

Stereospecific [2+2] cycloaddition reactions of diphosphorus with alkenes

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Abstract

[2+2] Cycloaddition reactions of P_2 with alkenes were predicted to have concerted paths, that is, pseudoexcitation, distorted $2\pi_s+2\pi_s$, and $2\pi_s+2\pi_a$ processes without any interventions of intermediates. The pseudoexcitation and/or distorted $2\pi_s+2\pi_s$ paths with retention of configuration of alkenes are kinetically preferred to the $2\pi_s+2\pi_a$ path with inversion of configuration. The reactions were predicted from the appreciable difference in the calculated enthalpies of activation to be stereospecific.

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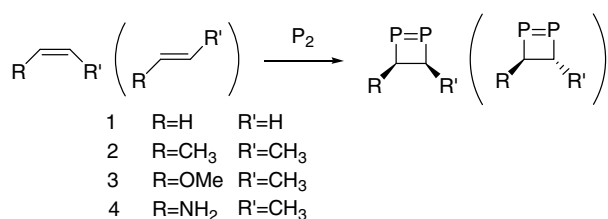
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Diphosphorus P_2 was generated only upon heating white phosphorus to more than 1100 K.¹ This procedure is not realistic for organic synthesis. Recently, a mild method has been developed and applied to Diels–Alder reaction with 1,3-cyclohexadiene.² The successful [4+2] cycloadditions have prompted us to investigate the [2+2] cycloadditions of diphosphorus with alkenes, especially their stereochemical courses (Scheme 1). In this Letter, we predict that the [2+2] cycloaddition reactions of P_2 with alkenes could not proceed via any intermediates but

through concerted reaction paths and that the retention of configuration of alkenes could be preferred.

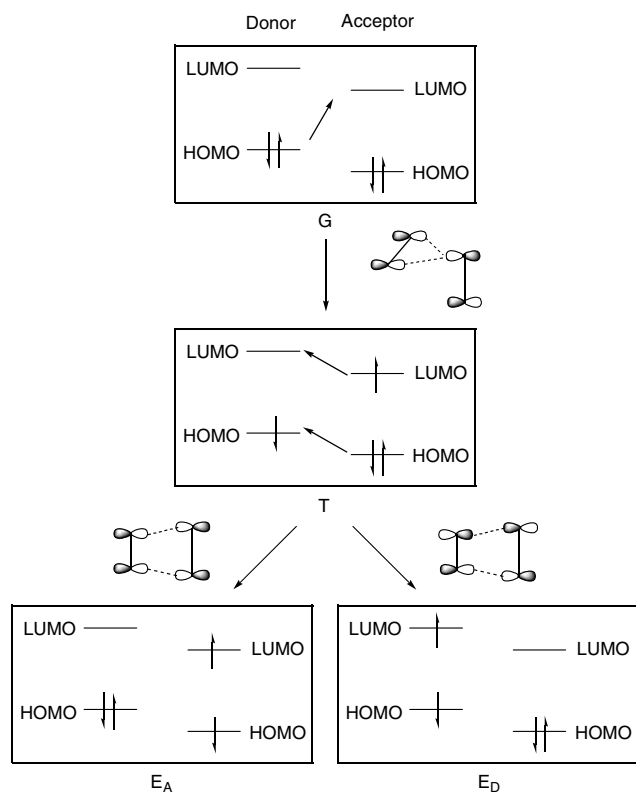
According to the Woodward–Hoffmann rules, the $2\pi_s+2\pi_s$ and $2\pi_a+2\pi_a$ processes are symmetry-forbidden and the $2\pi_s+2\pi_a$ process is symmetry-allowed.³ The antarafacial interaction is geometrically difficult to occur. In general, the thermal [2+2] cycloaddition reactions proceed stepwise via a biradical intermediate in a non-stereospecific manner. The $2\pi_s+2\pi_a$ process has rarely been documented.⁴ A different process was proposed for stereospecific [2+2] cycloadditions between the electron donors and acceptors.⁵ The strong three-centered HOMO–LUMO interaction accompanied by the induced HOMO–HOMO and LUMO–LUMO interactions can provide the reactions with the features similar to the photochemical reaction (pseudoexcitation as illustrated in Scheme 2).⁶

Diphosphorus has the π^* -LUMO low enough to be a strong electron acceptor. The [2+2] cycloaddition reactions of P_2 can proceed through the pseudoexcitation path (Scheme 2) with retention of configuration. The interaction between the HOMO of an alkene and the LUMO of P_2 prefers a three-membered ring structure at the initial stage (Fig. 1A). The HOMO–LUMO interaction between the strong donor and acceptor mixes the electron



Scheme 1.

