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HETERO DIELS-ALDER REACTION OF β -TRIFLUOROACETYLATED VINYL ETHERS WITH VINYL ETHERS TO ACCESS FLUORINE-CONTAINING DIHYDROPYRAN DERIVATIVES – A MOLECULAR ORBITAL CALCULATION STUDY

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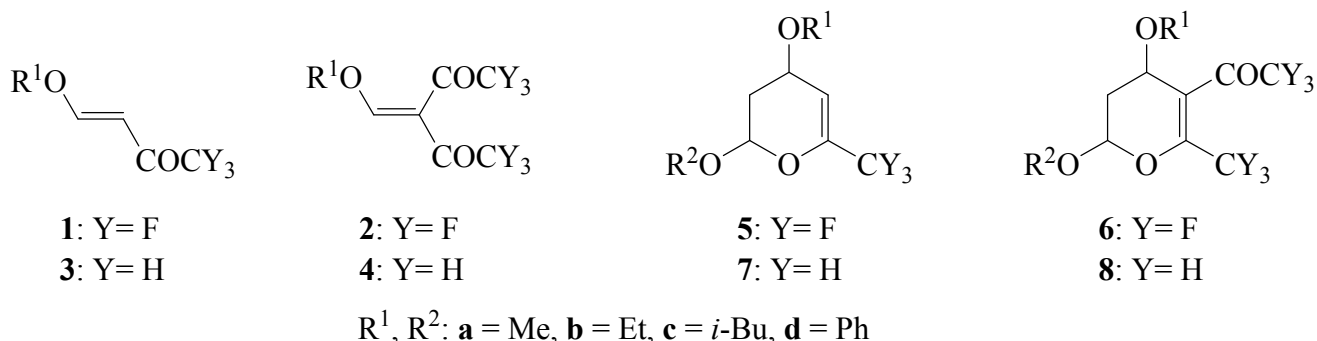
Abstract – The reactivity differences between β -trifluoroacetylvinyl ethers (**1**), β,β -bis(trifluoroacetyl)vinyl ethers (**2**), β -acetylvinyl ethers (**3**), and β,β -diacetylvinyl ethers (**4**) in the hetero Diels-Alder reaction with vinyl ethers giving dihydropyrans (**5**, **6**, **7**, and **8**, respectively) are discussed on the basis of molecular orbital calculations. Frontier orbital interactions and activation energies of these reactions were estimated using DFT calculations.

INTRODUCTION

In recent years, research efforts have focused on developing new methodologies for the syntheses of fluorine-containing heterocycles. These compounds are widely recognized as important organic materials, showing specific functions as well as biological activities that are of interest.¹⁻⁴ Previously, we reported efficient and convenient synthetic methods to obtain fluorine-containing dihydropyrans (**5**, **6**) from β -trifluoroacetylvinyl ethers (**1**)⁵ and β,β -bis(trifluoroacetyl)vinyl ethers (**2**).⁶ We found that the hetero Diels-Alder reaction of **1** with vinyl ethers readily occurred at 80 °C and that of **2** with vinyl ethers proceeded smoothly below 40 °C.^{5,6} On the other hand, the hetero Diels-Alder reaction of β -acetylvinyl ethers (**3**) bearing no fluorine atoms with vinyl ethers required high reaction temperatures (190-210 °C) to access the corresponding dihydropyrans (**7**).⁷ Even in the case of β,β -diacetylvinyl ethers (**4**) with two electron-withdrawing acetyl groups, elevation of the reaction temperature (over 100 °C) was necessary for the corresponding cycloaddition to afford dihydropyrans (**8**).⁸

In general, Lewis acid catalysis is necessary for inverse-electron-demand Diels-Alder reaction of heterodienes with electron-rich alkenes under mild conditions.⁹ Therefore, it is worth noting that the reaction of **2** with vinyl ethers proceeded, even at ambient temperatures, in the absence of a catalyst.⁶

We were thus very interested in the effect of trifluoromethyl and trifluoroacetyl groups on the present hetero Diels-Alder reaction.



