

A Comparison of Semi-empirical and *ab initio* SCF-MO Potential Energy Surfaces for the Reaction of $\text{H}_2\text{C}=\text{O}$ with $\text{R}_3\text{P}=\text{CH}_2$ and $\text{RP}=\text{CH}_2$

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The reaction between $\text{HP}=\text{CH}_2$ and $\text{H}_2\text{C}=\text{O}$ is predicted at the MNDO, PM3 and 3-21G* *ab initio* SCF-MO levels to proceed *via* a non-planar, unsymmetrical and relatively high energy transition state corresponding to a distorted $\pi 2_s + \pi 2_a$ cycloaddition, in contrast to the planar, symmetrical and lower energy saddle point located for the allowed cycloaddition between $\text{H}_3\text{P}=\text{CH}_2$ and $\text{H}_2\text{C}=\text{O}$. The 'allowed' character of the latter reaction is attributed to contributions from the P-H bonds and not to asymmetry in the reactant orbitals or to ionic character in the wavefunction. The methyl analogue $\text{Me}_3\text{P}=\text{CH}_2$ reveals a less synchronous transition state for cycloaddition, with a significant orbital contribution from the axial P-Me bond in particular.

There is considerable interest in the structure, reactions and differences in reactivity between compounds containing multiple bonds to phosphorus(III) and (V).¹ Most theoretical studies of molecules containing this element have hitherto been carried out at the *ab initio* SCF-MO level, since the errors at the semi-empirical MNDO/3 or MNDO levels have been reported² to be large, particularly for 'hypervalent species'. Where observed, these errors have been attributed to the lack of d-functions in the orbital basis set used in these methods.² Major differences between semi-empirical SCF (MNDO/3, MNDO, AM1) and *ab initio* (SCF and MCSCF)MO predictions of the degree of synchronisation of multiple bond formation or cleavage for pericyclic reactions have also been reported.³

Recently a re-parametrised semi-empirical SCF-MO procedure (PM3) has been reported‡ which appears to be a significant advance over MNDO and AM1 in three areas; the energetics and structures of 'hypervalent' compounds containing third period elements (Al, Si, P, S, Cl),‡ and the symmetries of transition states involving second period elements where the wave function is dominated by a single electronic configuration.⁴ This improvement over MNDO in particular is achieved *without* the inclusion of any d-functions, a result attributed to a more efficient parametrisation procedure.‡ In a study of the Beckmann rearrangement,⁴ the PM3 potential surface was found to more closely resemble the *ab initio* surface at the MP2/RHF level rather than the RHF level alone, and similarly the agreement in predicted vibrational spectra of water dimers and trimers was closest between PM3 and the correlated MP2/6-31G* level.⁵ Such effects were attributed by Stewart‡ to the Gaussian core-core repulsion functions in the PM3 method at least partially fulfilling the role of an effective operator for certain electron correlation effects such as dispersion forces, and we have suggested⁴ that certain features of closed shell (single configurational SCF) reaction surfaces may be similarly modified. In view of the biological and synthetic importance of hypervalent compounds of phosphorus, we felt it desirable to evaluate the PM3 method for reactions involving this element. We report in this paper a theoretical study of the Wittig reaction (Scheme) of $\text{R}_3\text{P}=\text{CH}_2$ (**2**; R = H, Me) and the analogous trivalent system $\text{RP}=\text{CH}_2$ (**7**) at the semi-empirical MNDO and PM3 level together with a comparison with single configurational *ab initio* calculations at two basis set levels.

Computational Details.—The MNDO and PM3 calculations were carried out using the MOPAC (V5.0) program system,‡ all

geometrical variables being optimised and transition states being characterised *via* the force constant matrix. Contour diagrams were constructed using the two forming P-O and C-C bonds as reaction co-ordinates. *ab initio* calculations were performed using the GAUSSIAN 86 program system, using the eigenvector following (EF) routine§ for location of transition states, and starting from PM3 optimised initial geometries.

