Pergamon

Tetrahedron, Vol. 53, No. 10, pp. 3545-3556, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00105-1

Substituent Effects on the Regiochemistry of Enone-Alkene 2+2-Photocycloadditions. Experimental Results and FMO Analysis.

Takaaki Suishu, Tetsuro Shimo, and Kenichi Somekawa*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Kagoshima University, Korimoto, Kagoshima 890, Japan

Abstract: The regiochemical selectivities (*i. e.*, head-to-head (hh) and head-to-tail (ht)) of 2+2-photocycloaddition reactions of cyclic α,β-unsaturated carbonyl compounds (**1**, **2**, **5**, **8**, **9**) with substituted alkenes have been determined experimentally. The observed preferences, associated with a two-step mechanism *via* biradical intermediates for addition of ground state alkenes to triplet enones, were analyzed by use of frontier molecular orbital (FMO) methods using molecular orbital energies and coefficients of corresponding species calculated by the PM3-CI method.

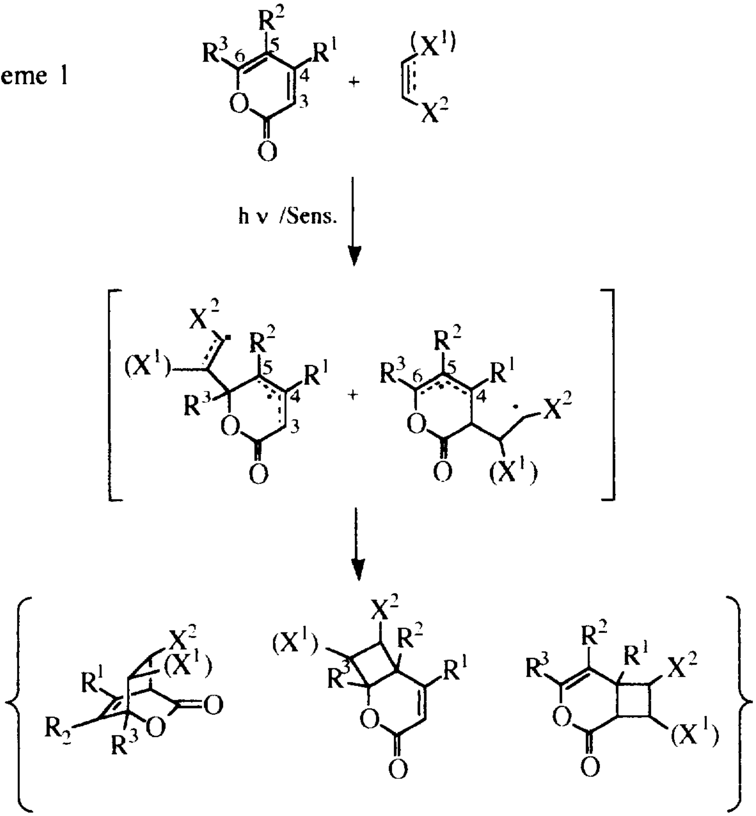
Regiochemical selectivities for the two-step 2+2-photocycloadditions were then analyzed in terms of two-center HSOMO-LUMO and LSOMO-HOMO interaction factors Sr1 corresponding to bonding between the enone triplet and alkene leading to formation of biradical precursors of the respective head-to-head and head-to-tail adducts. In addition, intramolecular interaction factors Sr2, corresponding to cyclization of the biradical intermediates were also determined. Good correlations were seen between the calculated interaction factor differences (*e.g.* $Sr1_{3\beta}$-$Sr1_{2\beta}$) and logarithims of the experimentally determined adduct ratios (*e.g.* log hh/ht). This observation suggests that the excited state 2+2-cycloaddition regioselectivities are mainly determined in the initial biradical producing step of this process but that they can be altered by partitioning of the biradical intermediates to product *vs.* ground state reactants.

Introduction

2+2-Photocycloaddition reactions of alkenes with α, β-unsaturated carbonyl compounds are among the most widely used excited state processes in synthetic organic chemistry.[1] The basic structural and mechanistic features of typical enone-alkene photoadditions were recently summarized and new insights into the mechanisms for these reactions have been provided.[2] Cycloaddition regioselectivity has remained a topic of great interest in this area.[2,3] The regiochemical preferences in cyclohexenone-alkene photoadditions have been nicely explained by using ab initio MO analysis of the first biradical producing step,[3] but the phenomenon associated with head-to-head *vs.* head-to-tail adduct formation from other α,β-unsaturated carbonyl compounds has not been similarly addressed. Recent biradical trapping experiments conducted on cyclic enone-alkene systems have led to the suggestion that the regioselectivities of these reactions is governed by the relative rates of biradical closure *vs.* their return to starting materials by bond fragmentation.[4] These contrasting conclusions clearly demonstrate that the mechanism and source(s) of regiochemical control in excited state 2+2-photocycloadditions are still not resolved issues.