The hetero Diels-Alder reaction to afford **5** and **6** is a potential route to prepare carbohydrates and related compounds bearing a CF_3 component. Furthermore, dihydropyrans (**5**, **6**) are potentially useful intermediates to access a variety of fluorine-containing organic compounds including heterocycles. We found the specific ring-opening reactions of **5** and **6** with nucleophiles, such as thiols,^{10,11} amines,¹² and aromatic compounds¹³ afford novel fluorine-containing dienone derivatives, which are expected to be versatile building blocks for various CF_3 -containing heterocycles. Despite its importance for the synthesis of various dihydropyran derivatives including **5** and **6**, there have been no reports of molecular orbital calculations elucidating the hetero Diels-Alder reaction of electron-deficient heterodienes (**1-4**) with electron-rich alkenes, such as vinyl ethers.

Here, we present hetero Diels-Alder reaction of these systems along with the results of molecular orbital calculations. The reactivity differences between compounds **1-4** in the hetero Diels-Alder reaction with electron-rich alkenes are elucidated on the basis of DFT calculations.

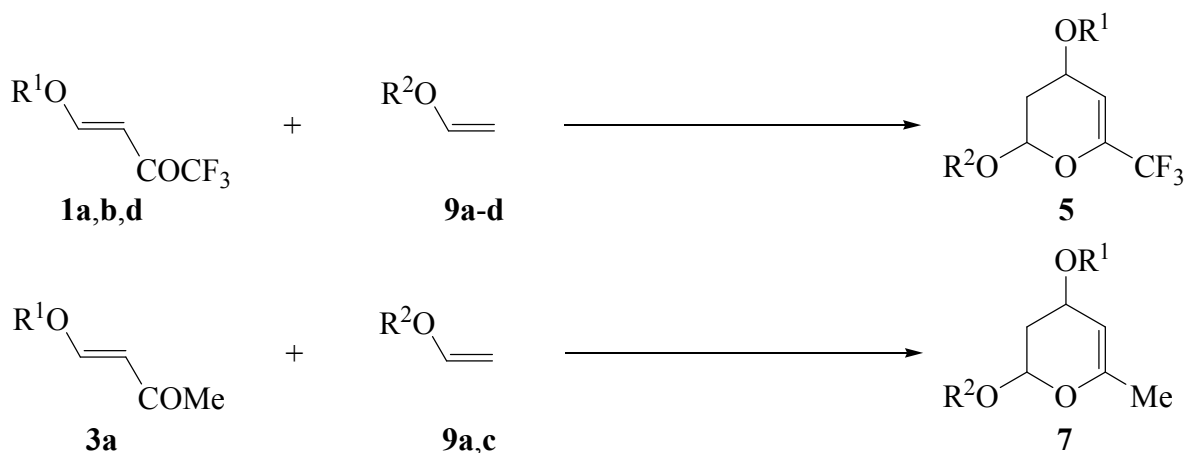
RESULTS AND DISCUSSION

Previously, we reported that the hetero Diels-Alder reaction of β -trifluoroacetylvinyl ethers (**1b,d**) with vinyl ethers (**9b-d**) readily occurred at 80 °C to give the corresponding 3,4-dihydro-2*H*-pyrans (**5bb,bc,db,dd**) in excellent yields (Scheme 1, Table 2, Entries 2, 3, 5 and 6).⁵ In contrast, the corresponding reaction of 4-methoxy-3-buten-2-one (**3a**) with isobutyl vinyl ether (**9c**), affording 2-isobutoxy-6-methyl-3,4-dihydro-2*H*-pyran (**7ac**), proceeded much slower, even at 190-210 °C, and the conversion did not exceed 45% (Scheme 1, Table 2, Entry 8).⁷ In order to understand the reactivity difference between **1** and **3** for the hetero Diels-Alder reaction with vinyl ethers (**9**), we carried out 6-31G* level DFT calculations (RB3LYP/6-31G*) on the reactions shown in Scheme 1.

The optimized structures and their energy values were computed for β -trifluoroacetylvinyl ethers (**1a,b,d**),

4-methoxy-3-buten-2-one (**3a**), and vinyl ethers (**9a-d**). The values of total energy and frontier orbital energy of these substrate molecules are summarized in Table 1.

