4SDTQ and QCISD(T) Levels on the MP2-Optimized Geometries[a]

	N	P	As	Sb	Bi
		Reaction 1			
MP2	132.4 (−2.3)	134.7 (0.0)	146.7 (12.0)	151.5 (16.8)	165.0 (30.3)
MP4SDTQ	113.4 (−4.6)	118.0 (0.0)	129.9 (11.9)	134.8 (16.8)	147.8 (29.8)
QCISD(T)	113.4 (−4.6)	118.0 (0.0)	130.0 (12.0)	135.1 (17.1)	148.8 (30.8)
MP4SDTQ/ 6-311+G(2d,p)// MP2/DZ+d	118.1	119.4			
QCISD(T)/ 6-311+G(2d,p)// MP2/DZ+d	117.9	119.6			
		Reaction 2			
MP2	−124.2 (30.7)	−154.9 (0.0)	−149.9 (−5.0)	−147.3 (−7.6)	−145.3 (−9.6)
MP4SDTQ	−99.3 (29.6)	−128.9 (0.0)	−124.4 (−4.5)	−122.5 (−6.4)	−121.5 (−7.4)
QCISD(T)	−101.0 (29.6)	−130.6 (0.0)	−126.2 (−4.4)	−124.5 (−6.1)	−124.1 (−6.5)
		Reaction 5			
MP2	66.2 (28.5)	37.7 (0.0)	54.7 (17.0)	62.1 (24.4)	77.6 (39.9)
MP4SDTQ	66.2 (25.0)	41.2 (0.0)	57.5 (16.3)	64.4 (23.2)	78.4 (37.2)
QCISD(T)	65.8 (24.7)	41.1 (0.0)	57.2 (16.1)	64.0 (22.9)	77.6 (36.5)
		Reaction 6			
MP2	68.2 (15.9)	52.3 (0.0)	68.2 (15.9)	77.3 (25.0)	93.0 (40.7)
MP4SDTQ	67.7 (13.5)	54.2 (0.0)	69.3 (15.1)	77.6 (23.4)	91.4 (37.2)
QCISD(T)	67.4 (13.2)	54.2 (0.0)	69.1 (14.9)	77.1 (22.9)	91.4 (36.3)

[a] The numbers not in parentheses are reaction energies, and those in parentheses are relative reaction energies with respect to M = P.

stable than M_{20} in all cases and is 33–45 kcal/mol lower in energy than the reactants. Vibration analysis indicated that all M_{10} are local minima on the potential energy surface. However, M_{20} was found to have one imaginary frequency corresponding to the pseudorotation at the M center for M = As, Sb, or Bi. Although P_{20} was calculated to be a minimum at the HF level, vibrational analysis at the MP2 level indicated that P_{20} is also the pseudorotational transition state at this level. Thus, the reaction may be regarded to proceed without any intermediate (local minimum) from M_{10} to the Wittig products.[41] The step from M_{10} to the products is exothermic by 12.5 kcal/mol for P but is endothermic for the other ylides. There is a large barrier (M_{2TS}) from M_{10} to the final products, and the barrier becomes progressively larger for P < As < Sb < Bi. The geometrical parameters of M_{2TS} listed in Table 5 show that the C–C bond length is longer in the order P > As > Sb > Bi; thus, the transition state is more reactant-like for the more reactive ylide.

It should be noted here that most of the extrema on the Wittig and the Corey reaction surface are lower in energy than the corresponding reactant state, indicating that the complexes and intermediates have excess energies, and therefore these reactions proceed without any activation in the gas phase. However, the situation would be different in solution; the interaction between the reacting molecules and solvent allows for the excess energies to disperse, and then various intermediates can be formed in the thermal ground state. The present calculations are consistent with the experimental results that, for the reaction of a nonstabilized P ylide with an aldehyde, oxaphosphetane forms rapidly as a persistent intermediate at low temperature and that the decomposition of the oxaphosphetane to alkene + phosphine oxide is the slowest step of the overall Wittig reaction.[1,2]

Among the four ylides considered here the Bi ylide is most reactive, forming the most stable complex (Bi_{1comp}) and having the lowest barrier height to the intermediate (Bi_{10}). This high reactivity results from the least stabilizing effect of Bi^+ and hence the largest carbanion character of the carbon center of $H_3Bi{=}CH_2$. However, since the Wittig-type reaction goes through a very stable intermediate, M_{10}, the overall reactivity is governed by the height of the second transition state, M_{2TS}, in solution. The barrier height from the intermediate of lowest energy increases in the order P (24.2 kcal/mol) < As (29.2) < Sb (32.4) < Bi (33.1). Therefore, the overall reactivity of the Wittig-type reaction is expected to decrease in this order.