Results and Discussion

A PM3 energy contour diagram (Figure 1) for the reaction between (**1**) and (**2**) (R = H) reveals an essentially symmetrical potential surface, corresponding to a synchronous transition state (**3**) similar in structure to that obtained previously¶,|| at the *ab initio* (double- ζ + polarisation) level (Table). For comparison, our own *ab initio* results at the smaller STO 3-21G* basis level are also included to illustrate that the geometries are not greatly sensitive to basis set effects. The MNDO structure⁶ for (**3**) is much less symmetrical, although the activation energy

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‡ PM3 (the third Parametric Method based on the NDDO approximations, following MNDO and AM1) differs from AM1 only in the values of the atomic parameters, obtained by simultaneous optimisation for twelve different elements; J. J. P. Stewart, *J. Comput. Chem.*, 1989, **209**, 221. These parameters are implemented in version 5.0 of the MOPAC program, available from *Quantum Chemistry Program Exchange*, University of Indiana, Bloomington, USA. AM1 level phosphorus parameters have also recently been reported, but these have not yet been evaluated for potential energy surfaces; M. J. S. Dewar and C. Jie, *J. Mol. Struct. (Theochem)*, 1989, **187**, 1.

Note added in proof. The AM1 surface for reaction of (**1**) and (**2**) shows a prominent ridge at P-O distances of 3.0 Å which is almost certainly an artifact (H. S. Rzepa, unpublished results.)

§ GAUSSIAN program systems available from Gaussian Inc., 4415 Fifth Avenue, Pittsburgh, PA, USA. The eigenvector following routine due to A. Banerjee, N. Adams, J. Simons, and R. Shepard, *J. Phys. Chem.*, 1985, **89**, 52 was as implemented by J. Baker, *J. Comput. Chem.*, 1986, **7**, 385.

¶ R. Holler and H. Lischka, *J. Am. Chem. Soc.*, 1980, **102**, 4632. The MNDO results quoted in this paper are clearly in error. We have checked our own calculations using MOPAC 5.0 against a version of the original MNDO program dating from 1976, finding deviations of <0.1 kcal mol⁻¹ from those reported (Table), and with numerical values entirely different from those quoted by Holler and Lischka.

|| For a comprehensive background to calculations on the Wittig reaction, see F. Volatron and O. Eisenstein, *J. Am. Chem. Soc.*, 1987, **109**, 1.

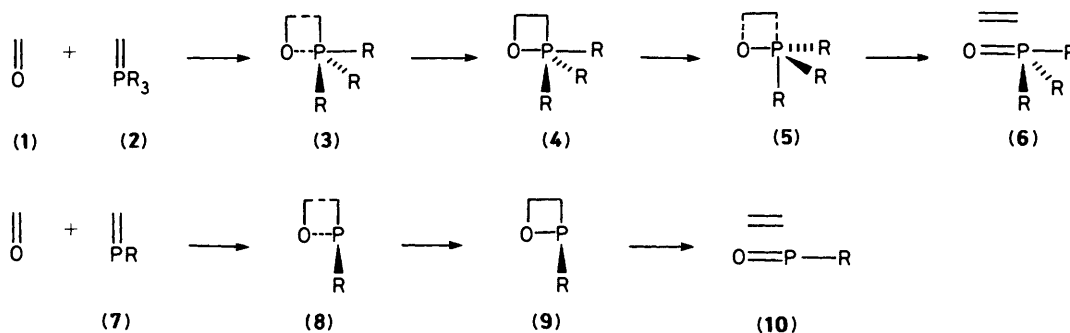


Table. Calculated properties for the reaction of R_3PCH_2 and RPCH_2 with H_2CO .