The energy level gaps (ΔE_f^1) between the HOMO of **9a-d** and the LUMO of **1a,b,d** and **3a**, and those (ΔE_f^2) between the HOMO of **1a,b,d** and **3a** and the LUMO of **9a-d** were calculated for all hetero Diels-Alder reactions depicted in Scheme 1 (Table 2). In all the cases, the values of ΔE_f^1 were much smaller than those of ΔE_f^2 , clearly indicating that the cycloaddition reactions in Scheme 1 are tentative inverse electron-demand Diels-Alder reaction of electron-deficient heterodienes (**1** and **3**) with electron-rich alkenes (**9**).



Scheme 1

Table 1. The total energy (E), and the energy levels of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) on **1a,b,d**, **3a** and **9a-d**

1, 3	R^1	E (au)	E_{HOMO} (eV)	E_{LUMO} (eV)	9	R^2	E (au)	E_{HOMO} (eV)	E_{LUMO} (eV)
1a	Me	-643.47522	-6.957	-1.824	9a	Me	-193.11042	-5.919	1.057
1b	Et	-682.79517	-6.888	-1.775	9b	Et	-234.42986	-5.874	1.101
1d	Ph	-835.21747	-6.702	-1.977	9c	<i>i</i> -Bu	-311.05832	-5.89	1.085
3a	Me	-345.76472	-6.360	-0.928	9d	Ph	-384.85540	-5.943	-0.114

The calculated ΔE_f^1 for the hetero Diels-Alder reactions of β -trifluoroacetylvinyl ethers (**1a,b,d**) with vinyl ethers (**9a-d**) were 3.896 - 4.123 eV (Entries 1-6) and the difference between each ΔE_f^1 did not exceed 0.23 eV. On the other hand, ΔE_f^1 for the reactions of 4-methoxy-3-buten-2-one (**3a**) with vinyl ethers (**9a,c**) were 4.970 - 4.991 eV (Entries 7, 8). The ΔE_f^1 values for the reaction of **1a**, **1b**, and **1d** were ca. 1 eV smaller than those for the reaction of **3a**.

The smaller ΔE_f^1 causes a stronger frontier orbital interaction between the heterodienes and alkenes, thus promoting the hetero Diels-Alder reaction more effectively. The results are compatible with the experimental results showing that cycloaddition of β -trifluoroacetylvinyl ethers (**1b,d**) with vinyl ethers (**9b-d**) occurs more readily than that of β -acetylvinyl ether (**3a**) with isobutyl vinyl ether (**9c**).^{5,7} The strong electron-withdrawing fluorine substituents effectively lower the LUMO level of **1** (Table 1), thereby decreasing ΔE_f^1 (Table 2) and making the hetero Diels-Alder reaction of **1** with **9** more facile than that of non-fluorinated **3** with **9**.

Table 2. The energy level gaps between HOMO and LUMO (ΔE_f^1 and ΔE_f^2) for hetero Diels-Alder reaction of β -acylvinyl ethers (**1a,b,d** and **3a**) with vinyl ethers (**9a-d**)

Entry	1, 3	R ¹	9	R ²	Product (Yield, %)	ΔE_f^1 (eV) ^a	ΔE_f^2 (eV) ^b
1	1a	Me	9a	Me	5aa	4.095	8.014
2	1b	Et	9b	Et	5bb (93) ⁵	4.099	7.989
3	1b	Et	9c	<i>i</i> -Bu	5bc (100) ⁵	4.123	7.973
4	1d	Ph	9a	Me	5da	3.942	7.759
5	1d	Ph	9b	Et	5db (72) ⁵	3.896	7.803
6	1d	Ph	9d	Ph	5dd (77) ⁵	3.965	6.588
7	3a	Me	9a	Me	7aa	4.991	7.417
8	3a	Me	9c	<i>i</i> -Bu	7ac (<45) ⁷	4.970	7.445