Previously, we reported the results of our studies of peri-, site-, regio- and stereo-selective 2+2-photoadditions of alkenes to 2-pyridones and 2-pyrones, both of which possess hetero-atom substituted 2,4-cyclohexadienone chromophores, and demonstrated how these selectivities associated with the mechanistic sequence shown in Scheme 1 can be theoretically analyzed by the use of FMO-PM3 methods.[5,6] Also, we have described regioselective photoadditions of alkenes to the heterocyclic-enones **5**, **8** and **9**.[7,8] We now report the results of an expanded study in this area in which we have explored photocycloaddition reactions occuring between electron-donating and -withdrawing group substitued alkenes and the α,β-unsaturated carbonyl compounds **1**, **2**, **5**, **8**, **9** and have applied FMO methods to elucidate the factors governing the observed regioselectivities.

Scheme 1



Photoreactions and MO Calculation

Photoadditions of acrylonitrile, methyl acrylate and ethyl vinyl ether to cyclopentenone (**1**), cyclohexenon (**2**), conjugated lactam **5** and furanones **8**, **9** (Scheme 2) result in the production of endo-exo diastereomeric

Scheme 2

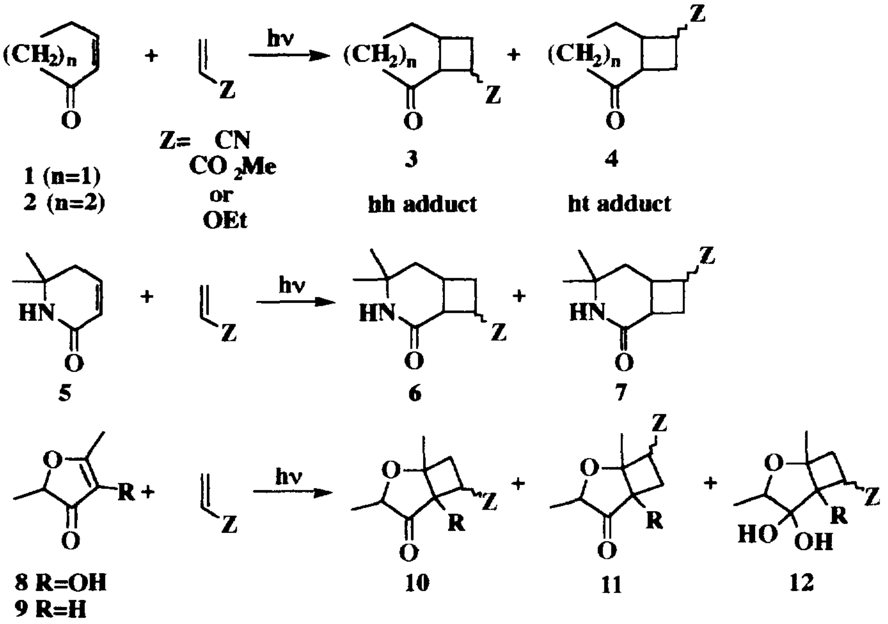


Table 1. Head-to-Head (hh) to Head-to-Tail (ht) Product Ratios from 2+2-Photoadditions of Substituted Alkenes to the α, β-Unsaturated Carbonyl Compounds.

Alkene (CH_2=CHZ)	hh : ht Ratios from cycloalkenones				
Z	**1**	**2**	**5**	**8**	**9**
CN	40/60[a]	76/24[b]	82/18[c]	100/0[d]	100/0[d]
CO_2CH_3	46/56[e]	-------	--------	60/40[d]	-------
OCH_2CH_3	20/80[f]	19/81[b]	5/95[c]	no[d,g]	0/100[d]

[a]Data taken from ref. 4b. [b]ref. 9. [c]ref. 7. [d]ref. 8. [e]ref. 2. [f]ref. 1. [g]no adduct.

