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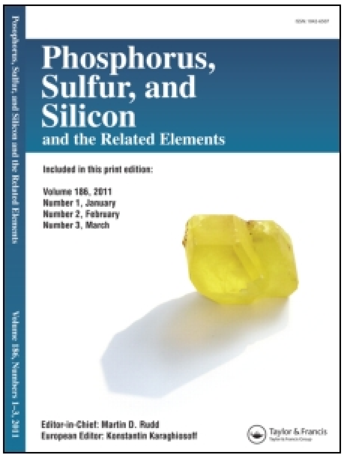

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Quantum-Chemical Aspects of Diene-Phosphaalkene Cycloadditions

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QUANTUM-CHEMICAL ASPECTS OF DIENE-PHOSPHAALKENE CYCLOADDITIONS

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Abstract Cycloaddition of dienes to phosphaalkenes was considered in the frames of the frontier MO approach. Quantum-chemical MNDO and ab initio calculations of frontier MO energies and structure for phosphaalkenes and pi electronic transition state stabilization energies of reactive systems confirmed that halogen-substituted phosphaalkenes are effective while diamino-substituted phosphaalkenes should not react with dienes. Satisfactory description was also obtained for regioselectivity of diene-phosphaalkene cycloadditions.

INTRODUCTION

The cycloaddition reactions of phosphaalkenes $R^1P{=}CR_2$ have attracted major interest since these compounds have been first prepared. The P=C double bond is an excellent candidate for (4+2)-cycloadditions with 1,3-dienes, and these reactions are of synthetic interest[1]. However, there are serious deficiences of knowledge concerning mechanism of these reactions because no relevant quantitative kinetic data are available. Furthermore, only one quantum-chemical work[2] has appeared hitherto in this field where reactions of butadiene with phosphaalkenes, iminophosphines and diphosphenes have been considered in terms of reactant HOMO-LUMO separations from MO LCAO SCF calculations using the STO-3G basis set.

QUANTUM-CHEMICAL TREATMENT

The aim of this work has been to give a wider quantum-chemical picture of diene-phosphaalkene cycloadditions including both their electron conditions and regioselectivity aspects.

The use of the frontier MO approach to the study of considered reactions seems to be reasonable. We have previously shown[3] that the use of the 4-31G(d) basis leads to fair description of the HOMO energies ε_i and the HOMO structure of phosphaalkenes; rather poor results are obtained with the STO-3G basis, and the semiempirical MNDO approximation is rather satisfactory. Direct verification of calculated LUMO energies is impossible, because no experimental values for electron affinities A_e of phosphaalkenes are available. But it is easy to show that for parent compounds a linear dependence should exist between the singlet-singlet electronic transition energy E_{00}, the ionization potential I_e and the calculated LUMO energy ε_j if the latter one is reliable:

$$E_{00} = aI_e - b\varepsilon_j + c \qquad (1)$$

where a, b and c are constants. The E_{00} and I_e values have been determined[4] for a series of compounds $RPC(SiMe_3)_2$ Using ε_j values from our MNDO calculations, we have obtained the relation (1) for this series (a = 0.934, b = 0.681, c = -2.041, r = 0.996). Furthermore, the I_e-A_e value for $HP{=}CH_2$ from MNDO calculations is close to the result of the 6-31G*-CI calculation (10.15 and 11.12 eV, respectively). We believe therefore that the frontier MO energies of phosphaalkenes calculated with the MNDO method may be applied at least for semi-quantitative evaluation of their reactivities. So we used them in our studies.

As HOMO and LUMO of phosphaalkenes are most frequently π-orbitals, a simple criterium of electron conditions for their Diels-Alder reactions is a comparison of reagent MO energy differences[5]:

$$\Delta\varepsilon_1 = \varepsilon_j^{RPCR_2} - \varepsilon_i^{diene} \qquad (2a)$$

$$\Delta\varepsilon_2 = \varepsilon_j^{diene} - \varepsilon_i^{RPCR_2} \qquad (2b)$$

We have normal electron conditions if $\Delta\varepsilon_1 < \Delta\varepsilon_2$

TABLE 1 Energetical data for phosphaalkenes in reactions with 1,3-butadiene from MNDO calculations