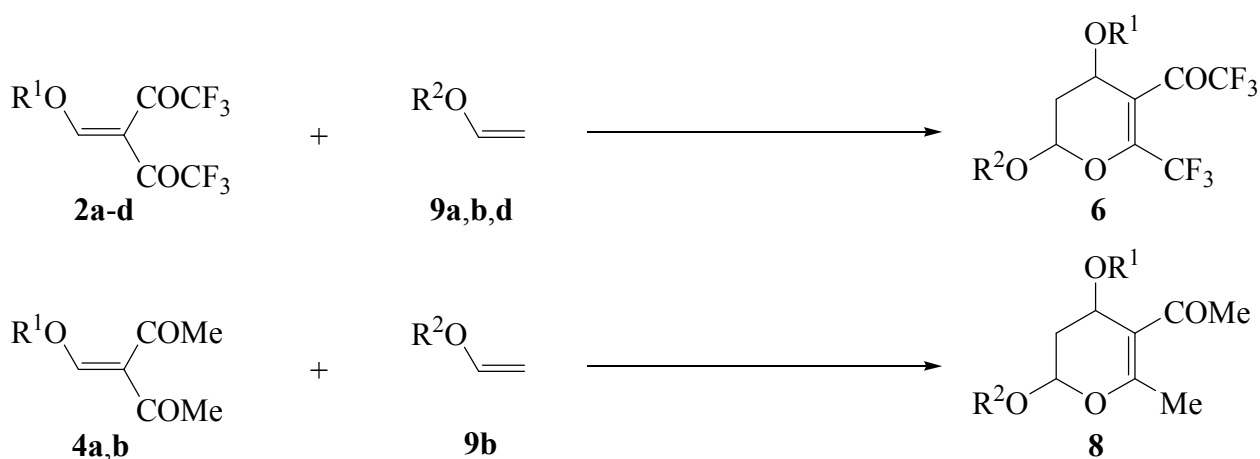
^a $\Delta E_f^1 = (E_{\text{LUMO}} \text{ of } \mathbf{1, 3}) - (E_{\text{HOMO}} \text{ of } \mathbf{9})$. ^b $\Delta E_f^2 = (E_{\text{LUMO}} \text{ of } \mathbf{9}) - (E_{\text{HOMO}} \text{ of } \mathbf{1, 3})$.

The hetero Diels-Alder reaction of β,β -bis(trifluoroacetyl)vinyl ether (**2**) with vinyl ether (**9**) occurs more readily than that of β -trifluoroacetylvinyl ether (**1**) with **9**.⁶ The reaction of alkyl β,β -bis(trifluoroacetyl)vinyl ethers (**2b,c**) with **9b** and **9d** and that of aryl β,β -bis(trifluoroacetyl)vinyl ether (**2d**) with **9d** proceeded successfully at ambient temperature and 40 °C, respectively, to afford the corresponding dihydropyrans (**6bb,cb,bd,dd**) in moderate to high yields (Scheme 2, Table 4).⁶ Furthermore, cycloaddition of **2b** with 1,1-diphenoxyethylene (**10d**) and that of **2b** and **2c** with ethyl vinyl sulfide (**11b**) also proceeded successfully under similar conditions to afford the corresponding **12bd**, **13bb**, and **13cb**, respectively (Figure 1, Table 4).⁶ In contrast, the hetero Diels-Alder reaction of β,β -diacetylvinyl ethers (**4a,b**) with ethyl vinyl ethers (**9b**) in Scheme 2 required a much higher reaction temperature (140 °C).⁸

The energy values and the frontier orbital energy levels of the most stable structures of β,β -bis(trifluoroacetyl)vinyl ethers (**2a-d**) and β,β -diacetylvinyl ethers (**4a,b**) are summarized in Table 3. As expected, the LUMO energies of **2a-d**, **4a**, and **4b** (Table 3) were lower than those of **1a-d** and **3a** (Table

1). These results clearly indicate that the hetero Diels-Alder reaction of **2a-d**, **4a**, and **4b** with electron-rich alkenes, such as **9a-d**, is also of the inverse electron-demand type reaction.

We calculated the energy level gaps (ΔE_f^1) between the HOMO of **9a**, **9b**, and **9d** and the LUMO of **2a-d**, **4a**, and **4b** for all cases of cycloaddition in Scheme 2 (Table 4). Moreover, for the cycloaddition of **2a** and **2b** with 1,1-diphenoxyethylene (**10d**) and vinyl sulfides (**11a,b**), which afforded the dihydropyrans (**12ad,bd** and **13aa-cb**; Figure 1), we evaluated the ΔE_f^1 values (Table 4).