It has been demonstrated experimentally that the oxaphosphetane derived from a nonstabilized P ylide with benzaldehyde undergoes "oxaphosphetane reversal" under typical reaction conditions.[1,2,42] This suggests that P_{1TS} is energetically not much higher than P_{2TS}. The present calculations indicate that P_{1TS} is less stable than P_{2TS} by 11.5 kcal/mol, which may seem too large. Of course, the difference in substituent between the simplest model used here and the highly substituted species in experiment should have a large influence on the relative stability. Besides, this apparent contradiction can be rationalized by considering the solvent effect. Since P_{1TS} was found much more polar than P_{2TS}, as indicated by the dipole moment listed in Table 7, the stabilization by solvation would be much larger for P_{1TS} than for P_{2TS}, which should make the energy difference smaller.

The Corey-type reaction to ethylene oxide + MH_3 goes through the initial formation of a complex (M_{comp}). Here again, the geometries of the ylides and the aldehyde change very little upon the complex formation (Table 5). The stabilization energy of the complex formation is smaller than that for M_{1comp} and is about 4 kcal/mol (Table 6). Complex M_{comp} gives the final products through the transition state (M_{TS}), whose geometrical parameters are shown in Table 5. The transition state has intramolecular S_N2 character, in which the carbonyl oxygen

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(41) The calculations indicated that the reaction goes from a local minimum (M_{10}) to a rotational transition state (M_{20}) and then to another transition state (M_{2TS}). In other words, if the reaction proceeds by crawling up on the potential energy surface from M_{10}, the reacting species first reaches a ridge (M_{20}), and further goes up to a transition state (M_{2TS}). This situation could be confirmed by the IRC calculations, which clearly indicated that M_{2TS} and M_{20} are directly connected on the reaction surface. In a real system with excess kinetic energy and random reaction trajectories, the reaction may go from M_{10} to M_{2TS} (not strictly via M_{20}).

(42) Yamataka, H.; Nagareda, K.; Takatsuka, T.; Ando, K.; Hanafusa, T.; Nagase, S. *J. Am. Chem. Soc.* **1993**, *115*, 8570.