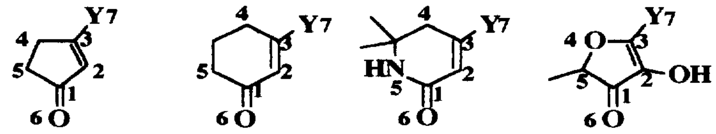
mixtures of head-to-head (hh, *e.g.* **3**) and head-to-tail (ht, *e.g.* **4**) adducts in the ratios shown in Table 1. The product **12** was taken as a hh adduct. In general, photoadditions with the electron-deficient ethylenes selectively afford hh adducts except for the case of cyclopentenone where a slight preference exists for the ht adducts. In contrast, photoadditions of substrates **1**, **2** and **5** with the electron-donating group sustituted ethyl vinyl ether in all cases yield ht adducts predominantly. The furanone **8** is an exception in this regard in that it does not yield 2+2-adducts in photoreaction with this alkene.

Molecular orbital calculations on the carbonyl triplet excited states and alkene ground states were carried out by use of the PM3 method. The optimized structure of the triplet excited state of each of the enones was calculated by using an unrestricted Hartree-Fock(UHF) wavefunction, and the energies and coefficients of all orbitals were estimated by use of the configuration interaction (CI) method considering thirty-six configurations. The optimized structures of the ground state alkenes were calculated by a restricted Hartree-Fock (RHF) wavefunction and the energies and coefficients were estimated by CI taking account of the 36 configurations. In addition, calculations were performed to determine the orbital properties of each of the radical components in the cycloadditon biradical intermediates and their orbital energies and coefficients were determined by use of UHF calculations.

FMO Results and Discussion

In Table 2 is shown the optimized geometries for the first-triplet excited states (T_1) of the four unsaturated carbonyl compounds **1**, **2**, **5**, **8** as well as for the ground state of **1** arrived at by PM3-CI calculations.[5,6] The large C_1, C_2, C_3, H_3 (Y7) dihedral angles found for the triplets (*e. g.* 73.0° for **2** and 69.1° for **5**) show that C2-C3 π-bonds are highly twisted (see Figure 1) for the six-membered compounds and to a lesser degree for the five membered ring compounds. The energies and coefficients of higher (HSOMO) and lower (LSOMO) energy singly occupied molecular orbitals of the enone triplets and the LUMO and HOMO levels of the alkenes are given in Table3.

Table 2. Optimized Geometries for the First Triplet Excited State(T_1) of **1**, **2**, **5** and **8** by the PM3-CI-UHF calculation.



1 **2** **5** **8**

	1(S_0)	1(T_1)	2(T_1)	5(T_1)	8(T_1)
A. Bond length (Å)[a]					
C1-C2	1.49	1.48	1.46	1.47	1.46
C2-C3	1.34	1.48	1.44	1.45	1.49
C3-X4	1.53	1.52	1.53	1.47	-
X5-C1	1.52	-	-	-	1.54
C1-O6	1.21	1.22	1.22	1.23	1.22
B. Dihedral angle (Å)[b]					
C1-C2-C3-X4				54.3	
C1-C2-C3-Y7	0.0	36.6	73.0	69.1	20.6
O6-C1-C2-C3	0.0	9.1	20.4		1.5

[a] X=C, N or O. [b] Y=H or C.

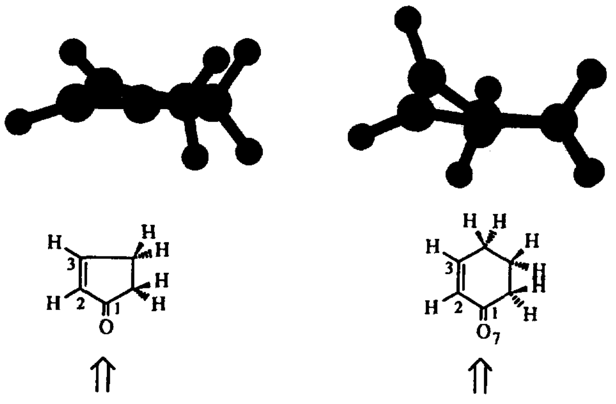


Figure 1. Twisted **1**(T_1) and **2**(T_1) structures by the PM3-CI-UHF calculations.