Scheme 2

Table 3. The total energy (E), and the energy levels of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) on **2a-d** and **4a,b**

2	R ¹	E (au)	E_{HOMO} (eV)	E_{LUMO} (eV)	2, 4	R ²	E (au)	E_{HOMO} (eV)	E_{LUMO} (eV)
2a	Me	-1093.81611	-7.556	-2.532	2d	Ph	-1285.55773	-7.159	-2.623
2b	Et	-1133.13671	-7.477	-2.457	4a	Me	-498.40763	-6.473	-1.578
2c	<i>i</i> -Bu	-1211.76615	-7.467	-2.454	4b	Et	-537.72748	-6.431	-1.519

The values of ΔE_f^1 for the hetero Diels-Alder reaction of β,β -bis(trifluoroacetyl)vinyl ethers (**2a-d**) with vinyl ethers (**9a-d**) were in the range of 3.319 – 3.486 eV (Entries 1-6). These ΔE_f^1 values were ca. 0.8 eV smaller than those for the reaction of β,β -diacetylvinyl ethers (**4a,b**) with **9b** (Entries 7, 8), and ca. 0.6 eV smaller than those for the reaction of β -trifluoroacetylvinyl ethers (**1a,b,d**) with **9a-d** (Entries 1-6 in Table 2). These results are consistent with the experimental results, showing that the cycloaddition of β,β -diacetylvinyl ethers (**4a,b**) with ethyl vinyl ether (**9b**) requires elevated reaction temperature up to 140 °C⁸ and that of β -trifluoroacetylvinyl ethers (**1b,d**) with vinyl ethers (**9b-d**) occurs at 80 °C,⁵ whereas

the corresponding cycloaddition of β,β -bis(trifluoroacetyl)vinyl ethers (**2b-d**) with **9b-d** readily occurs below 40 °C.⁶

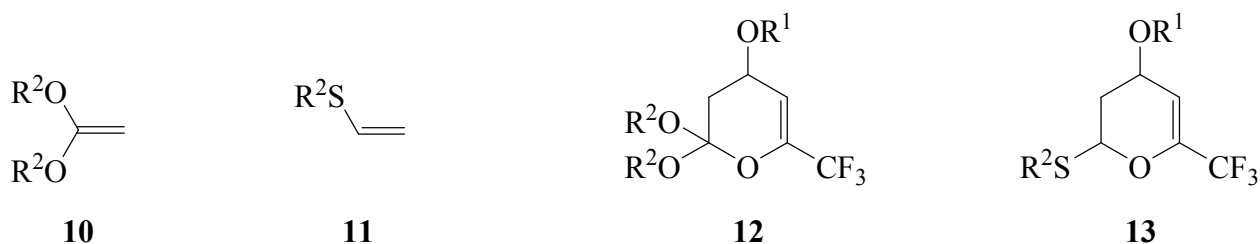


Figure 1

Table 4. The energy level gaps between HOMO and LUMO, ΔE_f^1 for hetero Diels-Alder reaction of β,β -diacylvinyl ethers (**2a-d** and **4a,b**) with electron-rich alkenes (**9a,b,d,10d** and **11a,b**)

Entry	2, 4	R^1	9-11	R^2	Product (Yield, %)	ΔE_f^1 (eV) ^a
1	2a	Me	9a	Me	6aa	3.387
2	2b	Et	9b	Et	6bb (95) ⁶	3.417
3	2c	<i>i</i> -Bu	9b	Et	6cb (98) ⁶	3.420
4	2a	Me	9d	Ph	6ad	3.410
5	2b	Et	9d	Ph	6bd (85) ⁶	3.486
6	2d	Ph	9d	Ph	6dd (50) ⁶	3.319
7	4a	Me	9b	Et	8ab	4.296
8	4b	Et	9b	Et	8bb (87) ⁸	4.355
9	2a	Me	10d	Ph	12ad	3.592
10	2b	Et	10d	Ph	12bd (77) ⁶	3.667
11	2a	Me	11a	Me	13aa	3.148
12	2b	Et	11b	Et	13bb (100) ⁶	3.169
13	2c	<i>i</i> -Bu	11b	Et	13cb (100) ⁶	3.172

^a $\Delta E_f^1 = (E_{LUMO} \text{ of } \mathbf{2, 4}) - (E_{HOMO} \text{ of } \mathbf{9-11})$.