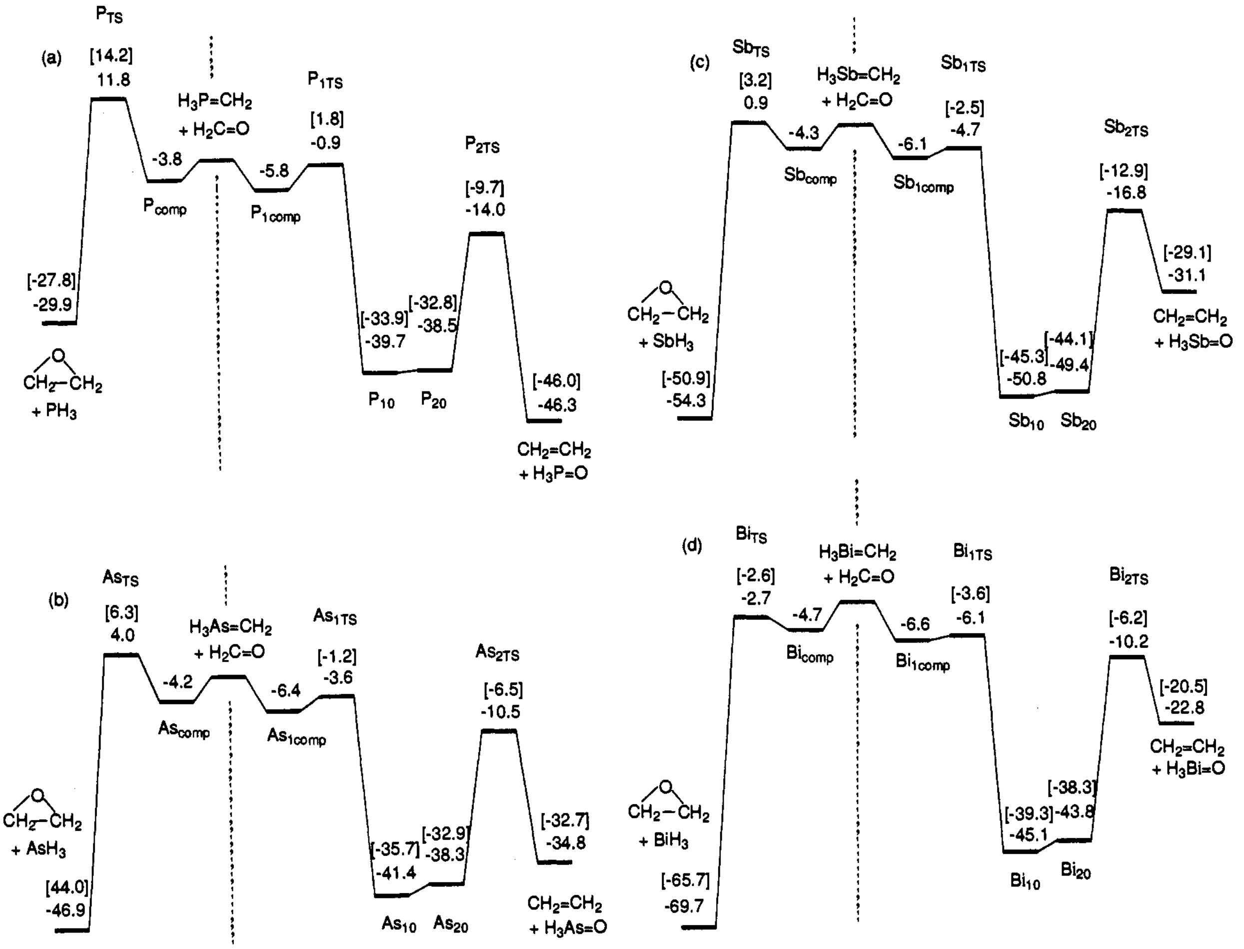

Figure 4. Energy profile for the Wittig and Corey reactions for (a) phosphorus ylide, (b) arsine ylide, (c) antimony ylide, and (d) bismuth ylide. The numbers not in brackets are the relative energies at the MP2/DZ+d//MP2/DZ+d level. Those in brackets are the values with the zero-point correction.

attacks the ylide carbon, displacing the MH_3 leaving group. The relative energy to the reactants decreases dramatically from P (14.2 kcal/mol) to Bi (−2.6), indicating that BiH_3 is a much better leaving group than PH_3. The transition structure also becomes progressively reactant-like in this order.

The energy profiles for the two reaction routes are illustrated in Figure 4. Figure 4 indicates that the Wittig products are less stable than the intermediates especially for M = Sb and Bi, suggesting that the Wittig-type reaction may not complete for these cases. In an actual experimental system, however, $Ph_3Sb{=}O$ (probably $Ph_3Bi{=}O$ also) readily dimerizes[43] and no back-reaction is likely to occur, and therefore discussion based on the M_{2TS} energy would be appropriate. In the case of the P ylide, the Wittig reaction is favored over the Corey reaction both kinetically and thermodynamically. In contrast, the Corey-type reaction becomes progressively favorable thermodynamically and the barrier height becomes lower for As < Sb < Bi in this order. For the As ylide, the Wittig reaction is kinetically favored by 7.5 kcal/mol while it is disfavored thermodynamically by 11.3 kcal/mol. The energy profiles clearly explain the experimental observation that the Wittig reaction exclusively occurs for phosphorus ylides, while either or both of the Wittig- and the Corey-type reactions may be observed for arsine ylides depending on the structures of the reactants and the reaction conditions.[3–6,44–48] The dipole moment of As_{TS} was found to be the largest among the extrema on the reaction surface (Table 7), which further suggests the feasibility of the Corey-type reaction for the As ylide in solution. The main driving force in the Wittig reaction of P ylides is the strong oxygen affinity of P as expressed by eq 7. It is interesting to note that the oxygen affinity of P, As, Sb, and Bi in eq 7 linearly correlates with the feasibility of the ylide formation shown in eq 5. The driving force in the Corey-type reaction for As, Sb, and Bi can be the relative leaving ability of MH_3 or the bond strength of $MH_3{=}CH_2$ shown in eq 8.

