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2-*H*-Methoxyoxete: a reactive intermediate en route to methyl acrylate from methoxyacetylene and formaldehyde under BF_3 catalysis. An ab initio HF and DFT study

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Abstract—The formation of methyl acrylate from formaldehyde and methoxyacetylene, and the influence of BF_3 as a model Lewis acid are studied by means of ab initio HF and DFT calculations (HF/6-31G* and B3LYP/6-31G*). In both cases calculations are in favour of a pathway involving the asynchronous (or stepwise) formation (the C–C bond being formed first) of the reactive intermediate methoxy oxete, and its further electrocyclic ring-opening into methyl acrylate. © 2001 Elsevier Science Ltd. All rights reserved.

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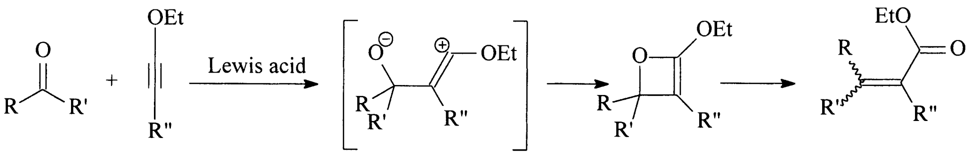
1. Introduction

The formation of α,β-unsaturated esters from aldehydes or ketones and alkoxyalkynes under Lewis acid catalysis was first reported by Vieregge et al. in 1959.[1] The reaction immediately met with success as demonstrated in a review article published seven years later by the same authors.[2] In the same paper, the authors proposed a mechanism involving the nucleophilic attack of the alkoxyacetylenic derivative on the Lewis acid-activated carbonyl compound, the formation of an intermediate alkoxyoxete and finally its electrophilic ring-opening to give the corresponding α,β-unsaturated ester (Scheme 1).

The strongest evidence supporting such a mechanism at that time was the isolation by Middleton of an ethoxyoxete derivative resulting from the *non-catalyzed* reaction between hexafluoroacetone and ethoxyacetylene.[3] Furthermore, this oxete underwent a rearrangement to yield the corresponding unsaturated ester. Since then, this reaction has attracted many experimental studies[4] and has even found some application in total synthesis.[5] However, due to their instability, oxetes have only been seldom isolated or characterized,[6] and examples of alkoxyoxetes are even fewer: in addition to the example reported by Middleton,[3] three others can be found in the literature.[7,8]. We reported in 1998 the first experimental evidence of the occurrence of ethoxyoxetes in a Lewis acid-catalyzed process involving a carbonyl compound.[9] From a theoretical point of view, only the non-catalyzed ring opening of the parent oxete into acrolein has been studied.[10] The calculated activation energy associated with that rearrangement was found to be of 26 kcal/mol (MP4/6-31G*). This value is in good agreement with experimental data.[11] More recently, the reverse reaction (acrolein into oxete) was also studied in detail.[12] As part of our theoretical studies on [2+2] cycloaddition reactions,[13] we wish to report here on the ab initio Hartree-Fock (HF) and DFT study of the formation of methyl acrylate from methoxyacetylene and formaldehyde. We have carried a comparison between the uncatalyzed and BF_3-catalyzed[14] reactions.



Scheme 1. Formation of α,β-unsaturated esters from carbonyl compounds and ethoxyalkynes under Lewis acid catalysis. Mechanism proposed by Vieregge et al. in 1966.[2]

Keywords: methoxyoxete; methylacrylate; Lewis acid; boron trifluoride; ab initio; HF; DFT; [2+2] cycloaddition; ring opening.

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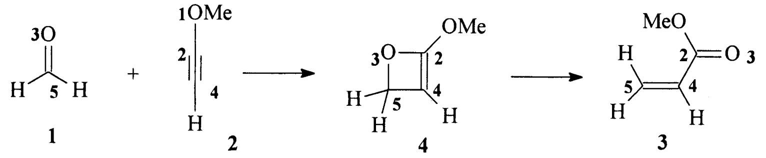


Scheme 2. Formation of methylacrylate **3**, via oxete **4**, from formaldehyde **1** and methoxyacetylene **2**.