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Scheme 2. Pseudoexcitation.

transferred configuration (T) into the ground configuration (G) to a great extent. The shift of the electron in the LUMO of P_2 to the LUMO of the alkene and the electron shift from the HOMO of P_2 to the electron hole to the HOMO of the alkenes in T give the locally excited configurations of the donor (E_D) and the acceptor (E_A), respec-

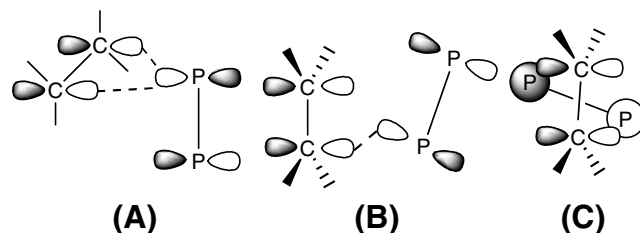


Fig. 1. Interactions between the HOMO of an alkene and the LUMO of P_2 in the (A) pseudoexcitation, (B) the distorted $2\pi_s+2\pi_s$, and (C) the $2\pi_s+2\pi_a$ paths.

tively. The electron shifts are accompanied by the HOMO–HOMO and the LUMO–LUMO interactions, which promote the transformation of the transient three-membered ring structure to the four-membered ring product.

P_2 has the high π -HOMO together with the low π^* -LUMO. The small HOMO–LUMO energy gap suggests that P_2 could be pseudoexcited on weak perturbation. The symmetry-forbiddenness of $2\pi_s+2\pi_s$ process can be easily lifted if the transition geometry is slightly distorted (Fig. 1B). The reactions via the distorted $2\pi_s+2\pi_s$ path proceed with retention of configuration. Furthermore, the long P–P bond may make an antarafacial interaction feasible on an alkene (Fig. 1C). The $2\pi_s+2\pi_a$ reaction proceeds with inversion of configuration.

We calculated the [2+2] cycloaddition of ethylene (**1**) with P_2 at the DFT (RB3LYP and UB3LYP) and MP2 levels with the 6-31G* basis set.⁷ The same results were given by the calculations at the restricted (R) and unrestricted (U) B3LYP levels. The transition structures were characterized by one imaginary frequency. Three transition