$$MH_3 + {}^1/_2O_2 \rightarrow H_3M{=}O \qquad (7)$$

$$\Delta E\ (\text{kcal/mol}) = -46.5\ (\text{P}), -16.0\ (\text{As}), -4.8\ (\text{Sb}), 18.9\ (\text{Bi}), 28.8\ (\text{N})$$

$$MH_3 + CH_2\ ({}^1A_1) \rightarrow H_3M{=}CH_2 \qquad (8)$$

$$\Delta E\ (\text{kcal/mol}) = -70.6\ (\text{P}), -53.6\ (\text{As}), -46.2\ (\text{Sb}), -30.8\ (\text{Bi}), -42.2\ (\text{N})$$

N Ylide. The character of the N ylide is different from other ylides as described previously. The HOMO of the N ylide has little π-bond character, and the ylide behaves as a carbanion. Therefore, the ylide and the aldehyde form a rather strong complex (N_{comp}) that is about 19 kcal/mol[49] more stable than the separated reactants. The geometry of N_{comp} is different from those of the other M_{comp}; the C–C bond is much shorter and the C–O bond is longer for N_{comp} (Table 5). From these characteristics N_{comp} may be regarded as a betaine intermediate. This intermediate gives ethylene oxide + NH_3 through transition state N_{TS} with a very low barrier. Thus, the over Corey-type process is quite feasible for the N ylide.

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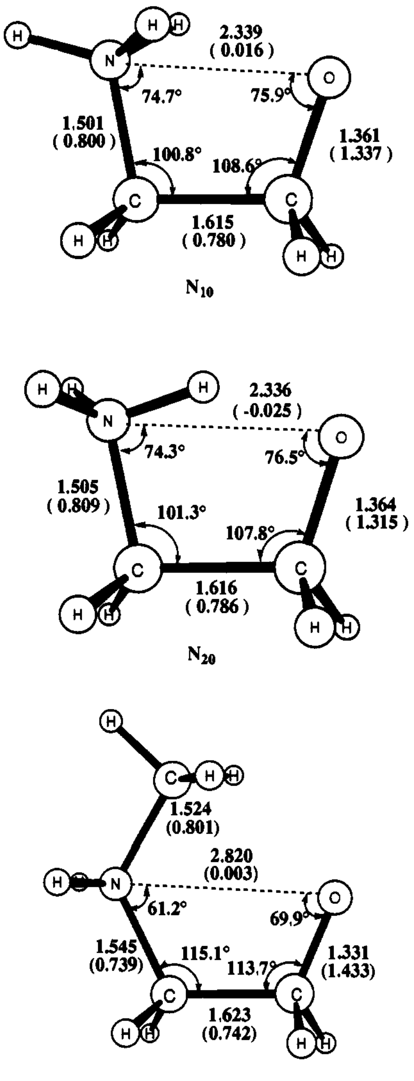
(43) Border, J.; Doak, G. O.; Everett, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 4206.
(44) Henry, M. C.; Wittig, G. *J. Am. Chem. Soc.* **1960**, *82*, 563.
(45) Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1981**, *103*, 1283.
(46) Kendurkar, P. S.; Tewari, R. S. *J. Organomet. Chem.* **1973**, *60*, 247.
(47) Kendurkar, P. S.; Tewari, R. S. *J. Organomet. Chem.* **1975**, *85*, 173.
(48) Huang, Y.; Shi, L.; Yang, J. *Tetrahedron Lett.* **1985**, *52*, 6447.



N_{10}

N_{20}

N_{20}(Me)

Figure 5. Geometries of extrema on the Wittig reaction route between nitrogen ylide and formaldehyde.

Because of the negligible π-bond character of the N–C bond, the N ylide does not form a stable complex with formaldehyde in the Wittig pathway. Instead, proton transfer occurs from the ylide nitrogen to the aldehyde oxygen to give β-hydroxyethylamine, which is 87.8 kcal/mol[49] more stable than the reactants. In order to investigate the Wittig route of the N ylide, we have to avoid the proton transfer. For this purpose, calculations of N_{10} were carried out under the constraint of C_s symmetry. The geometry of the intermediate corresponding to N_{10} thus located is shown in Figure 5. N_{10} is more stable than the reactants by 39.8 kcal/mol,[49] a magnitude similar to that for P_{10}. However, the geometrical features are quite different; the C–C bond is longer (by 0.076 Å) and the N–O bond is extremely longer (by 0.549 Å) in N_{10} as compared to P_{10}. The N–O bond is too long to have bonding interaction. The conformation is stable because of the attractive interaction between the carbonyl oxygen and the two hydrogens on the ylide nitrogen.