2. Methodology

All calculations reported in the present paper were performed with the standard version of GAUSSIAN 94.[15] Geometries of reactants, intermediates and products were determined by minimization of energy with respect to all geometric parameters. Transition states were located by minimizing the gradient norm of the energy and characterized by one, and only one, negative eigenvalue of the Hessian matrix. Ab initio HF and DFT calculations were performed with the 6-31G* basis set. Finally, transition states reported were shown to belong to the studied reaction by intrinsic reaction coordinate (IRC).[16]

3. Results discussion

3.1. Uncatalyzed reaction

Although the reaction does not occur experimentally in the

Table 1. Main parameters of the critical points involved in the formation of methyl acrylate **3**

Critical points		Total energy (au)	ΔE (kcal/mol)	C_4–C_5 (Å)	C_2–O_3 (Å)	$C_5C_4C_2$ (d°)	$O_3C_5C_4C_2$ (d°)
1+2	HF	−304.560148	0	3.560	3.831	79.5	40.6
	B3LYP	−306.3470393	0	3.851	3.978	78.2	29.2
TS_a	HF	−304.481761	49.2	1.690	2.316	100.4	5.0
	B3LYP	−306.2869888	37.7	1.709	2.260	96.3	−3.3
4	HF	−304.602893	−26.8	1.511	1.344	85.3	0.0
	B3LYP	−306.3987391	−32.4	1.512	1.371	85.5	0.0
TS_b	HF	−304.5550547	3.5	1.426	1.263	94.4	−4.9
	B3LYP	−306.3640177	10.7	1.432	1.300	94.5	−5.1
3	HF	−304.6641823	−65.0	1.320	1.186	119.6	−0.1
	B3LYP	−306.4536229	−66.9	1.336	1.210	119.7	0.0

ΔE: relative energy. (HF/6-31G* and B3LYP/6-31G*).

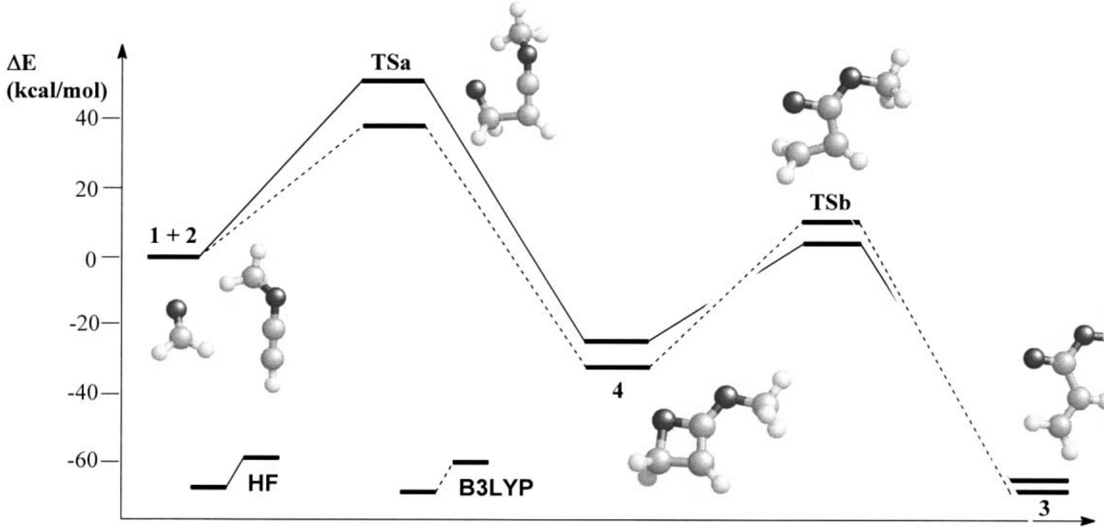
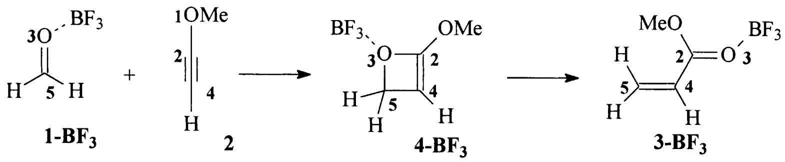


Figure 1. Formation of methyl acrylate **3** via methoxy oxete **4**. Reaction paths (HF and B3LYP) and structures of critical points (B3LYP).



Scheme 3. Formation of methylacrylate complex **3**-BF_3, via oxete complex **4**-BF_3, from formaldehyde complex **1**-BF_3 and methoxyacetylene.

absence of Lewis acid except with hexafluoroacetone,[3] we started our work with the study of the uncatalyzed process on the parent reaction (Scheme 2). Our aim was to set a reference to evaluate the role of the Lewis acid (BF_3) catalysis. HF/6-31G* calculations predict that the formation of oxete **4** occurs in a concerted but asynchronous way, the C_4–C_5 bond being formed first. This first step is exothermic (−26.8 kcal/mol) and the activation energy is high (49.2 kcal/mol, Table 1). Finally, the approach of formaldehyde **1** and methoxyacetylene **2** is *syn*periplanar. No reaction path involving an *anti*periplanar approach could be found by us.

