J. Am. Chem. Soc. 1980, 102, 4632–4635

# A Theoretical Investigation on the Model Wittig Reaction $PH_3CH_2 + CH_2O \rightarrow PH_3O + C_2H_4$

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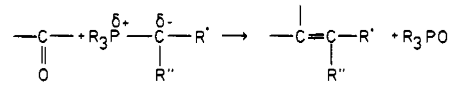
*Received December 3, 1979*

**Abstract:** Ab initio SCF calculations have been performed for the model Wittig reaction given in the title. The basis sets used range from STO-3G to double-$\zeta$ plus polarization quality. Full geometry optimization has been performed with the STO-3G and double-$\zeta$ basis sets. The reaction takes place in an essentially concerted way. Starting from $PH_3CH_2 + CH_2O$ an oxaphosphetane ring is formed via a very small energy barrier. This ring system corresponds to a local minimum on the energy hypersurface. An energy barrier of ~25 kcal/mol is found for the dissociation of the oxaphosphetane ring into $PH_3O$ and $C_2H_4$. The total reaction energy is calculated to be about –45 to –50 kcal/mol.

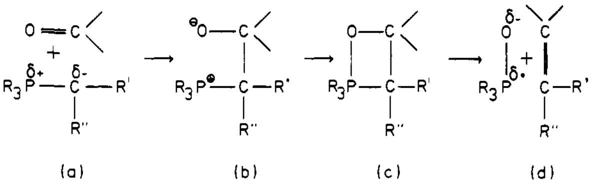
## I. Introduction

The Wittig reaction[1] is a very useful tool for the experimental chemist. According to the scheme of eq 1 a carbonyl group is



$$-\underset{\underset{O}{\|}}{C}- + R_3\overset{\delta+}{P}-\underset{\underset{R''}{|}}{\overset{\delta-}{C}}-R' \longrightarrow -\overset{|}{C}=\underset{\underset{R''}{|}}{C}-R' + R_3PO \qquad (1)$$

substituted by a methylene group. In spite of the importance of the Wittig reaction, its mechanism is still not completely clear. As intermediate steps of the reaction a betaine-type structure and a oxaphosphetane ring are discussed[2,3] (eq 2).



(2)

In some cases it could be shown that an oxaphosphetane structure (c) exists at low temperatures.[2,3] The question whether the reaction passes through a betaine-type structure or not could not be answered satisfactorily.

In terms of theoretical chemistry the just-mentioned question concerns primarily the characteristics of the energy hypersurface. If one assumes the existence of a $d_\pi$–$p_\pi$ bond in methylenephosphorane, there is a formal analogy of the Wittig reaction with the cycloadition of two ethylene molecules. The latter case is a standard for a symmetry-forbidden $[2_s + 2_s]$ addition. However, it has been shown[4–9] that the electronic structure of simple methylenephosphoranes and other related compounds is better represented by a dipolar structure. Thus one would expect that the symmetry rules for pericyclic reactions will not be valid for the Wittig reaction. On the contrary, easy formation of an oxaphosphetane ring corresponding to a local minimum on the energy hypersurface should occur. However, the question whether the oxaphosphetane ring is formed in one step (concerted) or via a betaine structure (nonconcerted) cannot be answered by simple qualitative arguments.

To our knowledge only one quantum-chemical investigation has been published so far.[10] In ref 10 partial geometry optimization has been performed by means of a charge model and some selected geometries have been computed by the CNDO/2 method. With the quantum chemical computer programs and the increased computer capacity available nowadays much more reliable calculations can be performed.

Table I. Basis Sets[a]

| nucleus | basis no. 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| P | STO-3G | 10s6p | 10s6p<br>+ 1s(0.04)[b]<br>+ 1p(0.05) | 11s7p | basis set 2<br>+ 1d(0.6) |
| C | STO-3G | 7s3p | 7s3p<br>+ 1s(0.1)[b]<br>+ 1p(0.06) | 8s4p | basis set 2<br>+ 1d(0.6) |
| O | STO-3G | 7s3p | 7s3p<br>+ 1s(0.12)[b]<br>+ 1p(0.13) | 8s4p | basis set 2<br>+ 1d(0.7) |
| $H_P$ | STO-3G | 3s[c] | basis set 2 | basis set 2 | basis set 2<br>+ 1p-(0.65) |
| $H_C$ | STO-3G | 3s[d] | basis set 2 | basis set 2 | basis set 2<br>+ 1p-(0.65) |

[a] The following contraction schemes have been used: (10s6p) [5,5 × 1/3,3 × 1], (11s7p) [6,5 × 1/4,3 × 1], (7s3p) [4,3 × 1/2,1], (8s4p) [4,4 × 1/2,2 × 1], and (3s) [2,1]. The primitive atomic basis sets have been taken from Huzinaga.[16] [b] Functions added to the atomic bases. Exponents are given in parentheses. [c] Scaled by a factor of 1.69. [d] Scaled by a factor of 1.44.