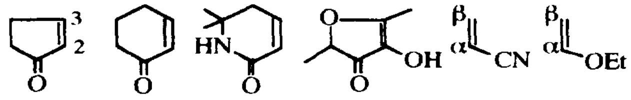
The triplet photoaddition reactions are believed to proceed by a two step mechanism involving formation and collapse of 1,4-biradical intermediates. The regiochemistry of the first step in this addition process will be influenced by the coefficients and energies of the component FMOs of the interacting partners, *i. e.* HSOMO(enone triplet)-LUMO(ground state alkene) and LSOMO(enone triplet)-HOMO(ground state alkene).[5c,10,11,12] The expected preferences for formation of the biradical intermediates **13** and **14** (Scheme 3) may be deduced from these FMO properties and reside in the magnitudes of the two-center FMO interaction factors Srl and the main factors Srl* in the equation (1) (in $\Delta\beta^2$/eV unit).

$$Srl = (Ci^{*}.Cj)^2/\Delta E(\text{HSOMO-LUMO}) + (Ci^{*}.Cj)^2/\Delta E(\text{LSOMO-HOMO}) = Srl^{*} + Srs^{*} \qquad (1)$$

Where $\Delta\beta$ is a resonance integral.[13] Ci* is the reaction point coefficient of HSOMO or LSOMO of photoexcited

Table 3. Frontier Orbitals of Triplet Enones and Ground-state Alkenes.

			HSOMO			LUMO	
HSOMO or LUMO	level (eV)	-3.84	-4.19	-4.19	-3.37	-0.19	1.30
	coeff. β	-0.735	-0.772	-0.761	-0.676	-0.673	-0.676
	α	0.522	0.487	0.530	0.566	0.551	0.707
			LSOMO			HOMO	
LSOMO or HOMO	level (eV)	-6.49	-5.64	-5.61	-5.78	-10.80	-9.51
	coeff. β	0.557	0.494	0.521	0.470	0.638	0.671
	α	0.699	0.734	0.733	0.628	0.595	0.495



enones, and Cj is the reaction point coefficient of the HOMO or LUMO of ground-state alkenes. Srl* and Srs* are also the larger part and smaller part of Sr1.

The Srl and Srl* values calculated by using values in Table 3 are given in Table 4 (and Table 7). By viewing these factors, it can be seen that $\mathrm{Sr1}_{3\beta}$ are larger for reactions in which initial bonding occur between the enone triplet and alkene β-carbons in the cases of electron-withdrawing group substituted alkenes. This suggests a preference for formation of biradical **13w** and a selectivity for production of head-to-head adducts in the 2+2-photoadditions of electron-deficient alkenes to the α,β-unsaturated carbonyl compounds **1**, **2**, **5**, **8** and **9**. With an electron-donating group substituted alkenes the interaction factors are trending in the other direction with $\mathrm{Sr1}_{2\beta}$ and $\mathrm{Srl}^{**}_{2\beta}$ corresponding to bonding between the triplet enone α- and alkene β-carbons being larger. The predicted trend here is that formation of biradicals **14d** and, thus, head-to-tail adducts would be preferred. Interestingly, the remarkably small $\mathrm{Srl}^{*}_{2\beta}$ and $\mathrm{Sr1}_{2\beta}$ values calculated for addition of furanone **8** with ethyl vinyl ether parallels the observation that 2+2-adducts are not formed in this photoreaction.

Scheme 3

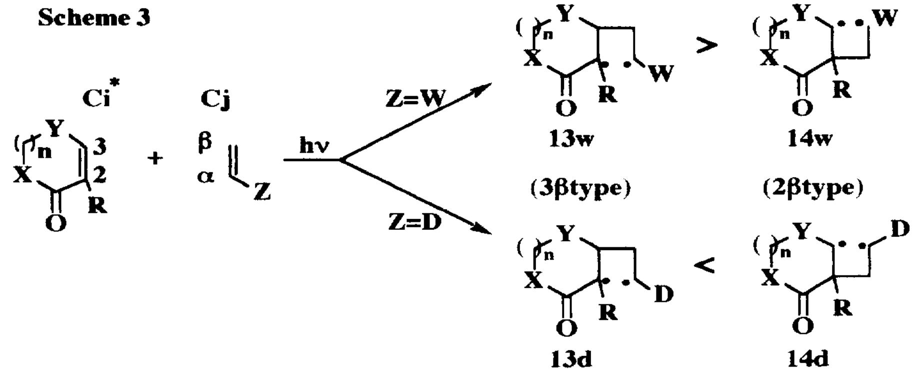


Table 4. Frontier Molecular Orbital Interaction Factors, Sr1 and Srl* for Additions of Ground State Alkenes to Triplet α,β-Unsaturated Carbonyl Compounds.

