Pseudorotational Isomers of Wittig Intermediates. Structures and Relative Energies

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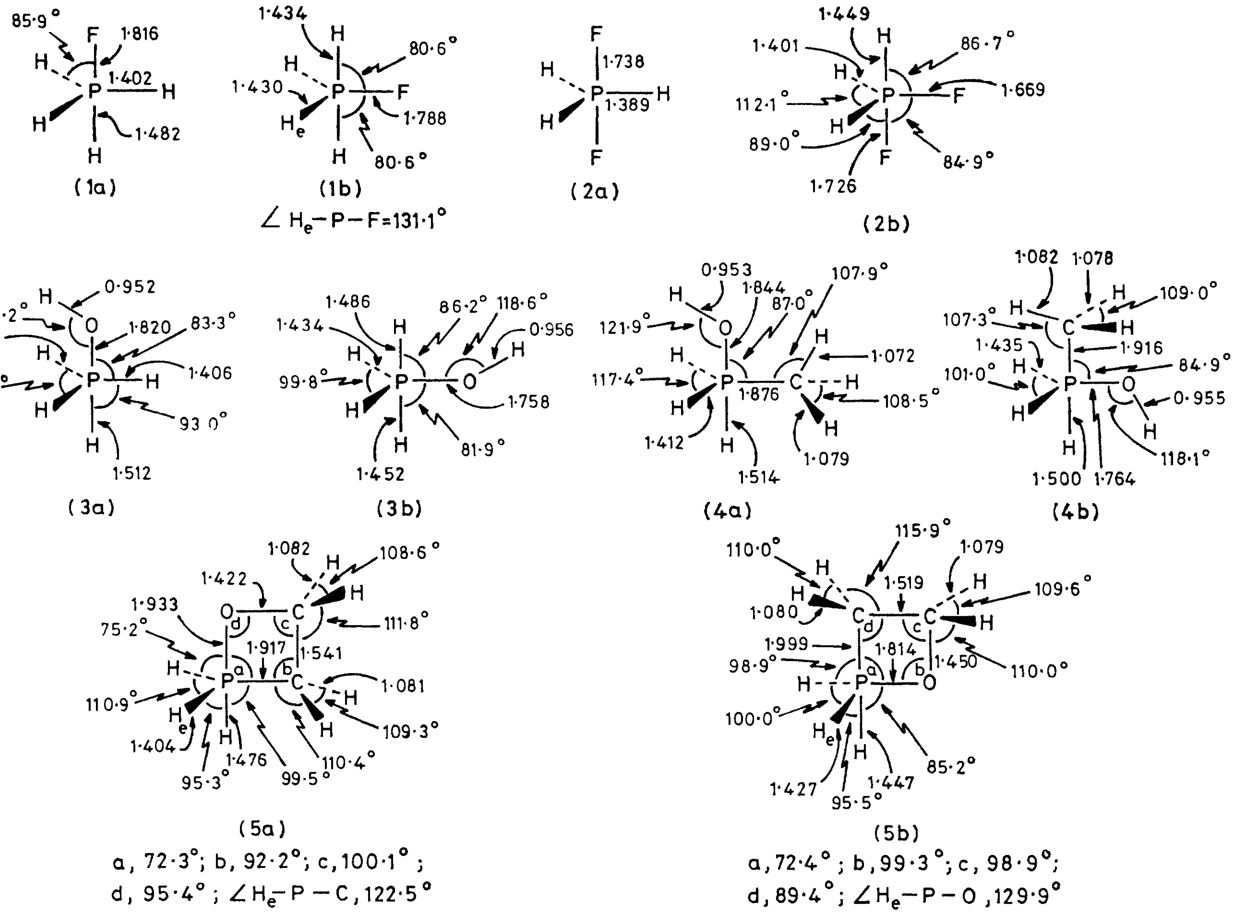
Summary *Ab initio* molecular orbital calculations indicate the pseudorotational oxaphosphetan Wittig intermediates to have unexpectedly small energy differences