The aim of the present investigation is to perform ab initio SCF calculations on the most simple model reaction $PH_3CH_2 + CH_2O \rightarrow PH_3O + C_2H_4$ where all of the substituents in eq 1 are hydrogen atoms. The following limitations were decisive for this particular choice of substituents. We find it absolutely necessary to perform extensive geometry optimization. This would be possible for larger systems using semiemperical methods. Thus, we have tried at the beginning of our investigations the MNDO method,[11] which is the most recent semiempirical method available. However, the results for the Wittig reaction were very unencouraging. We found that stability differences were predicted completely wrong; e.g., the reaction energy computed with MNDO amounts to +72 kcal/mol whereas about –50 kcal/mol is obtained from our most elaborate ab initio calculations. Thus we decided to use the much more time-consuming ab initio techniques exclusively. Moreover, in order to get reliable energy differences larger basis sets of at least double-$\zeta$ quality have to be used here.

It is clear that comparison with experiment is made difficult by the fact that the experimental investigations on the Wittig

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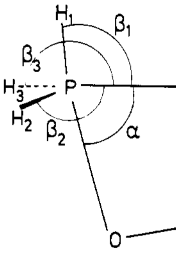

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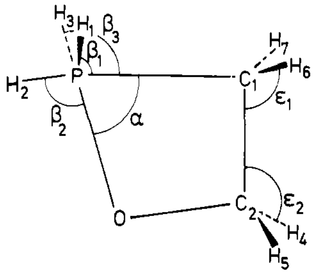

II

**Figure 1.** Definition of geometry parmeters for the two oxaphosphetane ring structures investigated. The torsional angles are defined as follows: $\pi = \mathrm{TORS}(P,O,C_1,C_2)$, $\gamma_1 = \mathrm{TORS}(H_1,P,C_1,C_2)$, $\gamma_2 = \mathrm{TORS}(H_2,P,C_1,C_2)$, $\gamma_3 = \mathrm{TORS}(H_3,P,C_1,C_2)$, $\theta_1 = \mathrm{TORS}(P,C_1,C_2,H_4)$, $\theta_2 = \mathrm{TORS}(O,C_2,C_1,H_7)$. TORS(*a,b,c,d*) defines the torsional angle between the planes *abc* and *bcd*.

reaction are performed in solution and that the substituents are not hydrogen atoms but bulkier groups such as alkyl or phenyl groups.

## II. Computational Details

The ab initio calculations have been performed at the SCF level with the basis sets presented in Table I. The two smallest basis sets (no. 1 and 2) are of STO-3G and double-$\zeta$ type, respectively. Basis set 3 is derived from set no. 2 by addition of diffuse s and p functions important for regions in space bearing partial negative charge (e.g., around the carbon atom in $PH_3CH_2$). Basis set 4 consists of 11s7p and 8s4p sets on the heavy atoms. Finally, basis set 5 is derived from basis set 2 by addition of polarization functions.

The geometry optimization has been performed by means of a gradient program developed by Pulay[12,13] using basis sets 1 and 2. The geometries thus obtained are used for calculations with the larger basis sets 3–5.

## III. Results and Discussion

**1. The Oxaphosphetane Ring.** Two isomeric structures have been investigated (see Figure 1). In both bases the phosphorus atom shows approximate trigonal-bipyramidal coordination. In structure I the oxygen atom is in an axial position and in structure II in an equatorial one. A complete geometry optimization has been performed with basis sets 1 and 2. The resulting geometries and total energies are shown in Tables II and III.

Structure I is slightly more stable than structure II with basis sets 1 and 2 (1.9 and 2.8 kcal/mol, respectively), whereas with basis set 5 both structures are practically equal in energy. The four heavy atoms are found to be situated exactly in a plane which also constitutes a plane of symmetry for the whole molecule.