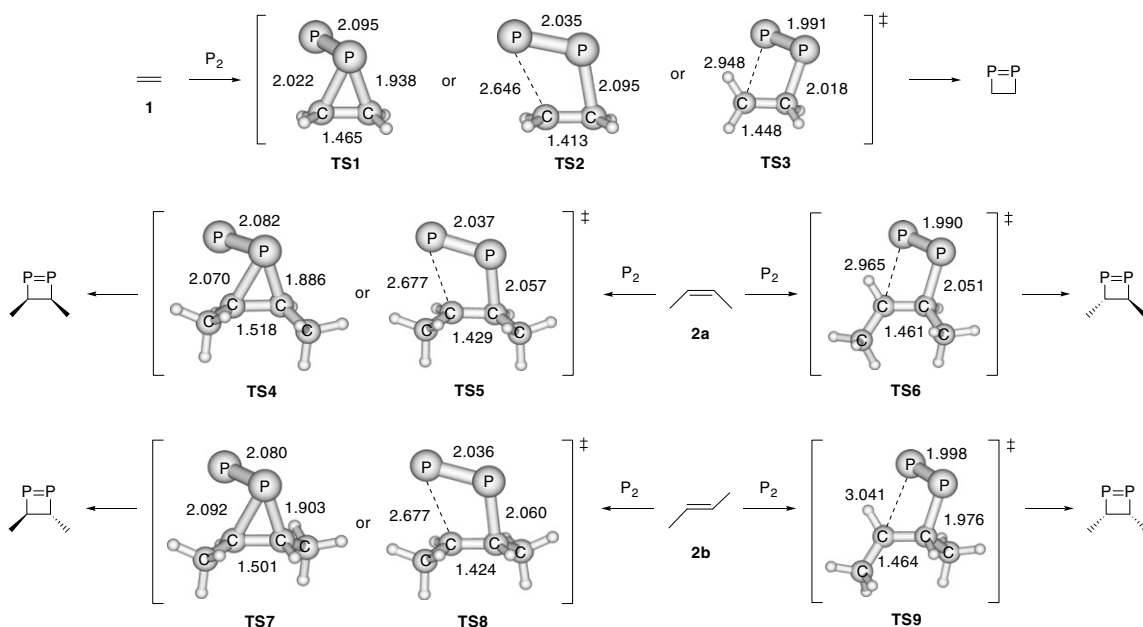


Fig. 2. The transition structures for the pseudoexcitation, the distorted $2\pi_s+2\pi_s$, and $2\pi_s+2\pi_a$ paths of the [2+2] cycloaddition of P_2 with ethylene (TS1–TS3), *cis*-2-butene (TS4–TS6), and *trans*-2-butene (TS7–TS9). Distances are in Angstrom (R(U)B3LYP/6-31G*).

Table 1
The enthalpies of activation ΔH^\ddagger (kcal/mol) for the [2+2] cycloaddition reaction of P_2 with ethylene (**1**)^a

Reactants	Paths	Transition structures	ΔH^\ddagger	
			R(U)B3LYP ^b	MP2 ^b
1	Pseudoexcitation	TS1	40.0	49.0
1	Distorted $2\pi_s+2\pi_s$	TS2	45.1	55.3
1	$2\pi_s+2\pi_a$	TS3	49.8	56.5

^a A temperature of 298 K and a pressure of 1 atm were assumed.

^b With the 6-31G* basis set.

structures (**TS1**, **TS2**, and **TS3**) were located for the pseudoexcitation, the distorted $2\pi_s+2\pi_s$, and the $2\pi_s+2\pi_a$ paths (Fig. 2). The intrinsic reaction coordinate (IRC) calculations showed that the reactions via the three transition structures could occur in concerted manners. No intermediates were located. The enthalpies of activation (Table 1) calculated at the R(U)B3LYP/6-31G* and MP2/6-31G* levels showed that the preference of the pseudoexcitation path with retention of configuration is most favored.

We chose *cis*-2-butene (**2a**) and *trans*-2-butene (**2b**) to examine the stereospecificity of the reactions. The optimized geometries of transition structures (**TS4–TS9**) are shown in Figure 2. The $2\pi_s+2\pi_a$ paths have higher enthal-

Table 2
The enthalpies of activation ΔH^\ddagger (kcal/mol) for the [2+2] cycloaddition reaction of P_2 with *cis*- (**2a**) and *trans*-2-butene (**2b**)^a

Reactants	Paths	Transition structures	ΔH^\ddagger	
			R(U)B3LYP ^b	MP2 ^b
2a	Pseudoexcitation	TS4	43.6	47.1
2a	Distorted $2\pi_s+2\pi_s$	TS5	44.6	50.0
2a	$2\pi_s+2\pi_a$	TS6	48.3	51.6
2b	Pseudoexcitation	TS7	43.7	47.4
2b	Distorted $2\pi_s+2\pi_s$	TS8	45.0	50.4
2b	$2\pi_s+2\pi_a$	TS9	51.8	56.9

^a A temperature of 298 K and a pressure of 1 atm were assumed.

^b With the 6-31G* basis set.

pies of activation than the pseudoexcitation and the distorted $2\pi_s+2\pi_s$ paths (Table 2). The [2+2] cycloaddition reactions of 2-butenes with P_2 may proceed stereospecifically via the pseudoexcitation and the distorted $2\pi_s+2\pi_s$ paths.