The values of ΔE_f^1 for the cycloaddition of **2a** and **2b** with 1,1-diphenoxyethylene (**10d**; Entries 9, 10) were slightly (ca. 0.2 eV) larger than those for the corresponding cycloaddition of **2a** and **2b** with phenyl vinyl ether (**9d**; Entries 4,5). In contrast, ΔE_f^1 for the cycloaddition of **2a-c** with vinyl sulfides (**11a,b**; Entries 11-13) were slightly (ca. 0.2 eV) smaller than those for the corresponding cycloaddition of **2a-c** with vinyl ether (**9a,b**; Entries 1-3). However, differences in the ΔE_f^1 smaller than 0.3 eV would show

no significant effect on the reaction. These results are also in good agreement with experimental results, showing that the cycloaddition of β,β -bis(trifluoroacetyl)vinyl ether (**2**) with ketene acetals (**10d**) and vinyl sulfides (**11a,b**) occurs as readily as that of **2** with vinyl ethers (**9**).⁶

In order to confirm these findings on the hetero Diels-Alder reactions of heterodienes (**1-4**) with electron-rich alkenes (**9-11**), we computed transition state structures for representative cases of these reactions and estimated their energies. Two pairs of optimized transition state structures (*endo*-TS5bb and *exo*-TS5bb; *endo*-TS6bb and *exo*-TS6bb) corresponding to the *endo*- and *exo*-[4+2]cycloaddition of **1b** with **9b** and those of **2b** with **9b** are depicted in Figure 2 together with their energy values. The transition state structure, *endo*-TS5bb, was estimated to be 0.8 kcal/mol more stable than *exo*-TS5bb, and *endo*-TS6bb was estimated to be 2.1 kcal/mol more stable than *exo*-TS6bb. These findings are in good agreement with our experimental results, in which *endo*-[4+2]cycloaddition occurs preferentially in both cases of the reaction of **1b** with **9b** and **2b** with **9b** to give dihydropyrans (*cis*-5bb and *cis*-6bb, respectively) as the major products together with *trans*-5bb and *trans*-6bb as the minor products, respectively.^{5,6}