Deficiencies of the STO-3G basis (basis set 1) are observed especially in the case of $R_{PC}$, which is too small by 0.05–0.1 Å if compared to the more reliable results of basis set 2 (see Table II). On the other hand, the STO-3G basis gives a much too large PC bond distance for the isolated $PH_3CH_2$ (see Table V). Nevertheless, the following facts hold for both basis sets: $R_{PC}$ is larger and $R_{PO}$ is somewhat smaller in structure II than in structure I. These results agree well with the general experience that for pentacoordinated phosphorus axial bonds are somewhat larger than equatorial ones (see, e.g., ref 14). Thus, structure I is better prepared to dissociate into $PH_3CH_2$ and $CH_2O$, whereas for structure II dissociation into $PH_3O$ and $C_2H_4$ seems to be favored.

Table II. Geometries Obtained for Structures I and II[a]

| | structure I | | structure II | |
|---|---|---|---|---|
| | 1[d] | 2[d] | 1[d] | 2[d] |
| $R_{PC_1}$ | 1.875 | 1.937 | 1.922 | 2.030 |
| $R_{C_1C_2}$ | 1.544 | 1.548 | 1.532 | 1.524 |
| $R_{C_2O}$ | 1.430 | 1.427 | 1.446 | 1.460 |
| $R_{PO}$ | 1.781 | 1.888 | 1.730 | 1.749 |
| $R_{PH}$[b] | 1.404 | 1.473 | 1.402 | 1.452 |
| $R_{PH}$[c] | 1.388 | 1.418 | 1.389 | 1.430 |
| $R_{C_2H_4}$ | 1.096 | 1.078 | 1.094 | 1.074 |
| $R_{C_1H_7}$ | 1.085 | 1.076 | 1.084 | 1.075 |
| $\alpha$ | 76 | 73 | 83 | 73 |
| $\beta_1$ | 96 | 98 | 97 | 98 |
| $\beta_2$ | 125 | 124 | 163 | 160 |
| $\beta_3$ | 125 | 124 | 97 | 98 |
| $\epsilon_1$ | 116 | 117 | 114 | 116 |
| $\epsilon_2$ | 112 | 111 | 114 | 114 |
| $\pi$ | 180 | 180 | 180 | 180 |
| $\gamma_1$ | 180 | 180 | 129 | 128 |
| $\gamma_2$ | 82 | 80 | 0 | 0 |
| $\gamma_3$ | −82 | −80 | −129 | −128 |
| $\theta_1$ | 119 | 119 | 117 | 113 |
| $\theta_2$ | 244 | 247 | 243 | 244 |

[a] For the definition of the geometry parameters see Figure 1. Distances are given in ångstroms, angles in degrees. [b] Axial position. [c] Equatorial position. [d] Basis set.

Two mechanisms are being discussed for the intramolecular exchange of axial and equatorial position in a trigonal-bypyramidally coordinated structure: the Berry pseudorotation and the turnstile rotation.[15] The situation is somewhat more complicated here since two of the ligands belong to the same four-membered-ring system. Thus, the question of ring strain is of additional importance.

In this connection we chose the following treatment of the interconversion of structures I and II. In a first step we computed with basis set 1 the matrix of force constants for those internal (angular) coordinates which describe the coordination of the phosphorus atom (i.e., $\alpha$, $\beta_1$, $\beta_2$, $\beta_3$, $\gamma_1$, $\gamma_2$, and $\gamma_3$; see also Figure 1). For both structures diagonalization of the matrix of force constants gave one very small eigenvalue. The corresponding eigenvector is expected to indicate the way in which structures I and II start to interconvert. In fact, we found that the deformations corresponded essentially to a rotation of the $PH_3$ group. Thus, in our particular case the exchange of ligands seems to be closer to the turnstile mechanism than to the Berry pseudorotation. These findings are in nice accord with the analysis given by Ugi et al. in ref 17.

The angle $\gamma_2$ was chosen as an approximate reaction coordinate. In addition to the values $\gamma_2 = 82°$ (structure I) and $\gamma_2 = 0°$ (structure II), intermediate values $\gamma_2 = 75$, 45, and 20° were selected and all the other geometrical parameters were optimized with basis set 1. The saddle point for the transformation I → II is situated between $\gamma_2 = 20$ and 45° and an approximate energy barrier of 5 kcal/mol has been claculated with basis set 1.