Structure	(1) + (2)	(3)	(4)	(5)	(6)	(1) + (7)	(8)	(9)	(10)
MNDO (R = H)									
ΔH	43.9 (+0.6) ^a	8.5 ^b	-17.3	+17.1	-19.1	-16.3	40.2	-40.5	-5.0
$r_{\text{P-O}}^c$	5.51	3.130	1.733	1.539	1.503	4.46	1.688	1.636	1.445
$r_{\text{C-C}}^c$	4.14	2.176	1.546	1.384	1.335	5.07	2.445	1.557	1.355
ν_i^d		343i		597i			753i		
PM3 (R = H)									
ΔH	-25.2(+2.2)	11.5	-30.9	+6.1	-29.7	-5.9	22.2	-42.8	-7.5
$r_{\text{P-O}}$	5.33	2.718	1.830	1.581	1.494	4.41	1.894	1.772	1.485
$r_{\text{C-C}}$	3.34	2.065	1.522	1.377	1.322	4.51	2.303	1.534	1.322
ν_i		269i		632i			890i		
PM3 (R = Me)									
ΔH	-3.50	14.6	-25.0	+9.9	-30.3	-17.7	22.9	-43.1	-11.9
$r_{\text{P-O}}$		2.839	1.822	1.579	1.483	4.57	1.896	1.769	1.479
$r_{\text{C-C}}$		1.907	1.519	1.383	1.322	4.63	2.307	1.532	1.322
ν_i		340i		662i			871i		
ab initio (3-21G*, R = H)									
E	-492.7757(3.2) ^e	5.9	-41.3	-19.8	-57.3	-491.6705(0.6)	42.8	-37.4	-11.7
$r_{\text{P-O}}$		2.633		1.538	1.472		1.908	1.665	1.429
$r_{\text{C-C}}$		2.124		1.402	1.315		2.443	1.564	1.315
ν_i		399i		727i			907i		
ab initio (DZ + P,R = H)									
E	-495.0011 ^f	5.0	-34.1	-9.6	-50.0				
$r_{\text{P-O}}$		2.726	1.749	1.718	1.572				
$r_{\text{C-C}}$		1.912	1.524	1.375	1.312				

^a Heat of formation of reactant pair. All energies in kcal mol^{-1} . The energy of the *isolated* reactants relative to the supermolecule is shown in parentheses. ^b Energy relative to reactant pair. ^c Bond lengths in Å. ^d Value of normal frequency corresponding to the reaction co-ordinate, in cm^{-1} . ^e In hartree, at the 3-21G* basis level. The energy of the isolated reactants is shown in parenthesis. All subsequent energies are relative to the reactant pair. ^f Ref. 8.

is comparable with the other methods. Transition state (3) [and also (5)] reveals the apical character of the forming P-O bond [or cleaving P-C bond in (5), Figure 2], which implies that a turnstile type rotation[‡] must occur in the cyclic intermediate (4) prior to completion of the reaction. The PM3 energy of (4) relative to (1) is similar to that predicted at the *ab initio* level.

The calculated properties for the second transition state (5; R = H) apparently show more divergence between the various methods. The PM3 breaking P-C and C-O bond lengths (2.467 and 1.839 Å, respectively) suggest a more symmetrical transition state than the corresponding 4-31G* *ab initio* values reported in the literature[‡] (2.359 and 2.527 Å), whilst at the MNDO level, a substantially asymmetrical saddle point is located (3.431 and 1.673 Å). Our own 3-21G* results for (5) (2.426 and 1.831 Å respectively) actually agree very well with the PM3 values. The

MNDO energy of (5) is well above the reactants making this the rate-determining transition state at this level, whereas (3) is clearly the highest point in the reaction path at both the PM3 and *ab initio* levels. Finally, it should be noted that the congruence between the *ab initio* and PM3 approaches for the overall heat of reaction is much better than that achieved at the MNDO level.[‡]

The PM3 transition state (8; R = H) is radically different in character from the PV analogue (Figure 2). Both the semi-empirical and the *ab initio* methods predict a significantly non-planar and a highly asymmetrical structure where P-O bond formation very much precedes C-C bond formation, corresponding closely to the zwitterionic representation (11). The PM3 and 3-21G* geometries are in particularly close agreement (Table). There is also a marked antarafacial component to the transition state (Figure 2), with a barrier to reaction of (7) significantly higher than for (2) at all theoretical levels, as is the value of the imaginary frequency corresponding to the reaction

^{†‡} See footnotes ¶ and || on p. 2115.