Enones	1		2		5		8		9	
Ethylene R/Z	H/CN (H/CO_2Me)	H/OEt	H/CN	H/OEt	H/CN	H/OEt	OH/CN	OH/OEt	H/CN	H/OEt
HSOMO-LUMO (3-β = hh)	6.7/9.6 [a] (6.2/9.1)		6.8/8.5		6.6/8.7		6.5/8.3		7.0/8.3	
LSOMO-HOMO (2-β = ht)	4.6/8.0 (4.5/7.6)		4.3/6.6		4.2/7.4		3.2/7.8		5.5/7.6	
HSOMO-LUMO (3-β = hh)		4.8/9.4		5.0/7.6		4.8/8.0		4.5/7.1		4.9/6.9
LSOMO-HOMO (2-β = ht)		7.3/9.7		6.3/8.1		6.2/8.5		4.8/7.9		8.8/10.2

[a] $(\mathrm{Srl}^{*}\times 10^2)/(\mathrm{Sr1}\times 10^2)$. Sr1 and Srl* are in equation (1).

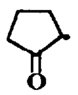
Also, the FMO evaluation of photocycloaddition regioselectivities needs to include factors which influence partitioning of the diradical intermediate by bonding to form the cyclobutane adduct or cleavage to regenerate ground state reactants. The entire process can be analyzed in terms of the FMO interaction factors Sr1 and Sr2 (eq. 2) which correspond to the first biradical forming and second closing steps, respectively.

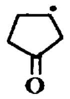
$$Sr2 = (Ci.Cj)^2/\Delta E\,(SOMO\text{-}LUMO) + (Ci.Cj)^2/\Delta E\,(LUMO\text{-}SOMO) = Sr1^{**} + Srs^{**} \qquad (2)$$

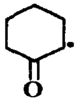
Sr1* and Sr1** correspond to the two main frontier orbital interactions included in Sr1 and Sr2. Large values for Sr1* and Sr1** and, thus, Sr1 and Sr2 would suggest that cyclobutane formation is the predominant reaction pathway while return of the biradical intermediate to the ground state alkene and unsaturated carbonyl compound would dominate when Sr2 are small. In Tables 5 and 6 are compiled the energies and coefficients of the frontier orbitals for the radical componets of each relevant biradical intermediate formed by bonding between triplet cyclohexenone and electron rich and poor alkenes. These values were employed to calculate Sr2 by using UHF methods. The calculated values for Sr1 and Sr2, which are energy terms, along with logarithms of the

Table 5. MO Property of Radicals from 2-Cycloalkenones.

		αspin	βspin	αspin	βspin	αspin	βspin	αspin	βspin
LUMO	level (eV)	1.07	-0.64	0.81	0.58	1.06	-0.58	0.81	0.65
	coeff.	0.25	0.75	0.02	0.90	0.25	0.75	0.01	0.91
SOMO	level (eV)	-9.87	-10.60	-9.34	-10.64	-9.83	-10.52	-9.27	-10.54
	coeff.	0.85	0.00	0.88	0.00	0.85	0.01	0.88	0.00







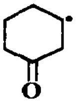


Table 6. MO Property of Radicals from Alkenes.

		αspin	βspin	αspin	βspin	αspin	βspin	αspin	βspin
LUMO	level (eV)	1.34	-0.71	1.29	0.37	2.45	1.46	2.67	0.95
	coeff.	0.00	0.80	0.00	0.95	0.00	0.89	0.00	0.95
SOMO	level (eV)	-9.87	-12.36	-10.04	-12.39	-8.33	-11.21	-9.40	-10.60
	coeff.	0.83	0.00	0.91	0.01	0.84	0.21	0.89	0.08

hh/ht product ratios for photocycloadditions of cyclohexenone and cyclopentenone to electron rich and poor alkenes are given in Table 7. Linear correlations between log(hh/ht) and ($Sr1_{3\beta}$-$Sr1_{2\beta}$) were found for small

Table 7. Frontier Orbital Interaction Factors Sr1, Sr2 and the main factors Sr*, Sr** and Logarithms of Photoaddition Product Ratio (hh/ht)exp.