**2. The Wittig Reaction. a. Geometrical Aspects.** Starting from structure I the dissociation of the oxophosphetane ring into $PH_3O$

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Table III. Total Energies (au)[a]

| | basis | | | | | |
|---|---|---|---|---|---|---|
| | 1[b] | 2[b] | 2[c] | 3[b] | 4[b] | 5[c] |
| structure I[d] | 489.497 66 | 494.865 87 | 494.874 15 | 494.898 88 | 495.128 81 | 495.055 27 |
| structure II[d] | 489.494 71 | | 494.869 74 | | | 495.055 39 |
| structure III[e] | 489.399 89 | | 494.831 08 | | | 494.993 16 |
| structure IV[e] | 489.390 86 | | 494.835 86 | | | 495.016 39 |
| $PH_3CH_2$ | 377.050 48 | 381.126 10 | 381.134 92 | 381.138 77 | 381.269 80 | 381.254 47 |
| $CH_2O$ | 112.354 34 | 113.688 19 | 113.689 48 | 113.703 23 | 113.809 13 | 113.746 62 |
| $PH_3O$ | 412.356 73 | 416.941 92 | 416.948 57 | 416.977 08 | 417.148 51 | 417.101 95 |
| $C_2H_4$ | 77.073 95 | 77.936 87 | 77.937 67 | 77.943 96 | 77.999 99 | 77.976 10 |

[a] All values are negative. [b] Geometry obtained with basis set 1. [c] Geometry obtained with basis set 2. [d] See also Figure 1 and Table II. [e] See also Figure 1 and Table IV.

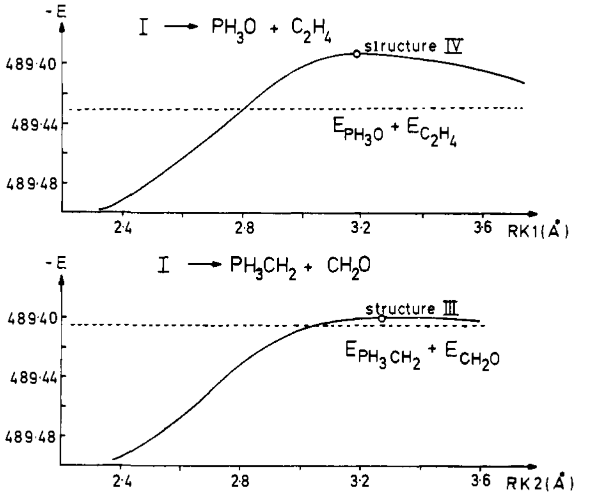

**Figure 2.** Decomposition of structure I into $PH_3O + C_2H_4$ and $PH_3CH_2 + CH_2O$, respectively, calculated with basis set 1.

$+ C_2H_4$ (reaction D1) and into $PH_3CH_2 + CH_2O$ (reaction D2) was discussed. As reaction coordinates linear combinations of those distances were chosen which determine the dissociation: $RK1 = 2^{-1/2}(R_{PC} + R_{CO})$ for D1 and $RK2 = 2^{-1/2}(R_{PO} + R_{CC})$ for D2.

For a given value of RK1 and RK2, respectively, the corresponding coordinates $2^{-1/2}(R_{PC} - R_{CO})$ and $2^{-1/2}(R_{PO} - R_{CC})$ show directly the orientation of the dissociating subunits.

Different values for RK1 and RK2, respectively, were chosen and all the other coordinates have been optimized with basis set 1. Energy curves and the changes in the characteristic distances are shown in Figures 2 and 3. The Wittig reaction starts in Figure 3b on the right-hand side. Initially, $R_{PO}$ and $R_{CC}$ decrease simultaneously. At RK2 ~3 Å, mainly $R_{PO}$ is decreased, and starting from RK2 = 2.5 Å both distances decrease simultaneously again. At the beginning of the decomposition of the ring (Figure 3a) the distances $R_{PC}$ and $R_{CO}$ are increased at the same time. Later on the PC bond is stretched preferentially and from RK1 ~3.1 Å on the CO bond is increased mainly. Although in different stages of the reaction a slight preference of formation or cleavage of one of the bonds is observed, Figure 3 shows essentially a concerted mechanism for the Wittig reaction.