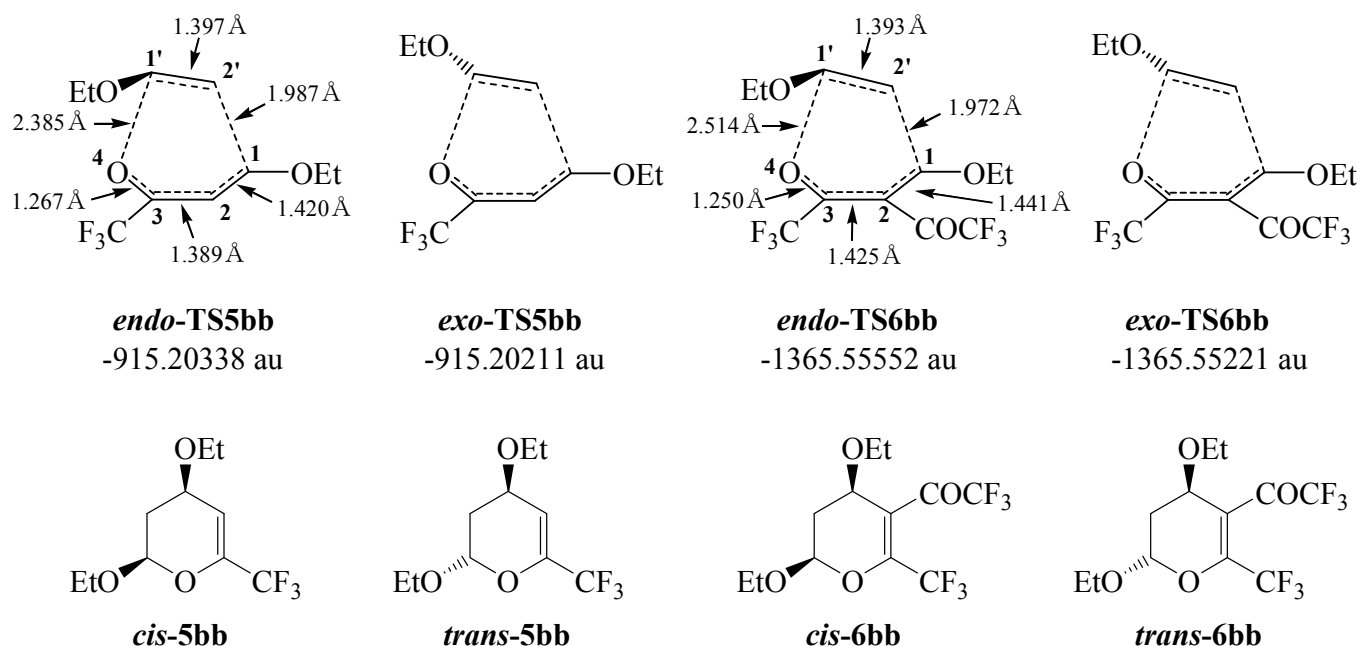


Figure 2

Some interatomic distances in *endo*-TS5bb and *endo*-TS6bb are also indicated in Figure 2. In both cases, the C(1')–O(4) bond was longer (0.398 Å and 0.542 Å, respectively) than the C(2')–C(1) bond.

From the energy values of the *endo* type transition state structures, we estimated the activation energies (ΔE^\ddagger)¹⁴ of hetero Diels-Alder reactions of β -acylvinyl ethers (**1a,b,d** and **3a**) and β,β -diacylvinyl ethers (**2a,b** and **4a,b**) with electron-rich alkenes (**9a-d**, **10a**, and **11a,b**) (Table 5). The estimated ΔE^\ddagger values of

the cycloaddition of β -trifluoroacetylvinyl ethers (**1a,b,d**) with vinyl ethers (**9a-c**; Entries 1-5) were 12-14 kcal/mol, which was over 6 kcal/mol lower than that of the reactions of β -acetylvinyl ethers (**3a**) with **9a** and **9c** (Entries 6, 7). The ΔE^\ddagger for the cycloaddition of β,β -bis(trifluoroacetyl)vinyl ethers (**2a,b**) with **9a** and **9b** (Entries 8, 9) was 7-8 kcal/mol, which was over 7 kcal/mol lower than that of the corresponding reaction of β,β -diacetylvinyl ethers (**4a,b**; Entries 11,12), and at least 4 kcal/mol lower than the corresponding reaction of β -trifluoroacetylvinyl ethers (**1a,b,d**; Entries 1-5). The ΔE^\ddagger for the cycloaddition of **2b** with phenyl vinyl ether (**9d**; Entry 10) was estimated to be 12.2 kcal/mol, which was ca. 5 kcal higher than that of the corresponding reaction with ethyl vinyl ether (**9b**; Entry 9). This relatively high activation energy corresponds to the fact that the cycloaddition of **2b** with phenyl vinyl ether **9d** required a prolonged reaction time (24 h) compared to that of **2b** with **9b** (15 min).⁶

Table 5. Estimated activation energy (ΔE^\ddagger) for hetero Diels-Alder reactions of β -acylvinyl ethers (**1a,b,d** and **3a**) and β,β -diacylvinyl ethers (**2a,b** and **4a,b**) with electron-rich alkenes (**9a-d**, **10a**, and **11a,b**)

Entry	1-4	R ¹	9-11	R ²	Product	ΔE^\ddagger (kcal/mol)
1	1a	Me	9a	Me	5aa	13.9
2	1b	Et	9b	Et	5bb	13.6
3	1b	Et	9c	<i>i</i> -Bu	5bc	13.4
4	1d	Ph	9a	Me	5da	13.0
5	1d	Ph	9b	Et	5db	12.4
6	3a	Me	9a	Me	7aa	20.0
7	3a	Me	9c	<i>i</i> -Bu	7ac	20.0
8	2a	Me	9a	Me	6aa	8.0
9	2b	Et	9b	Et	6bb	6.9
10	2b	Et	9d	Ph	6bd	12.2
11	4a	Me	9b	Et	8ab	15.4
12	4b	Et	9b	Et	8bb	15.6
13	2b	Et	10a	Me	12ba	3.3
14	2a	Me	11a	Me	13aa	10.7
15	2b	Et	11b	Et	13bb	9.8