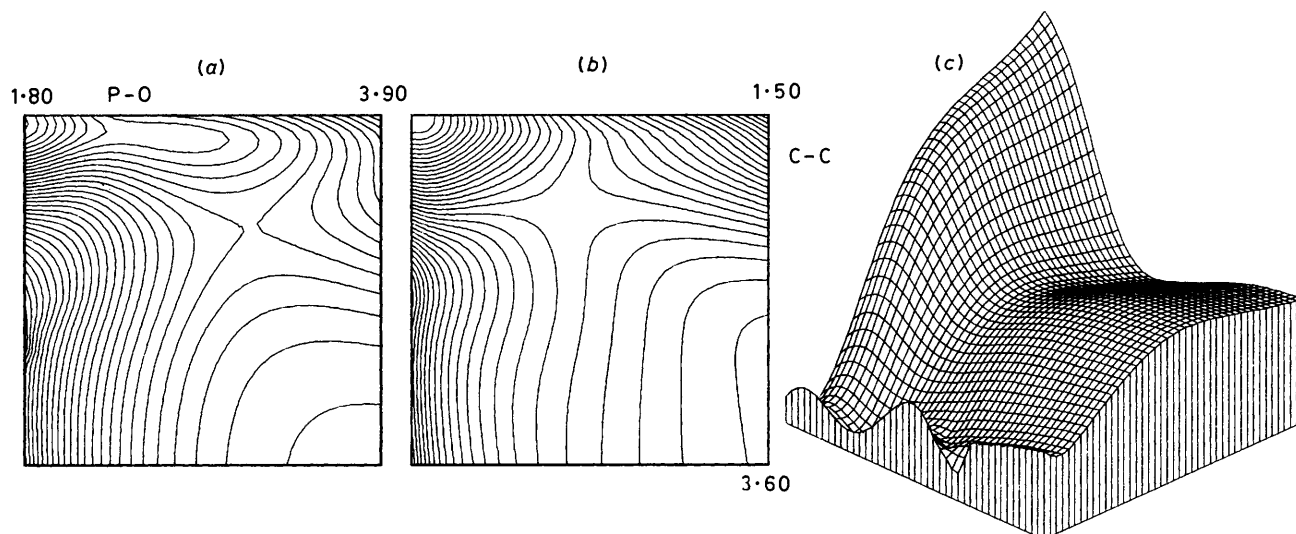


Figure 1. Contour maps for the reaction between (1) and (2) as a function of the P-O and C-C bond lengths for (a) MNDO and (b) PM3. The difference between the two surfaces is shown (c) as an isometric projection.

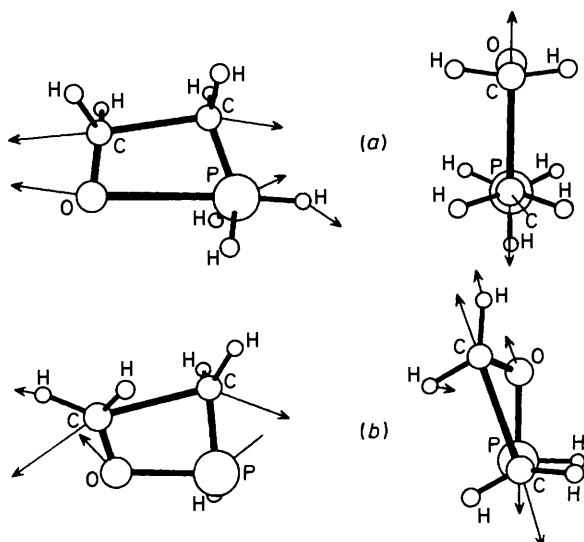
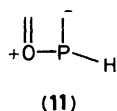