For both dissociation reactions D1 and D2 saddle points are found with basis set 1 (structures III and IV in Figure 2). Taking the values of the reaction coordinates at these points (RK1 = 3.17 Å, structure IV, and RK2 = 3.28 Å, structure III) the other geometry parameters have been reoptimized with basis set 2. Resulting geometries are given in Table IV. It is interesting to note that for structure III the phosphorus atom has the same coordination as in structure I and that for structure IV the same coordination as for structure II is found. This means that in the course of the Wittig reaction starting from $PH_3CH_2 + CH_2O$ one arrives (via structure III) at the oxaphosphetane ring given by structure I. In the subsequent dissociation (via structure IV) a reorganization of the coordination of the phosphorus atom is found. The tendency for such a behavior has been discussed already in

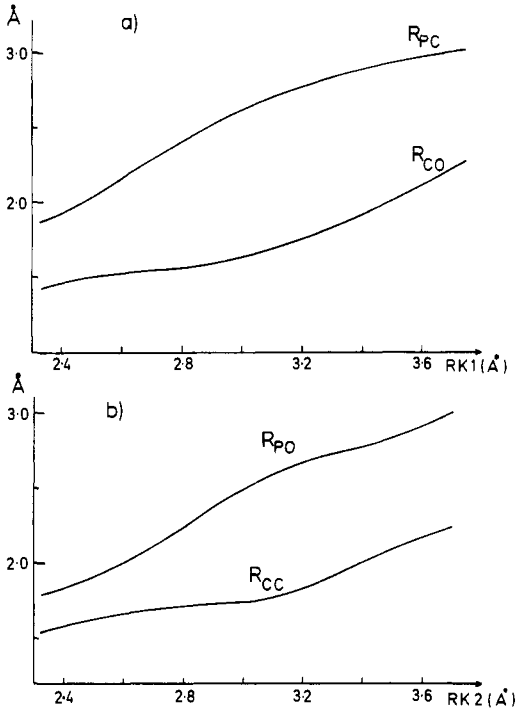

**Figure 3.** Dependency of characteristic internal coordinates on the reaction coordinates RK1 and RK2, respectively.

Table IV. Geometries of the Saddle-Point Structures III and IV for the Decomposition of the Oxaphosphetane Ring[a]

| | structure III[b] | | structure IV[c] | |
|---|---|---|---|---|
| | 1[f] | 2[f] | 1[f] | 2[f] |
| $R_{PC_1}$ | 1.844 | 1.879 | 2.725 | 2.588 |
| $R_{C_1C_2}$ | 1.912 | 1.914 | 1.375 | 1.381 |
| $R_{C_2O}$ | 1.274 | 1.289 | 1.756 | 1.892 |
| $R_{PO}$ | 2.726 | 2.724 | 1.718 | 1.618 |
| $R_{PH}$[d] | 1.375 | 1.418 | 1.375 | 1.422 |
| $R_{PH}$[e] | 1.375 | 1.391 | 1.375 | 1.404 |
| $R_{C_2H_4}$ | 1.114 | 1.093 | 1.092 | 1.070 |
| $R_{C_1H_7}$ | 1.089 | 1.082 | 1.071 | 1.068 |
| $\alpha$ | 67 | 67 | 67 | 69 |
| $\beta_1$ | 118 | 113 | 83 | 83 |
| $\beta_2$ | 113 | 116 | 174 | 175 |
| $\beta_3$ | 113 | 116 | 83 | 83 |
| $\epsilon_1$ | 118 | 118 | 119 | 120 |
| $\epsilon_2$ | 96 | 96 | 120 | 120 |
| $\pi$ | 181 | 181 | 180 | 180 |
| $\gamma_1$ | 180 | 180 | 128 | 128 |
| $\gamma_2$ | 60 | 60 | 0 | 0 |
| $\gamma_3$ | −60 | −60 | −128 | −128 |
| $\theta_1$ | 125 | 125 | 102 | 102 |
| $\theta_2$ | 245 | 245 | 252 | 255 |

[a] Distances are given in ångstroms, angles in degrees. For the definition of the geometry parameters see Figure 1. [b] Saddle point for the dissociation reaction D2, RK2 = 3.28 Å. [c] Saddle point for the dissociation reaction D1, RK1 = 3.17 Å. [d] Axial position. [e] Equatorial position. [f] Basis.