As for the ring-opening step, the activation energy is of 30.3 kcal/mol, which is close to the value reported by Goddard for the formation of acrolein from the parent oxete (26 kcal/mol).[10] The electrocyclic process is concerted and exothermic (−38.2 kcal/mol). The whole process is therefore highly exothermic (−65 kcal/mol) and the first step is the rate determining one. It should also be noted that TS_b, involved in the ring-opening step, has an energy value only 3.5 kcal/mol higher than the reactants (Fig. 1, Table 1).

We then performed DFT calculations. Results are similar to the ab initio HF ones. Indeed, the first step is concerted and exothermic (−32.4 kcal/mol) and so is the second. The whole process is therefore once again greatly exothermic (−66.9 kcal/mol). The only significant difference deals with activation energies. In the first step (oxete formation), it is reduced from 49.2 kcal/mol (HF value) to 37.7 kcal/mol (DFT value). The electronic correlation is certainly responsible for this reduction. Indeed, although transition state TS_a is slightly earlier in the DFT calculations (1.709 Å (DFT) vs 1.690 Å (HF) for C_4–C_5), this small structural variation cannot account for such a variation of the activation energy of the reaction. Nevertheless, in both cases (HF and DFT), TS_a is the highest stationary point of the reaction profile.

3.2. BF_3-Catalyzed reaction

We then undertook both ab initio HF and DFT calculations on the BF_3-catalyzed reaction (Scheme 3).[17] We first calculated the energy associated to the formation of the formaldehyde–BF_3 complex (**1**-BF_3). The values we obtained (HF: 9.7 kcal/mol; DFT: 12.7 kcal/mol) are in good agreement with previously published calculations[18] and also with a recent experimental value obtained for a closely related complex (11 ± 2 kcal/mol for the CH_3CHO–BF_3 complex).[19] The introduction of a Lewis acid induces a wider range of possible approaches for the two reactants and modifications of the reaction profile and energies associated. However, despite extensive searches[20] we only found one reaction path leading to the formation of the oxete complex **4**-BF_3 and therefore to ester complex **3**-BF_3. As shown in Fig. 2, the approach of the reactants is *syn*periplanar with BF_3 and the CH_3 groups being *syn* with respect to the future ring system. We refer to this approach as the *syn*(*syn*) approach.

3.3. Influence of the Lewis acid

Not surprisingly, the introduction of BF_3 as a model Lewis acid has a dramatic effect on the first part of the reaction, i.e. the formation of the oxete complex **4**-BF_3: the activation energy is greatly reduced, especially in DFT calculations (from 37.7 to 2.1 kcal/mol), and the reaction profile is

Table 2. Main parameters of the critical points involved in the formation of methyl acrylate complex **3**-BF_3