No.	Compound	$\Delta\varepsilon_1$ (eV)	$\Delta\varepsilon_2$ (eV)	E^{π}_{st} (eV)
1	$HP=CH_2$	8.65	10.89	0.636
2	$FP=CH_2$	8.47	10.71	0.579
3	$ClP=CH_2$	8.24	10.92	0.589
4	$HSP=CH_2$	8.47	10.17	0.501
5	$H_2NP=CH_2$	9.32	9.23	0.503
6	$HP=CHNMe_2$	9.26	9.93	0.487
7	$F_3CP=CF_2$	6.72	11.70	0.616
8	$FP=C(SiH_3)_2$	8.13	10.59	0.573
9	$ClP=C(SiH_3)_2$	7.94	10.83	0.560
10	$ClP=C(SiMe_3)_2$	8.02	10.75	0.542
11	$Me_2NP=C(SiH_3)_2$	8.88	9.38	0.443
12	$HP=C(NH_2)_2$	9.72	8.52	0.500

and inversed electron conditions if $\Delta\varepsilon_1 > \Delta\varepsilon_2$.[5] As is shown in Table 1, normal conditions are typical for phosphaalkenes; we obtained similar result in 4-31G calculations for compounds 1-5. This is in contrast with results in[2], perhaps due to shortcomings of the STO-3G basis set. Only for the compound 12 inversed conditions are observed; in this case, however, HOMO is delocalized, with a minor contribution of the carbon p AO and hence is not matched with the LUMO of a diene.

To evaluate the reactivity of phosphaalkenes towards dienes, one may use the conception of the delocalized transition state electronic system.[6,7] Then the π electronic stabilizing contribution E^{π}_{st} is the most important. It can be evaluated on the base of the second-order perturbation theory, according to[7], but transition state resonance integrals β should be known for this purpose. We have found the energy maximum in a model system at phosphorus-carbon distance of 209 pm; this gives $\beta_{PC} = -1.811$, $\beta_{CC} = -1.317$ eV. The calculated E^{π}_{st} values are given in

Table 1. Obviously, influence of electron-withdrawing substituents leads to the increase of E_{st}^{π} values and that of electron-donating ones - to their decrease, due both to high $\Delta\varepsilon_1$ values and to delocalization of frontier MOs.

Thus, both factors influencing the course of Diels-Alder reactions of phosphaalkenes - the $\Delta\varepsilon$ and the E_{st} values - are most effective for halogen-substituted phosphaalkenes which indeed are the best dienophiles.[1] The higher is E_{st}, the easier should be the reaction: this is the case for cycloadditions of dienes to compounds 7 and 10.[1] Compound 12 and thits derivatives should not react with dienes; indeed, such reactions are unknown.

We have also considered regioselectivity in cycloaddition of the compound 10 to the diene $CH_2=C(OH)-CH=CHOH$ (13). The highest contribution to the HOMO of 13 is from the unsubstituted terminal carbon C_m (-0.67), and that of the LUMO of 10 - from P AO (0.71). The E_{st} value of the transition state with the new P-C bond is higher than that of alternative transition state (50.6 and 45.8 kJ/mole, respectively). Thus, the adduct with the P-C_m bond should be formed preferrably. This is the case in the reaction of 10 with the diene $CH_2=C(OSiMe_3)-CH=CHOMe$ (14)[8] which is modelled by 13.

REFERENCES

1. D.L.Boger, S.M.Weinreb, Hetero Diels-Alder Methodology in Organic Synthesis (New York, 1987).
2. W.W.Schoeller, J.Chem.Soc.Chem.Communs, 334 (1985).
3. L.N.Alexeiko, V.V.Penkovsky, V.I.Kharchenko, Teoret. i Eksperiment.Khimiya, 26, 547 (1990).
4. D.Gudat, E.Niecke, W.Sachs, and P.Rademacher, Z.anorg. allg.Chem., 545, 7 (1987).
5. J.Sauer, R.Sustmann, Angew.Chem., 62, 773 (1980).
6. N.Epiotis, J.Am.Chem.Soc., 94, 1924 (1972).
7. M.V.Basilevsky, Adv.Chem.Phys., 33, 345 (1975).
8. P.Pellon, Y.Y.C.Y.L.Ko, P.Cosquer, P.Hamelin, and R.Carrie, Tetrahedron Lett., 27, 4299 (1986).