Table V. Geometries for $PH_3O$, $C_2H_4$, $PH_3CH_2$, and $CH_2O$[a]

| | $PH_3CH_2$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| basis | $R_{PC}$ | $R_{PH_1}$ | $R_{PH_2}$ | $R_{CH}$ | $\angle H_2PC$ | $\angle H_1PC$ | $\angle H_7CP$ | *b* | *c* |
| STO-3G | 1.897 | 1.387 | 1.373 | 1.101 | 111 | 132 | 100 | 125 | 53 |
| 10s6p/7s3p/3s | 1.717 | 1.448 | 1.424 | 1.061 | 114 | 126 | 119 | 122 | 85 |

| $C_2H_4$ | | | | $PH_3O$ | | | | $CH_2O$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| basis | $R_{CC}$ | $R_{CH}$ | $\angle HCC$ | basis | $R_{PO}$ | $R_{PH}$ | $\angle HPO$ | basis | $R_{CO}$ | $R_{CH}$ | $\angle HCO$ |
| STO-3G | 1.306 | 1.082 | 122 | STO-3G | 1.656 | 1.383 | 119 | STO-3G | 1.217 | 1.101 | 123 |
| 7s3p/3s | 1.312 | 1.069 | 122 | 10s6p/7s3p/3s | 1.572 | 1.418 | 117 | 7s3p/3s | 1.207 | 1.081 | 122 |

[a] Geometry parameters are defined in Figure 1. Distances are given in angstroms, angles in degrees. [b] TORS($H_1PCH_2$). [c] TORS($H_1PCH_7$).

Table VI. Energy Differences (kcal/mol)[a]

| | basis | | | | | |
|---|---|---|---|---|---|---|
| | 1[b] | 2[b] | 2[c] | 3[b] | 4[b] | 5[c] |
| $\Delta E$ | −16.2 | −40.5 | −38.8 | −49.6 | −43.7 | −48.3 |
| $\Delta E_1$ | 58.3 | 32.4 | 31.2 | 35.7 | 31.3 | 34.0 |
| $\Delta E_2$ | 42.0 | −8.1 | −7.6 | −13.9 | −12.4 | −14.3 |
| $\Delta E_{II}$ | 1.9 | | 2.8 | | | −0.08 |
| $\Delta E_{III}$ | 61.4 | | 27.0 | | | 39.0 |
| $\Delta E_{IV}$ | 67.0 | | 24.0 | | | 24.4 |
| $E_1^A$ | 3.1 | | −4.2 | | | 5.0 |
| $E_2^A$ | 25.0 | | 31.6 | | | 38.7 |

[a] For definition see Figure 4. [b] The geometry calculated with basis set 1 has been used. [c] The geometry calculated with basis set 2 has been used.

section 1 by means of the bond distances $R_{PC}$ and $R_{PO}$.

The formation and dissociation of the oxaphosphetane ring may be illustrated also in two other ways: by correlation diagrams in terms of orbital energies and by population analysis.

The connection of the Wittig reaction with the $[2_s + 2_s]$ addition has been discussed already in the Introduction. Correlation diagrams for the orbital energies have been constructed. It is possible to correlate all occupied orbitals of the reactants with all occupied orbitals of the products in the case of the Wittig reaction.

Moreover, a Mulliken population analysis has been performed. Since the deficiencies of such an analysis are well known, qualitative features are described only. When the reactants $PH_3CH_2$ and $CH_2O$ approach each other, a charge transfer from $PH_3CH_2$ to $CH_2O$ takes place. For example, in the case of structure III 0.3 $e_0$ is transferred. This charge is supplied almost exclusively by the $CH_2$ group of $PH_3CH_2$. In structure I the $PH_3O$ and $C_2H_4$ subunits are almost neutral so that on dissociation into $PH_3O$ and $C_2H_4$ no additional charge transfer is necessary. In structure IV ethylene acts as a weak electron acceptor (it carries a surplus of $\sim$0.1 $e_0$). However, it is still quite strongly polarized (the net charges are −0.4 $e_0$ on the $CH_2$ group originally bonded to the phosphorus and +0.3 $e_0$ on the other $CH_2$ group).