Figure 2. Two views of the transition state (3) (a) and the transition state (8) (b) calculated at the PM3 level. Arrows represent the form of the normal mode corresponding to the imaginary frequency.

co-ordinate (Table). In this context, it has been suggested⁷ that the $\pi_2^s + \pi_2^a$ mode of concerted cycloaddition between alkenes and ketenes leads to the more sterically hindered cyclobutanone, and it is interesting to speculate that if a species such as (7) did react with a carbonyl group, the sterically more hindered *cis* alkene could be the eventual product!



The contrast between transition states (3) and (8) (R = H) is usefully discussed in terms of 'forbidden' or 'allowed' pericyclic reactions. The PM3 potential energy surface surrounding (3) is both continuous and symmetrical (Figure 1), suggestive of a symmetry-allowed concerted reaction with no avoided crossing involving excited state electronic configurations. In previous *ab initio* single configuration SCF calculations on (3) for the specific substituent R = H, the 'allowed' characteristics of the

Wittig reaction have been attributed to either the considerable ionic character of the transition state (3)* or to asymmetry in the HOMO/LUMO orbitals of the reactants increasing what would otherwise be an orthogonal overlap in the $\pi_2^s + \pi_2^s$ sense.[†] However, such explanations are more in accord with significantly asynchronous transition states, which for R = H at least appears not to be the case, and imply the importance of excited state or open shell configurations. Such configurations are clearly important for highly asynchronous or stepwise pathways in cycloaddition reactions, the study of which requires a multi-configurational (MCSCF) approach.^{3b} The MCSCF method when applied to non-polar cycloaddition reactions such as that between butadiene and ethene leads to concerted and symmetrical transition states similar to those obtained at the single configuration SCF level, although this cannot in general be guaranteed.^{3b} The synchronous nature of (3; R = H) predicted using PM3 suggests that this reaction too can be treated at least qualitatively at the SCF level and such a conclusion is supported by a relatively large HOMO/LUMO energy gap for (3) (10.80 eV). The form of the canonical PM3 eigenvector for (3) corresponding most closely to the forming P-O and C-C bonds suggests an alternative explanation to that previously suggested*[†] for the 'allowed' nature of this reaction. This reveals an in-phase overlap of what formally corresponds to the four p_π nodes in a $\pi_2^s + \pi_2^s$ reaction, and by involving the P-H σ bonds indicates a substantial role for the three R-substituents (Figure 3). Indeed when R = Me, the transition state (3) becomes less synchronous, with C-C bond formation being more advanced than P-O formation, along with a small increase in the activation energy and a larger wavenumber for the imaginary mode (Table). Qualitatively, this can be rationalised by invoking greater stabilisation of a positive phosphorus centre *via* the inductive effect of the three R groups. The corresponding molecular orbital (Figure 4) is higher in energy than with R = H, and while still strongly bonding in the C-C region, is less bonding in the P-O region. Also prominent is the significant involvement of the axial P-R bond, which accords with experimental observations that the R groups are critical to the reactivity of the Wittig reagent. On this basis, it is possible that the reaction of $\text{Ph}_3\text{P}=\text{CH}_2$ may be even less synchronous than for R = Me.

The situation for the transition state (8) is quite different. The

*[†] See footnotes ¶ and || on p. 2115.