THE apical electronegativity rule has long been central to the interpretation of the behaviour of pentaco-ordinate phosphorus compounds[1] Electronegative substituents are expected to favour the apical position strongly However, quantitative estimates of the apicophilicities of different groups have varied over a wide range[1,2] We have used *ab initio* molecular orbital theory to investigate systematically a series of substituted model phosphoranes Geometry optimization was carried out with the split-valence 4-31G basis set,[3] the symmetry constraints are implied in the



(1a) (1b) $\angle H_e{-}P{-}F = 131{\cdot}1°$ (2a) (2b)

(3a) (3b) (4a) (4b)

(5a) a, 72·3°; b, 92·2°; c, 100·1°; d, 95·4°; $\angle H_e{-}P{-}C$, 122·5°

(5b) a, 72·4°; b, 99·3°; c, 98·9°; d, 89·4°; $\angle H_e{-}P{-}O$, 129·9°

FIGURE. Optimized 4-31G geometries. Angles are given in degrees and bond lengths in Å (10^2 pm).

Figure and include a planar ring for (**5**). These geometries (Figure) were employed in another set of calculations which included a set of d-orbitals on phosphorus (4-31G+d);† the results (Table) should provide the best estimates for energy comparisons.‡

TABLE. Calculated energies (E/hartree) and relative energies (ΔE/kJ mol^{-1}) of substituted phosphoranes

	4-31G		4-31G+d	
Molecule	E	ΔE	E	ΔE
(**1a**)	−441·83894	0·0	−441·94541	0·0
(**1b**)	−441·81466	63·6	−441·92422	55·7
(**2a**)	−540·63270	0·0	−540·74851	0·0
(**2b**)	−540·59458	100·1	−540·71952	76·1
(**3a**)	−417·83401	0·0	−417·93704	0·0
(**3b**)	−417·81863	40·2	−417·92999	18·4
(**4a**)	−456·83023	0·0	−456·92877	0·0
(**4b**)	−456·81427	41·9	−456·91875	26·4
(**5a**)	−494·62397	0·0	−494·71694	0·0
(**5b**)	−494·61100	34·8	−494·70965	19·3

In agreement with previous *ab initio* calculations,[4] fluorine prefers the axial site in PH_4F by 55·7 kJ/mol. For PH_3F_2, the diapical isomer (**2a**) is 76·1 kJ/mol more stable than the apical–equatorial form (**2b**). The apical isomers are still the preferred forms for PH_4OH (**3**) and $PH_3(CH_3)OH$ (**4**) but the calculated energy differences are much smaller [4-31G+d: (**3a**) − (**3b**) = − 18·4; (**4a**) − (**4b**) = − 26·4 kJ/mol]. The model Wittig oxaphosphetan intermediate (**5**) behaves similarly; the pseudorotational energy difference is only 19·3 kJ/mol after the inclusion of the d-orbitals on phosphorus into the calculation. Höller and Lischka[5] calculate a similarly low energy difference between (**5a**) and (**5b**).

Our most important conclusion is that the apicophilicity of an OR group is surprisingly small. The introduction of the four-membered ring in the oxaphosphetan (**5**) results in an additional reduction in the energy difference between the pseudorotational forms [relative to (**4**)]. Qualitative MO analyses indicate that substituents which act principally as π-donors should prefer the equatorial rather than the apical

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† The exponent 0·39 is the one employed in the STO-3G* basis set (ref. 9).

‡ We have also examined these species at other theoretical levels, namely semi-empirical MNDO (ref. 10) and *ab initio* [STO-3G (ref. 11) and STO-3G* (ref. 9) basis sets], but the results do not appear to be trustworthy.

position[6] An OR group, being a better π-donor and a poorer σ-acceptor than F, exhibits reduced apicophilicity

Some recent experimental observations provide support to our results ^{31}P N m r investigations indicate the presence of two pseudorotational forms of Wittig intermediates[7] This suggests that the relative energies are not very different Some of us have utilised this surprising conclusion in detailed mechanistic proposals for the Wittig reaction[8] We are extending our calculations of apical–equatorial energy differences to a wide variety of substituents

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