**b. Energies.** In order to calculate reaction energies the geometry of reactants and products has been optimized with basis sets 1 and 2. Resulting geometry parameters and energies are given in Tables III and V. The definition of energy differences and a corresponding energy profile are shown in Figure 4. In Table VI numerical values are collected.

Table VI shows that the energy differences obtained with basis set 1 (STO-3G) are not satisfactory. E.g., in the case of $\Delta E_2$, which determines the stability of the oxaphosphetane ring with respect to $PH_3O$ and $C_2H_4$, even the sign is incorrect. However, if the STO-3G geometries are used in connection with basis set 2, the results are not so bad. Nevertheless, we prefer the geometries obtained with the more flexible basis set 2.

Of minor importance than the use of a double-$\zeta$ basis instead of the STO-3G basis but also quite significant is the addition of diffuse s and p functions (basis set 3) and of polarization functions (basis set 5). However, the effects of diffuse s plus p functions and of polarization functions are not mutually independent. The polarization functions contained in basis set 5 certainly compensate to some extent deficiencies due to the lack of diffuse s and p functions in this basis. Thus we think that our most accurate results are those obtained with basis set 5.

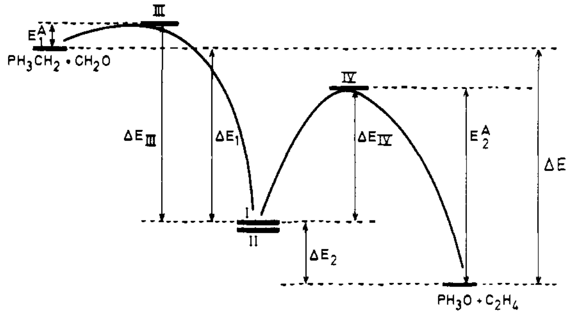

**Figure 4.** Energy profile for the reaction $PH_3CH_2 + CH_2O \rightarrow PH_3O + C_2H_4$. The energy differences are defined as follows: $E_1^A = E_{III} - E_{PH_3CH_2} - E_{CH_2O}$; $E_2^A = E_{IV} - E_{PH_3O} - E_{C_2H_4}$; $\Delta E_1 = E_{PH_3CH_2} + E_{CH_2O} - E_I$; $\Delta E_2 = E_{PH_3O} + E_{C_2H_4} - E_I$; $\Delta E_{II} = E_{II} - E_I$; $\Delta E_{III} = E_{III} - E_I$; $\Delta E_{IV} = E_{IV} - E_I$; $\Delta E = E_{PH_3O} + E_{C_2H_4} - E_{PH_3CH_2} - E_{CH_2O}$. Roman numbers refer to the structures I–IV defined in Figure 1 and Tables II and IV.

Following the course of the Wittig reaction (see also Figure 4) we find a very small energy barrier $E_1^A$ for the formation of the oxaphosphetane ring formed from $PH_3CH_2$ and $CH_2O$. The barrier even vanishes with basis set 2 so that the question is still open as to whether this barrier exists at all. The energy $\Delta E_1$ gained by the formation of the ring system lies in between 30 and 35 kcal/mol. For the dissociation of structure I a much larger amount of activation energy is necessary ($\Delta E_{IV}$ $\sim$25 kcal/mol) than for its formation. The products $PH_3O + C_2H_4$ are more stable than structure I by 10–15 kcal/mol. The total reaction energy amounts to from −45 to −50 kcal/mol.

## IV. Conclusions

From our calculations on the model Wittig reaction we find that the reaction occurs in an essentially concerted way. Although a charge transfer occurs during the formation of the oxaphosphetane ring, the resulting effect is not interpreted as the formation of a betaine-type structure. This observation is confirmed by the almost simultaneous changes of $R_{CC}$ and $R_{PO}$ for the formation and of $R_{PC}$ and $R_{CO}$ for the dissociation of the oxaphosphetane ring.

It is possible to draw a correlation diagram for the orbital energies along the reaction path in which all occupied orbitals of the reactants can be correlated with all the occupied orbitals of the products. No crossing of occupied and unoccupied orbitals is observed in contrast to the symmetry-forbidden $[2_s + 2_s]$ addition. As already emphasized in the Introduction this difference is due to the polar structure of the molecules involved in the Wittig reaction.

**Acknowledgments.** The computations were performed on the CDC CYBER 73/74 computers of the University and the Technical University of Vienna. Generous supply of computer time is gratefully acknowledged.