		Srl* and Srs*			Srl** and Srs**					
		HSOMO-LUMO	LSOMO-HOMO	Sr1	SOMO-LUMO	LUMO-SOMO	Sr2	$Sr1_{3\beta}$-$Sr1_{2\beta}$	$Sr1^*_{3\beta}$-$Sr1^*_{2\beta}$	$\log(hh/ht)_{exp}$
cyclopentenone (1) vs. acrylonitrile										
2-α	hh	0.023	0.040	0.063	0.071	0.064	0.135	0.016	0.021	-0.18[a]
3-β		0.067	0.029	0.096	0.050	0.043	0.093			
3-α	ht	0.045	0.026	0.070	0.063	0.050	0.113			
2-β		0.034	0.046	0.080	0.057	0.054	0.111			
cyclopentenone (1) vs. methyl acrylate										
2-α	hh	0.018	0.047	0.065	0.069	0.067	0.136	0.014	0.017	-0.06[a]
3-β		0.062	0.029	0.090	0.047	0.045	0.092			
3-α	ht	0.036	0.030	0.066	0.061	0.053	0.114			
2-β		0.031	0.045	0.076	0.054	0.057	0.111			
cyclopentenone (1) vs. 2-methylpropene										
2-α	hh	0.025	0.053	0.078	0.053	0.054	0.107	-0.001	-0.020	-0.41[b]
3-β		0.051	0.045	0.096	0.052	0.053	0.105			
3-α	ht	0.049	0.034	0.083	0.047	0.043	0.090			
2-β		0.026	0.071	0.097	0.058	0.066	0.124			
cyclopentenone (1) vs. ethyl vinylether										
2-α	hh	0.027	0.040	0.066	0.067	0.064	0.131	-0.003	-0.025	-0.60[a]
3-β		0.048	0.046	0.094	0.050	0.052	0.102			
3-α	ht	0.053	0.025	0.078	0.059	0.051	0.110			
2-β		0.024	0.073	0.097	0.056	0.064	0.120			
cyclohexenone (2) vs. acrylonitrile										
2-α	hh	0.016	0.038	0.053	0.071	0.065	0.136	0.019	0.025	0.72[a]
3-β		0.068	0.017	0.085	0.051	0.042	0.093			
3-α	ht	0.045	0.015	0.060	0.063	0.049	0.112			
2-β		0.023	0.043	0.066	0.058	0.055	0.113			
cyclohexenone (2) vs. 2-methylpropene										
2-α	hh	0.018	0.047	0.065	0.053	0.055	0.108	-0.002	-0.010	-0.79[c]
3-β		0.053	0.025	0.079	0.052	0.052	0.104			
3-α	ht	0.051	0.019	0.070	0.047	0.042	0.089			
2-β		0.018	0.063	0.081	0.059	0.067	0.126			
cyclohexenone (2) vs. ethyl vinylether										
2-α	hh	0.019	0.035	0.053	0.067	0.065	0.132	-0.005	-0.013	-0.63[a]
3-β		0.050	0.026	0.076	0.050	0.051	0.101			
3-α	ht	0.055	0.014	0.069	0.060	0.050	0.110			
2-β		0.017	0.063	0.081	0.056	0.065	0.121			

[a] Product ratios, (hh/ht)exp were taken from Table 1. [b] ref. 4e. [c] ref. 9. Underlines are for clearness.

slope, namely small correlation a=22.7 (r=0.93) with cyclopentenone and for large a=69.7 (r=0.98) with cyclohexenone in Figure 2. The correlations were similar to the correlations with Sr1*(3β-2β) (=$Srl^*_{3\beta}$-$Srl^*_{2\beta}$), and were better than the ones with Sr1(2α+3β-3α-2β). The better correlation with cyclohexenone

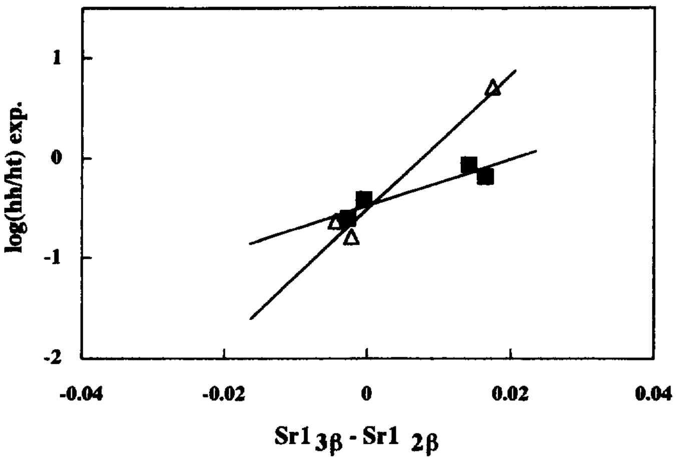


Figure 2 . Relationship between deference of predominant frontier orbital interactions ($Srl_{3\beta}$-$Srl_{2\beta}$) and experimental data log(hh/ht)exp. in Table 7. (■) cyclopentenone, (△) cyclohexenone.