The enthalpies of activation are high for the [2+2] cycloaddition reactions of 2-butene with P_2 . To lower enthalpies of activation, we designed [2+2] cycloaddition reactions of *cis*- and *trans*-1-methoxypropenes (**3a**, **3b**) and 1-amino-

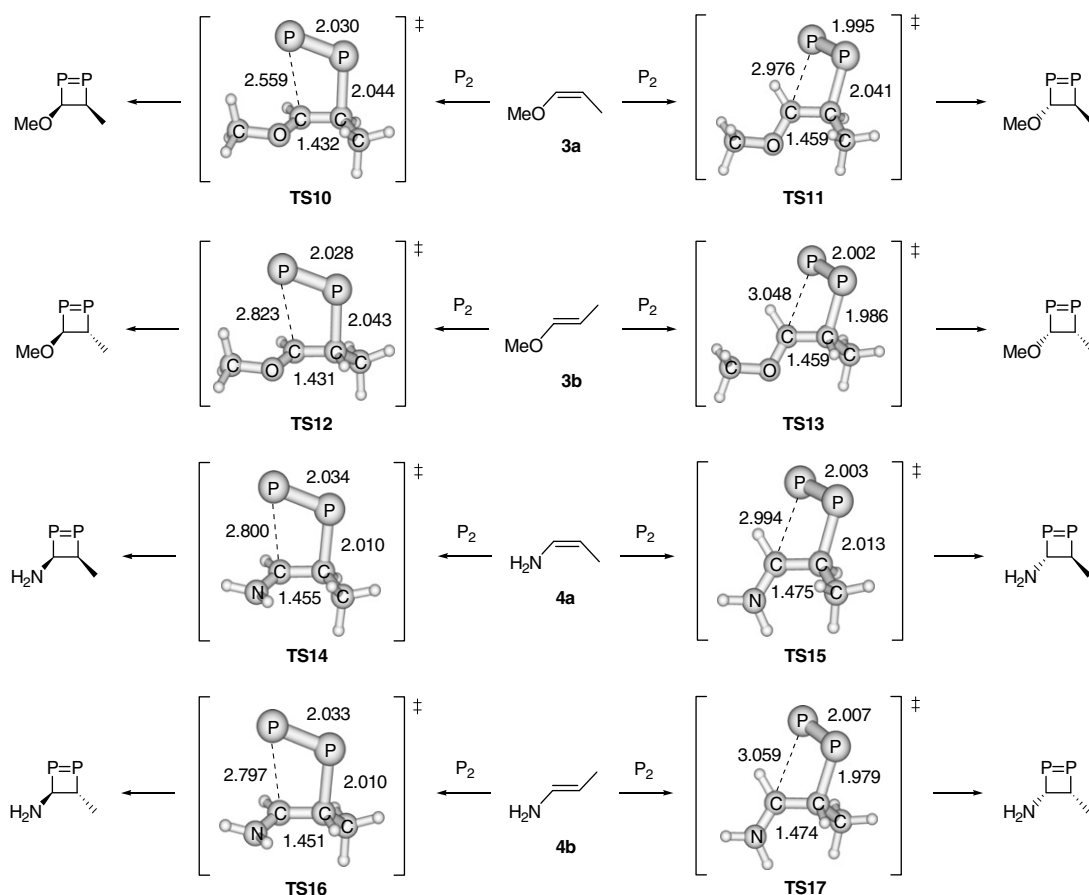


Fig. 3. The transition structures for the distorted $2\pi_s+2\pi_s$ and $2\pi_s+2\pi_a$ paths of the [2+2] cycloaddition of P_2 with *cis*- and *trans*-1-methoxypropenes (**TS10–TS13**) and 1-aminopropenes (**TS14–TS17**). Distances are in Angstrom (R(U)B3LYP/6-31G*).