Critical points	Method	Total energy (au)	ΔE (kcal/mol)	C_4–C_5 (Å)	C_2–O_3 (Å)	$C_2C_4C_5$ (d°)	$C_2C_4C_5O_3$ (d°)	$C_9O_1O_3C_5$ (d°)	$BO_3C_2O_1$
1-BF_3+2	HF/6-31G*	−627.7710769	0	3.220	3.553	78.1	42.2	151.0	101.6
	B3LYP/6-31G*	−630.9205793	0	2.720	3.286	89.8	29.9	142.7	92.9
	B3LYP (ZPE)	−630.814819	0						
TS_1	HF/6-31G*	−627.7482563	14.3	1.984	2.896	108.1	−9.2	136.3	83.6
	B3LYP/6-31G*	−630.9172997	2.1	1.980	3.008	111.7	27.5	141.7	88.2
	B3LYP (ZPE)	−630.810184	2.9						
I_1	HF/6-31G*	−627.7671238	2.5	1.537	2.411	111.8	−0.5	122.6	66.6
	B3LYP/6-31G*	−630.9222037	−1.0	1.625	2.759	116.2	−9.1	119.4	58.8
	B3LYP (ZPE)	−630.813560	0.8						
TS_2	HF/6-31G*	−627.766640	2.8	1.517	2.178	106.9	0.2	122.3	67.4
	B3LYP/6-31G*	−630.921281	−0.4	1.556	2.475	111.1	−1.8	122.6	66.9
	B3LYP (ZPE)	−630.812933	1.2						
4-BF_3 *syn*	HF/6-31G*	−627.8079804	−23.2	1.503	1.412	89.2	−0.9	124.6	58.3
	B3LYP/6-31G*	−630.9669739	−29.1	1.504	1.454	89.8	−1.4	135.8	67.2
	B3LYP (ZPE)	−630.855944	−25.8						
TS_3	HF/6-31G*	−627.804005	−20.7	1.596	1.377	87.1	−0.2	96.1	54.9
	B3LYP/6-31G*	−630.9644348	−27.5	1.507	1.423	88.7	−1.8	65.0	59.4
	B3LYP (ZPE)	−630.853978	−24.6						
4-BF_3	HF/6-31G*	−627.809647	−24.2	1.509	1.357	86.4	−0.5	2.5	52.8
	B3LYP/6-31G*	−630.9660533	−28.5	1.509	1.405	87.9	−1.6	4.2	61.0
	B3LYP (ZPE)	−630.855388	−25.5						
TS_4	HF/6-31G*	−627.7742789	−2.0	1.440	1.313	97.4	7.6	14.0	54.0
	B3LYP/6-31G*	−630.9390254	−11.6	1.439	1.348	96.8	−5.4	25.1	58.7
	B3LYP (ZPE)	−630.830546	−9.9						
3-BF_3	HF/6-31G*	−627.8753614	−65.4	1.323	1.217	119.9	0.0	−0.2	−0.1
	B3LYP/6-31G*	−631.0228238	−64.2	1.338	1.238	120.3	0.0	0.0	0.0
	B3LYP (ZPE)	−630.912898	−61.5						

ΔE: relative energy (HF/6-31G* and B3LYP/6-31G*).