indicates that Sr1* is the more influential factor in governing regiochemistry in this case. The relatively large $Sr^*_{3\beta}$ value for the first-step in reaction of triplet cyclopentenone with acrylonitrile suggests preferable formation of the hh biradical intermediate, but the small $Sr2_{3\beta}$ (0.092) for the second-step indicates a poorer partitioning of this biradical to the hh-cyclobutane adduct. The Sr1 and Sr2 values for photoadditions between cyclopentenone and acrylonitrile and methyl acrylate and between cyclohexenone and acrylonitrile also trend in opposite directions again signaling low hh/ht regioselectivities. Interestingly, the Sr1 and Sr2 values evaluated for photoadditions of cyclopentenone and cyclohexenone to methylpropene are relatively quite similar inferring that ht-adduct formation preferences in these cases will be similar.

We now postulate for the factors of the cycloaddition regiochemistry differences between cyclopentenone and cyclohexenone for electron-deficient alkenes. The biradical intermediates may bring about cleavage to the reactants and formation of the cycloadducts. As the reactions of cyclohexenone mainly give thermally unstable trans-fused adducts,[9] the twisted triplet biradical intermediates might pass through the kinetically control transition states. The process must be effective for intersystem crossing (ISC) to singlet biradicals and the two p-orbital overlaps for cycloadducts. The trans-fused adduct formation in cyclohexenone-methylpropene photoadditions could be also accounted by considering the possible pyramidal conformations of the 1, 4-biradical intermediates.[2, 14] It is like as conformational memory effects on the endo-selectivity of Paterno-Büchi photoadditions . The conformer with cyclohexene preferentially gives endo-photoadducts than the one with cyclopentene.[15]

From these considerations, the photocycloadditions with cyclohexenone are inferred that the first-step (Sr1) is effective (large slope in Figure 2) for the cycloadducts. The phenomena were also calculated by Houk et al.[3]

The additions with cyclopentenone must involve flatter triplet biradical conformers, and such ones cause slower ISC and/or the lower two p-orbital overlaps, and then the biradical intermediates might be brought about bond-cleavage to the reactants. It is inferred the first step ($Sr1_{3\beta}$) is not so effective (small slope), and the small $Sr2_{3\beta}$ might relatively cause back-reactions.[4b] The hh/ht ratio might be then less than 1.0.

The proper conformations of the biradical intermediates from cycloalkenones-alkenes photoreactions may be speculated for the PM3 calculations etc. in the next step.

Conclusion

Several conclusions can be drawn from the results of the PM3-CI-FMO treatments presented above. The regiochemical preferences for 2+2-photocycloadditions, occuring between cyclic α,β-unsaturated carbonyl compounds and substituted alkenes, can be analysed by considering the main FMO interaction factors Sr1 (Sr1*) and Sr2 for the respective biradical forming and cyclization steps. Thus, the head-to-tail regioselectivity observed in reactions of electron-donating substituted alkenes is well correlated with the interaction factor Sr1 associated with the first bonding step (*i. e.* a good linear correlation exists between log(ht/hh) and Sr1 (2β-3β) and it also appears to derive from relatively the large $Sr1^{**}_{2\beta}$ (LUMO-SOMO) values which suggest that ht-biradical bonding will be against relative to reversion to reactants. The few head-to-head selective electron-deficient alkene cycloadditions may be stem from large $Sr1^{*}_{3\beta}$ (HSOMO-LUMO) values but the generally small values calculated for $Sr2_{3\beta}$ suggest the existence of relatively efficient reversion of the hh-biradical intermediates[2b] to the reactants in these cases.[16]

As mentioned above, earlier Houk and his coworkers have provided a nice theoretical explanation for the photoaddition regioselectivity of cyclohexenone.[3] Weedon has also probed these photocycloadditions of cyclopentenone by use of biradical trapping techniques and concluded that reversion from these intermediates to ground-state reactants was more influential in determining regiochemistry than the initial biradical production step.[4] Weedon's conclusion is based on the expectation that the alkyl-cycloalkanone product ratios he observed were determined solely by H_2Se reduction of competitively formed biradical intermediates. However, we believe that these results must be viewed with some caution especially in the cases of photoaddition reactions with electron-deficient alkenes. Cyclopentenone itself reacts photochemically with H_2Se to give cyclopentanone *via* radical intermediates.[4d,e] We have calculated the FMOs of the ground state of H_2Se (E(HOMO) = -9.67eV, E(LUMO) = -0.57eV) and conclude that this substance would preferrentially transfer a hydrogen atom to the a-carbon of the triplet of cyclopentenone. The resulting b-oxoxyxlopentyl radical could very well add to electron deficient alkenes to give ultimately the same hydrogenated adducts which were presumed to arise exclusively by H_2Se trapping of head-to-head diradicals. Consequently, in this case the trapping product ratios might not truly reflect the ratios of the biradical intermediates formed.[2] It is inferred by the MO method that the biradical intermediate **13w** (3β) type ratio at the photoreaction between cyclopentenone and methyl acrylate is larger than the experimental data (e. g. under 1%) by the trapping method.[2b]