Table 3

The enthalpies of activation ΔH^\ddagger (kcal/mol) at the R(U)B3LYP/6-31G* level for the [2+2] cycloaddition reactions of P₂ with *cis*- and *trans*-1-methoxypropenes (**3a**, **3b**) and 1-aminopropenes (**4a**, **4b**)^a

Reactants	Paths	Transition structures	ΔH^\ddagger ($\Delta\Delta H^\ddagger$) ^b	Reactants	Paths	Transition structures	ΔH^\ddagger ($\Delta\Delta H^\ddagger$) ^b
2a	pseudoexcitation	TS4	43.6 (0.0)	2b	pseudoexcitation	TS7	43.7 (0.0)
3a	pseudoexcitation	NL ^c		3b	pseudoexcitation	NL ^c	
4a	pseudoexcitation	NL ^c		4b	pseudoexcitation	NL ^c	
2a	distorted $2\pi_s + 2\pi_s$	TS5	44.6 (0.0)	2b	distorted $2\pi_s + 2\pi_s$	TS8	45.0 (0.0)
3a	distorted $2\pi_s + 2\pi_s$	TS10	34.2 (−10.4)	3b	distorted $2\pi_s + 2\pi_s$	TS12	35.5 (−9.5)
4a	distorted $2\pi_s + 2\pi_s$	TS14	28.3 (−16.3)	4b	distorted $2\pi_s + 2\pi_s$	TS16	28.7 (−16.3)
2a	$2\pi_s + 2\pi_a$	TS6	48.3 (0.0)	2b	$2\pi_s + 2\pi_a$	TS9	51.8 (0.0)
3a	$2\pi_s + 2\pi_a$	TS11	37.0 (−11.3)	3b	$2\pi_s + 2\pi_a$	TS13	39.9 (−11.9)
4a	$2\pi_s + 2\pi_a$	TS15	30.9 (−17.4)	4b	$2\pi_s + 2\pi_a$	TS17	32.2 (−19.6)

^a A temperature of 298 K and a pressure of 1 atm were assumed.

^b Minus signs indicate enthalpies of activation lower than those for 2-butenes (**2a**, **2b**).

^c Not located.

propenes (**4a**, **4b**) with P₂. The HOMO energy level is raised by the interaction of π with the lone pair of methoxy and amino groups. The high HOMO promotes the delocalization (HOMO–LUMO interaction) and the pseudoexcitation (HOMO–HOMO and LUMO–LUMO interactions). The unsymmetrical substitutions of alkenes polarize the HOMO and reduce the symmetry-forbiddensness of the HOMO–LUMO interaction. We carried out only the DFT calculations because the MP2 level calculations have given similar results about the reactions of P₂ with ethylene and 2-butenes. The transition structures (TS10–TS13, TS14–TS17) were located for the distorted $2\pi_s+2\pi_s$ and the $2\pi_s+2\pi_a$ paths without any intermediates (Fig. 3). In fact, the enthalpies of activation were lowered by 9.5–11.5 kcal/mol by the methoxy substitution and by 16.3–19.6 kcal/mol by the amino substitution from those of 2-butenes (Table 3). According to the orbital mixing rule,⁸ the HOMOs of **3** and **4** are polarized by the lone pair and extend more at the β -carbon. A phosphorus atom preferentially attacks the β -carbon, as is seen in the transition structures for the distorted $2\pi_s+2\pi_s$ and $2\pi_s+2\pi_a$ paths. The missing of the three-membered ring transition structure may be due to the sufficient HOMO polarization.

The reactions of **3** and **4** proceed stereospecifically via the distorted $2\pi_s+2\pi_s$ paths with retention of configuration. The enthalpies of activation (~ 35 , ~ 28 kcal/mol) are low enough to be realistic and are sufficiently lower (2.8, 4.4, 2.6 and 3.5 kcal/mol) than those of the $2\pi_s+2\pi_a$ reactions of **3a**, **3b**, **4a**, and **4b** with inversion of configuration, respectively, to be stereospecific.

In summary, we propose concerted reaction paths without any intermediates for the [2+2] cycloaddition reactions of P₂ with alkenes: (A) the pseudoexcitation path with retention of configuration via the transition structure of a three-membered ring with a tailing atom; (B) the distorted $2\pi_s+2\pi_s$ path with retention of configuration; and (C) a symmetry-allowed $2\pi_s+2\pi_a$ path with inversion of configuration. The retention of configurations are kinetically preferred. The [2+2] cycloadditions are pre-

dicted to proceed stereospecifically with retention of configuration.

Supplementary data

The Cartesian coordinates and the sole imaginary frequencies of all transition structures optimized at the DFT (RB3LYP and UB3LYP) and MP2 levels with the 6-31G* basis set are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.04.026.

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