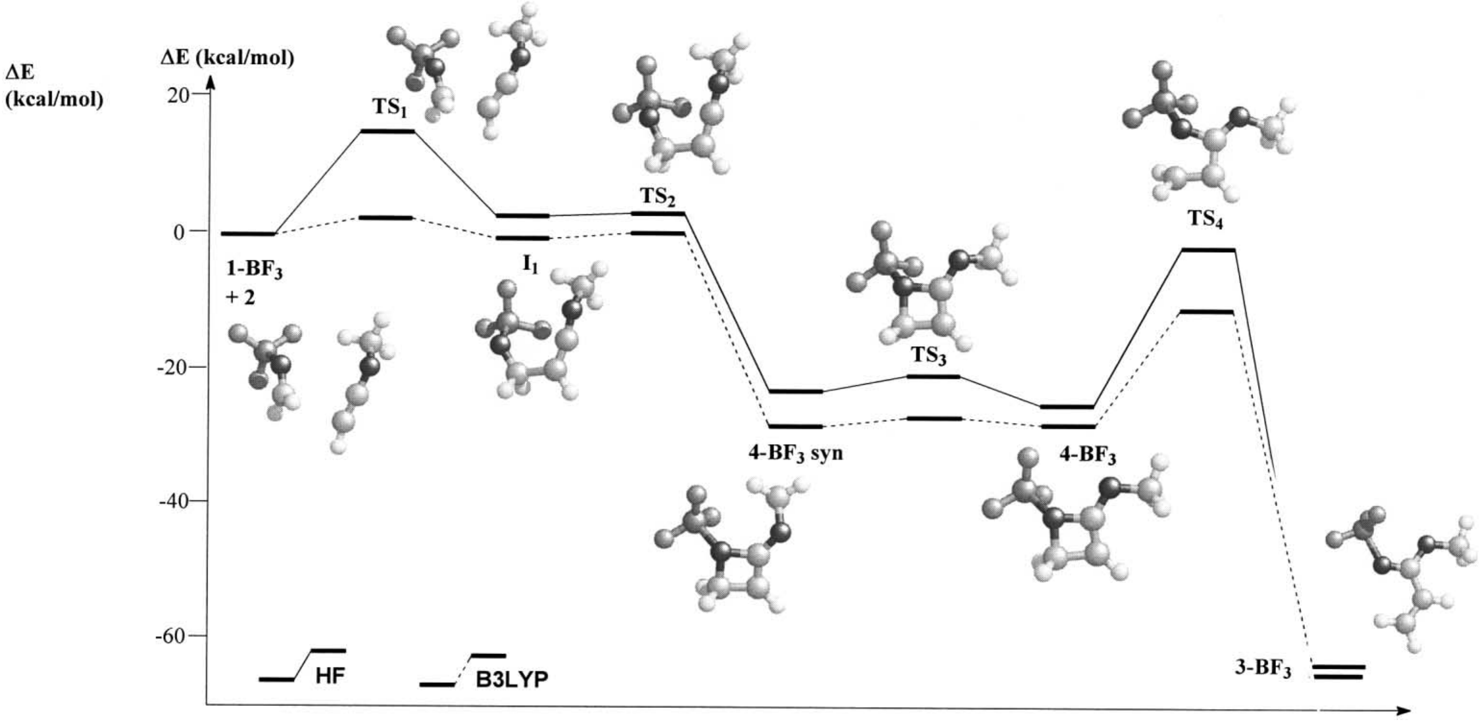


Figure 2. Formation of methyl acrylate complex **3**-BF$_3$ via intermediate I$_1$ and oxetene complex **4**-BF$_3$. Reaction paths (HF and B3LYP) and structures of critical points (B3LYP).

modified to incorporate an intermediate I_1 and, therefore, a second transition state TS_2 (Table 2). The formation of oxete **4**, from concerted although asynchronous in the uncatalyzed process, becomes clearly a stepwise process with prior formation of the C_4–C_5 bond in the first step and then the formation of the C_2–O_3 bond in a second step. The reduction of the activation energy and the modification of the reaction path are associated. Indeed, TS_1 is a much earlier transition state than TS_a (C_4–C_5: 1.980 Å vs 1.709 Å and C_2–O_3: 3.008 Å vs 2.260 Å (DFT values)) and if the C_4–C_5 bond is nearly formed in intermediate I_1, the distance C_2–O_3 is still larger than in TS_a (2.759 Å vs 2.260 Å (DFT values)). A second transition state, TS_2, is therefore necessary to complete the ring transformation. These observations based on geometrical values (Table 2) are corroborated by the examination of the Mulliken partial charges of the main atoms involved in the formation of oxete **4** and oxete complex **4**-BF_3 *syn* (Table 3). Indeed, the charge distribution on C_2 and O_3, particularly the partial negative charge on O_3, is greatly influenced by the introduction of the Lewis acid. Thus, from −0.64 e in TS_a, δO_3 falls to −0.40 e in TS_1 (and −0.49 e in I_1) and therefore the formation of the C_2–O_3 bond cannot occur in the first step and a second one is required. In TS_2, δC_2 and δO_3 values are closer to those obtained in TS_a. Taken apart a rotation of the methyl group (from **4**-BF_3 *syn* to **4**-BF_3 via TS_3) the influence of BF_3 is less spectacular on the ring-opening step. The process remains concerted and the reduction of the activation energy is smaller (from 43.1 to 16.9 kcal/mol, DFT values) but still significant. Despite these modifications an important point remains unchanged with respect to the uncatalyzed process.

TS_1 is, in both HF and DFT calculations, the highest stationary point of the reaction profile. Moreover, the heat produced by the oxete formation (HF: −23.2 kcal/mol; DFT: −29.1 kcal/mol) is greater than the energy required (HF: 21.2 kcal/mol; DFT: 17.5 kcal/mol) for its ring opening, or the energy of TS_4 (HF: −627.7742789 au; DFT: −630.9390254 au) is lower than the energy of the reactants (HF: −627.7710769 au; DFT: −630.9205793 au).[21] This observation is crucial since it accounts for the experimental difficulty to observe and isolate the alkoxyoxetes involved in this reaction.

Table 3. Mulliken partial charges (in electron) of main atoms involved in the formation of methyl acrylate complex 3-BF_3 and oxete complex **4**-BF_3 *syn*

Critical points		δO_1	δC_2	δO_3	δC_4	δC_5	δB
1+2	HF	−0.61	0.21	−0.44	−0.25	0.15	–
	B3LYP	−0.49	0.21	−0.33	−0.20	0.07	–
Ts_a	HF	−0.51	0.59	−0.83	−0.39	0.20	–
	B3LYP	−0.39	0.49	−0.64	−0.31	0.09	–
4	HF	−0.61	0.81	−0.64	−0.48	0.02	–
	B3LYP	−0.46	0.62	−0.51	−0.34	−0.04	–
1-BF_3+2	HF	−0.62	0.22	−0.49	−0.27	0.16	1.04
	B3LYP	−0.47	0.30	−0.34	−0.28	0.07	0.68
TS_1	HF	−0.55	0.57	−0.59	−0.47	0.13	1.04
	B3LYP	−0.41	0.45	−0.40	−0.34	0.00	0.67
I_1	HF	−0.50	0.61	−0.73	−0.27	0.06	1.04
	B3LYP	−0.37	0.50	−0.49	−0.23	0.00	0.67
TS_2	HF	−0.51	0.63	−0.76	−0.26	0.05	1.06
	B3LYP	−0.37	0.52	−0.54	−0.21	−0.01	0.68
4-BF_3 *syn*	HF	−0.63	0.79	−0.74	−0.38	0.01	1.09
	B3LYP	−0.47	0.61	−0.54	−0.26	−0.05	0.74