Acknowledgement. We thank Professor Patrick S. Mariano at University of Maryland for his suggestions regarding presentation of the results of our work. The studies were financially supported by a grant from The Naito Foundation and by a Grant-in-Aid for Scientific Research No.06651012 from the Ministry of Education, Science, Sports and Culture.

References and Notes

(1) (a) Demuth, M.; Mikhail, G. *Synthesis* **1989**, 145. (b) Keukeleire, D. D.; He, Shu-L. *Chem. Rev.* **1993**, *93*, 145.

(2) Schuster, D. I.; Chem. Rev. **1993**, *93*, 3. (b) Andrew, D.; Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1994**, *116*, 10870.

(3) Broeker, J. L.; Eksterowicz, J. E.; Belk, A. J.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 1847.

(4) (a) Andrew, D.; Hastings, D. J.; Oldroyd, D. L; Rudolph, A.; Weedon, A. C.; Wong, D. F.; Zhang,B. *Pure Appl. Chem.* **1992**, *64*, 1327. (b) Krug, P.; Rudolph, A.; Weedon , A. C. *Tetrahedron Lett.* **1993**, *34*, 7221. (c) Maradyn, D.J.; Sydnes, L. K.;Weedon, A. C.; *Tetrahedron Lett.* **1993**, *34*, 2413. (d) Maradyn, D. J.; Weedon, A. C. *Tetrahedron Lett.* **1994**, *35*, 8107. (e) Andrew, D.; Weedon, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 5647.

(5) (a) Somekawa, K.; Izumi, R.; Taniguchi, K.; Suishu, T.; Shimo, T. *Nippon Kagaku kaishi.* **1990**,

271. (b) Somekawa, K,; Okuhira, H.; Sendayama, M.; Suishu, T.; Shimo, T. *J. Org. Chem.* **1992**, *57*, 5708. (c) Somekawa, K.; Shimo, T.; Suishu,T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 354.

(6) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10.

(7) Somekawa, K.; Shimo, T.; Atsuchi, M.; Kumamoto, S. *Nippon kagaku Kaishi* **1978**, 1013.

(8) (a) Shimo, T.; Ohshima, K.; Somekawa, K.; Kawaminami, M. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2891. (b) Suishu, T.; Shimo, T.; Minamishin, H.; Somekawa, K. *J. Heterocyclic Chem.* in contribution.

(9) Corey, E. J.; Bass, J. D. j.; Lemahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

(10) Caldwell, R. A.; Ghali, N. I.; Ohien, C. K.; Macro, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857.

(11) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley, New York, **1976**; Chapter 5 and 6.

(12) Rao, V. P. ; Ramamurthy, V. *J. Org. Chem.* **1998**, *53*, 332.

(13) Imoto, M. Bunshi-Kidou Wo Tsukau-tameni, Kagaku Doujin, Kyoto, **1986**; Chapter 5.

(14) Bauslaugh, P. G. *Synthesis.* **1970**, 287.

(15) Griesbeck, A. G.; Mauder, H.; Stadtmuller, S. *Acc. Chem. Res.* **1994**, *27*, 70.

(16) Some one at the photochemistry conference has pointed out a potential problem associated with energy transfer in photoreactions with acrylonitrile. Specifically, the vertical triplet energies of some ethylenes such as acrylonitrile (E_T = 58 kcal/mol)[17] are below that of the relaxed triplets of enones, so that the reactions may not simply involve additions of triplet enones to the ground state alkenes. It should be mentioned that reactions with acrylonitrile were not so different from that with methyl acrylate[4b] in

terms of adduct distribution as shown by the data in Table 1. The clear theoretical prediction by Houk[3] may also serve as good evidence that the photocycloaddition reactions with acrylonitrile simply involve additions of triplet cycloalkenones with the ground state of this substance.

(17) Lavilla, J. A.; Goodman, J. L. *Chem. Phys. Lett.* **1987**, *141*, 149.

(*Received in Japan* 22 *November* 1996; *accepted* 23 *January* 1997)