The ΔE^\ddagger values were in decreasing order: β -acetylvinyl ethers (**3**; Entries 6, 7), β,β -diacetylvinyl ether (**4**; Entries 11, 12), β -trifluoroacetylvinyl ethers (**1**; Entries 1-5), and β,β -bis(trifluoroacetyl)vinyl ethers

(**2**; Entries 8-10). This order is consistent with the decreasing order of the reaction temperature required for the hetero Diels-Alder reactions of **1-4** with vinyl ethers (**9**); **3**: 190-210 °C,⁷ **4**: 140 °C,⁸ **1**: 80 °C,⁵ and **2**: rt-40 °C.⁶

We also estimated the ΔE^\ddagger for the hetero Diels-Alder reactions of β,β -bis(trifluoroacetyl)vinyl ethers (**2a,b**) with ketene acetals and vinyl sulfides instead of vinyl ethers. 1,1-Dimethoxyethylene (**10a**) was selected as a model compound for the ketene acetals. In the case of the cycloaddition of **2b** with **10a** (Entry 13), an ΔE^\ddagger of less than 4 kcal/mol was estimated. In contrast, the predicted ΔE^\ddagger of the reaction of **2a** and **2b** with vinyl sulfides (**11a,b**; Entries 14, 15) was relatively high in comparison with that of the corresponding reaction with vinyl ethers (**9a,b**; Entries 8, 9). These results explain why the reaction of **2b** with ethyl vinyl sulfide (**11b**) proceeds more slowly than that of **2b** with ethyl vinyl ether (**9b**),⁶ even when the HOMO-LUMO gap (ΔE_f^1) between **2b** and **11b** (Table 4, Entry 12) is narrower than that between **2b** and **9b** (Table 4, Entry 2).

The difference in ΔE^\ddagger on the reactions of **9**, **10**, and **11** would be attributed to stronger electron-donating ability of oxygen compared to sulfur. The terminal olefin carbon of the ketene acetal (**10a**) bearing two methoxy groups has more negative charge than that of vinyl ether (**9a**). On the other hand, the terminal olefin carbon of vinyl sulfide (**11a**) has less negative charge than **9a**. A stronger electrostatic interaction between **10a** and electron deficient **2b** would assist the molecular orbital interaction, in particular, that of C(2')-C(1) on the transition state (Figure 2), thus further decreasing ΔE^\ddagger . In contrast, the reverse would be true on the transition state of the reaction of **2b** with **11a**.

CONCLUSION

Molecular orbital calculations suggest that the efficiency of heterodienes (**1-4**) on hetero Diels-Alder reaction with electron-rich alkenes (**9-11**) can be attributed to energy level gaps (ΔE_f^1) between the LUMO of **1-4** and the HOMO of **9-11**. We confirmed these results by estimating the activation energies (ΔE^\ddagger) of these hetero Diels-Alder reactions. It is worth noting that one trifluoroacetyl group in the heterodienes (**1**) lowers the activation energy of the hetero Diels-Alder reaction more effectively than the two acetyl groups in **4**. A more stable *endo* type transition state in the hetero Diels-Alder reaction of β -trifluoroacetylvinyl ethers (**1**) and β,β -bis(trifluoroacetyl)vinyl ethers (**2**) with ethyl vinyl ether (**9**) explains the formation of the major product, the *cis*-isomers of dihydropyrans (**5**, **6**).

COMPUTATIONAL METHODS

All calculations employed in this paper were accomplished using the computer programs packages SPARTAN and PC SPARTAN 04.¹⁵ All calculations for geometrical optimizations were performed

with the 6-31G* basis set at B3LYP¹⁶ level. The starting geometries employed for all optimizations were resulted from molecular mechanics using SYBYL¹⁷ force field and subsequent semi-empirical PM3¹⁸ optimizations. The calculations for transition state geometries and their energies were also taken with the 6-31G* basis set at B3LYP level.

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