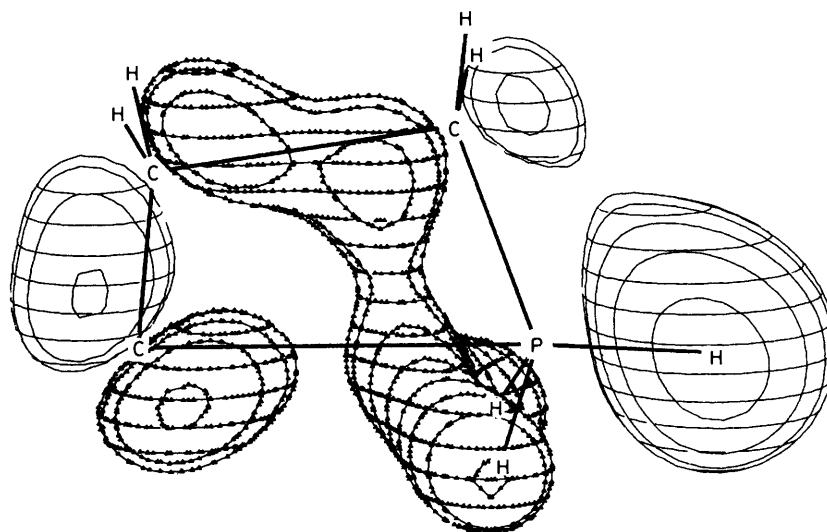


Figure 3. PM3 eigenvector (E , -14.05 eV) for transition state (3; R = H) revealing the participation of the P-H bonds in the P-O and C-C bond formation.

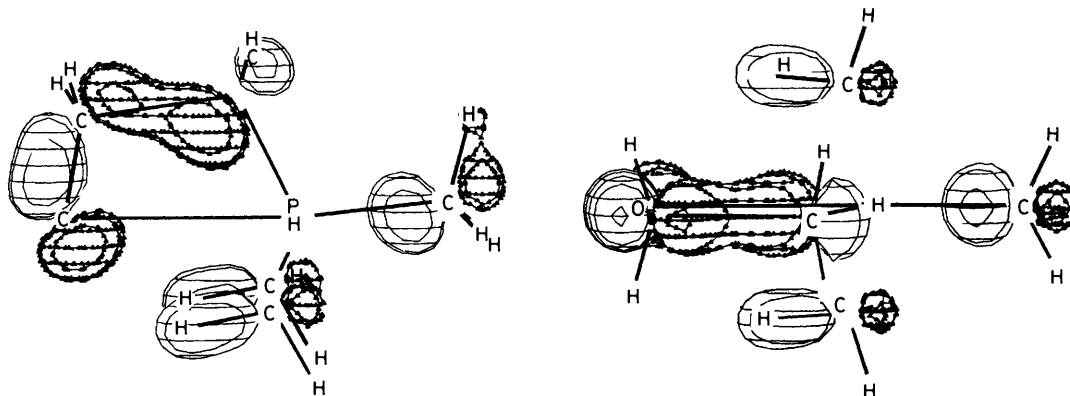


Figure 4. Two views of the PM3 eigenvector (E , -12.46 eV) for transition state (3; R = Me) corresponding to C-C bond formation, showing the contribution from the axial P-R bond.

much smaller predicted PM3 HOMO-LUMO energy gap (7.57 eV) suggests that excited-state configurations may make indeed a significant contribution. Furthermore, a major out-of-plane geometrical deformation, coupled with a large degree of asymmetry and no involvement of the P-H bond indicates all the characteristics of a $\pi_2s + \pi_2a$ reaction with the antarafacial component on the formaldehyde [Figure 2(b)]. In accord with this, substitution with R = Me has almost no effect on the properties of the transition state (8) (Table).

Conclusions

The PM3 s/p basis set SCF-MO method appears capable of modelling* the characteristics of Wittig-type reactions of Pv with similar accuracy to that obtainable using a medium basis set *ab initio* SCF approach, and is particularly useful in providing preliminary information for use in high accuracy *ab initio* approaches. It is found that the essential involvement of the P-R bonds makes a significant contribution to the symmetry of the transition state. Such an involvement is not possible in the transition state (8) and at a single configurational SCF level at least, phospho-alkenes are pre-

dicted to be less reactive than the classical Pv Wittig reagent in reactions with carbonyl groups. An MCSCF or similar correlated treatment of the Pv and particularly the P_{III} system would be required to provide a more definitive assessment of the reactivity of such species and the symmetry of the transition states involved.*

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