The second intermediate, N_{20}, was located by fixing the N—H bond that is on the symmetry plane at 1.0 Å. Without this constraint, the hydrogen atom migrates from N to O to give β-hydroxyethylamine. Here again, the N—O bond is quite long. Because of the H···O interaction, N_{20} is 6.7 kcal/mol[49] more stable than N_{10}. Full optimization without any constraint could be done for $N_{20(Me)}$, for which the hydrogen atom on the C_s plane was replaced by a methyl group. The geometry obtained at MP2/DZ+d has an even longer N—O bond than N_{20} because of the absence of NH···O interaction for $N_{20(Me)}$. The energy of $N_{20(Me)}$ is only 15.2 kcal/mol[49] more stable than that of the reactants, $H_2MeN{=}CH_2 + H_2C{=}O$. Thus, N_{20} is different from M_{20} of other ylides, and may correspond to *syn*-betaine. The transition state (N_{2TS}) connecting N_{20} with ethylene + $H_3N{=}O$ could not be located on the reaction surface.

The reason for the absence of the Wittig-type reaction route for the N ylide lies in the weakness of the N–O bonds for the pentavalent N atom. The N-O-bonded four-membered ring structure is unstable for the N ylide and becomes betaine with no bonding between N and O. We have already seen the example of electrostatic effects in the ylide molecules. The larger electronegativity of N (Pauling electronegativity 3.0) compared to those for P (2.1), As (2.0), Sb(1.9), Bi (1.9), and H (2.1) is the major reason for the instability of the N ylide as well as the higher barrier for the Wittig-type reaction.[50]

Summary

The present calculations reproduced the known trend that the phosphorus ylide is most suitable for the Wittig reaction, and offered the reasons for it. The P ylide is most easily formed among the group 15 ylides because (1) PH_3 is a strong nucleophile, nearly as good as NH_3, (2) $H_3P^+{-}CH_3$ is the strongest acid, much stronger than $H_3N^+{-}CH_3$, and (3) H_3P^+ is the best group stabilizing the adjacent carbanion among the analogous group 15 elements. The Wittig reaction is favored over the Corey-type reaction both kinetically and thermodynamically for the P ylide. It is interesting to note that it is only for the P ylide that the Wittig products are energetically more stable than the Wittig intermediates and the products of the Corey-type reaction. On the other hand, for the As ylide, the Corey-type reaction becomes favorable thermodynamically and kinetic preference for the Wittig-type reaction becomes small. For the Sb and Bi ylides, the thermodynamic preference for the Corey-type route becomes overwhelming. These characteristics in the ylide reactivity are judged to arise from two factors, the M–C bond strength and the M^+ stabilization of the adjacent electronegative group ($p\pi$–$d\pi$ interaction); the large oxygen affinity of P is another facet of this stabilization. Thus, the weak M–C bonds of Sb and Bi make the Corey-type reaction feasible, and the large $p\pi$–$d\pi$ stabilization effect for P makes the P ylide and the Wittig product stable.

The N ylide behaves quite differently from the P ylide. The nucleophilicities of NH_3 and PH_3 toward CH_3Cl are similar, but the proton abstraction from the ammonium salt is more difficult than from the phosphonium ion. The N ylide has little π-bond character and shows little reactivity toward the Wittig-type reaction. These differences are attributable to the large electronegativity of the N atom. The electronegativity of nitrogen is much larger than that of hydrogen, and therefore the nitrogen atom tends to bear a negative charge, because of which it cannot stabilize effectively the adjacent electronegative group such as CH_2^- in the ylide or O in amine oxide. Although the calculations were carried out for $H_3N{=}CH_2$ and $R_3N{=}CH_2$ (R = alkyl or aryl) is usually used in the real experimental system, nitrogen is still much more electronegative (3.0) than carbon (2.5), and thus the argument raised here will probably be justified for the real system.[50]

Supplementary Material Available: Lists of geometrical parameters and vibrational frequencies (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(49) Energies without zero-point correction.

(50) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.