4. Conclusions

Ab initio calculations support the Lewis acid-promoted mechanism proposed on experimental grounds[2,4] and which involves the stepwise formation of an alkoxyoxete followed by its ring opening to yield the corresponding α,β unsaturated ester (Scheme 1). Moreover, these calculations account in a satisfying way for the difficulty to isolate alkoxyoxetes in Lewis acid-promoted reactions. Introduction of substituents that would increase the activation energy of the ring-opening step should be helpful in trying to characterise the intermediate alkoxy oxetes. We are currently working on this aspect both from a theoretical and experimental[9] point of view.

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14. We used BF_3 as a model Lewis acid since an AM1/RHF IRC calculation with the simpler BH_3 led to a hydride transfer similar to the one we observed in our previous study of β-lactone formation.[13b]

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16. We ran IRC calculations (HF/6-31G*) from all transition states of both reaction paths, uncatalyzed and catalyzed. In the DFT study IRC calculations were run from transition states TS_1, TS_2 and TS_3.

17. Although CASSCF calculations on the ring opening of the parent oxetene to acrolein[10] proved to give the most reliable results (compared to the experiment), we did not perform such calculations for the following reasons: (a) Improvements were minor both for the energy barrier value (compared to MP2 calculations which are close to DFT ones) and for the structure of the transition state (compared to HF calculations). (b) Our system is much bigger and involves the whole process, formation and ring-opening of the oxete in the presence of a Lewis acid. CASSCF calculations would be very difficult to perform and therefore time consuming. (c) CASSCF calculations are particularly relevant when a crossing occurs between S0 and S1 surfaces. This is not the case in the studied system as shown by AM1 CI=20 calculations (more than 2 eV separates the two surfaces throughout the whole process).

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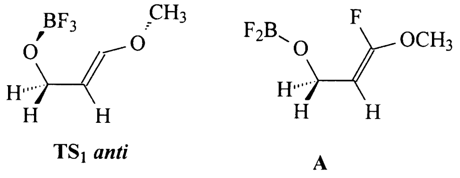
20. As in the uncatalyzed process, we did not find an *anti*-periplanar approach of the two reactants leading to the formation of the oxete complex 4-BF_3. We also searched for a *syn*(*anti*) approach (*syn* periplanar approach of the reactants with an *anti* position of BF_3 and –CH_3 with respect to the future ring). At the HF level we were able to find a transition state (TS_1 *anti*: − 627.7378875 au) leading to and *anti* intermediate (I_1 *anti*: − 627.748730 au) (Scheme 4). This approach is however clearly unfavoured since the activation energy of the first step (formation of the C4–C5 bond) rises from14.3 kcal/mol in the *syn*(*syn*) approach to 20.8 kcal/mol in this *syn*(*anti*) approach. Moreover, we were not able to fully characterize a reaction path towards 4-BF_3 and therefore 3-BF_3. Finally, using DFT calculations, no transition state leading to 4-BF_3 could be located. The difficulty we had in studying the potential energy surface associated with the *syn*(*anti*) approach arises from the absence of steric repulsion between BF_3 and CH_3 (in the *anti* configuration) which allows a greater mobility of the system. This mobility has, at least, two consequences: (a) a quasi flatness, only perturbed by small ondulations due to numerous small variations of the diedral angles, of the potential energy surface in that area, and (b) the possibility of a fluorine atom transfer from the boron atom to the C_2 carbon which bears a significant positive partial charge. This process, leading to A, is thermodynamically greatly favoured since A is a very stable compound (−627.8374103 au) (Scheme 4); it is analogous to the hydride transfer we reported in our study of the β-lactone formation.[13a]



Scheme 4. Transition state TS_1 *anti* and compound A.

21. A case similar to ours was described: Stahl, M.; Pidun, U.; Frenking, G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2234–2237.