JOC Article

[3 + 2] Cycloreversion of Bicyclo[*m*.3.0]alkan-3-on-2-yl-1-oxonium Ylides to Alkenyloxyketenes. Stereospecific Aspect

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Rhodium(II)-catalyzed intramolecular reaction of diazoketones **1** bearing a cyclic ethereal moiety transiently formed bicyclo[*m*.3.0]octan-3-one-1-oxonium-2-ylides (**2**), which underwent sigmatropic and stereospecific [3 + 2] cycloreversion reaction to form alkenyloxyketenes **3**. The ketenes were efficiently trapped by methanol to form the corresponding esters **4**. Mechanistic studies revealed that the size of ethereal ring can be variable at least from THF to the THP, oxepane, and oxocane moiety, i.e., $m = 3-6$. On the other hand, the size of the ylide ring containing the carbonyl unit is limited to a five-membered ring. The cycloreversion was found to be stereospecific as was proven by the reactions of diastereoisomeric pairs bearing a methyl group at the bond-cleaving position. From threo isomers **7**, (*E*)-alkenyloxyacetates **15** were exclusively formed (77−84%), whereas from erythro isomers **8**, (*Z*)-isomers **16** were formed (80−88%). Mechanism of the cleavage from diazoacetonyl-substituted cyclic ethers to alkenyloxyketenes via bicyclic oxonium ylides was analyzed on the basis of calculations employing the hybrid density functional B3LYP and the highly correlated quadratic configuration interaction QCISD method to reveal that the concerted [3 + 2] cycloreversion is the key step of this reaction.

Introduction

Ethereal oxonium ylides are highly reactive and short-lived intermediates compared with other onium ylides.[1] While they possess appreciable potential for synthetic use, systematic utilization for synthesis has been limited[2] due to their transient lifetime. The advantage of intramolecular formation of oxonium ylides was previously reported by Kirmse,[3] and we also reported[4] novel reactions to control the high reactivity of bicyclooxonium ylides by the design of intramolecular pathways.[3] In particular, we were intrigued by the behavior of bicyclo[3.3.0]octan-3-one-1-oxonium-2-ylide (**2**), which was transiently formed in the transition-metal-catalyzed reaction of THF-substituted diazoacetone **1**.[5a] In contrast to the ring-enlargement reaction that exclusively took place in the presence of relatively strong acids,[5b] we found that with a weakly acidic nucleophile such as MeOH, ylide **2** underwent a sigmatropic cleavage of the bicyclic ring, namely [3 + 2] cycloreversion reaction. Products were alkenyloxyacetates **4** that were unequivocally formed from **1** via ketene intermediates **3** (Scheme 1).[5b]

In contrast to a number of studies on [2 + 2] cycloaddition reactions of ketenes with alkenes,[6] a related reverse process such as [3 + 2] cycloreversion of bicyclic oxonium ylides to oxyketenes and olefins are yet unknown except our preliminary report.[5b] In this regard, our primary concern was how to control this reaction by structural factors, e.g., length of tethering side chain,[4a] ring size,[7] stereochemistry at the bond-cleaving site, and polar factors of attacking reagents.[8] The second concern was the mechanism of the reaction pathway and the structure of transient species involved therein.

Results and Discussion

Preparation of Diazoketones. Diazoketones bearing cyclic ethers with varying ring sizes were prepared from the corresponding acid chlorides by the treatment with

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(1) (a) Padwa, A.; Fryxell, G. E.; Zhi, L. *J. Am. Chem. Soc.* **1990**, *112*, 3100. (b) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (c) Ye, T.; Mckervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (d) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (e) Naito, I.; Oku, A.; Ohtani, N.; Fujiwara, Y.; Tanimoto, Y. *J. Chem. Soc., Perkin Trans. 2* **1996**, 725. (f) Tomioka, H.; Kobayashi, N.; Murata, S.; Ohtawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 8771.

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(6) (a) Snider, B. B. *Chem. Rev.* **1988**, *88*, 793. (b) Snider, B. B.; Hui, R. A. *J. Org. Chem.* **1985**, *50*, 5167. (c) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T. *Acc. Chem. Res.* **1995**, *28*, 265. (d) Hyatt, J. A.; Raynolds, P. W. *Org. React.* **1994**, *45*, 159.

(7) Oku, A.; Numata, M. *J. Org. Chem.* **2000**, *65*, 1899.

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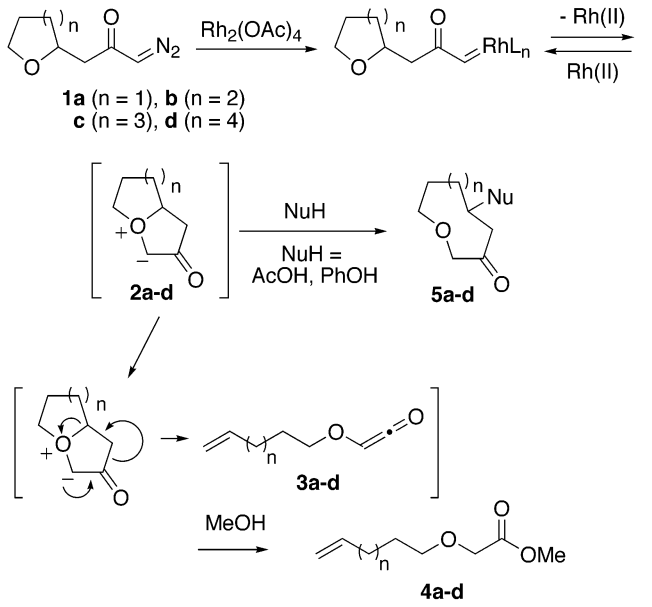
SCHEME 1. Rh(II)-Catalyzed Decomposition of Diazoketone 1



diazomethane. General preparative procedures are summarized in Scheme 2.

Cycloreversion of Diazoacetonyl-Substituted Cyclic Ethers with Different Ring Sizes. First of all, the effect of ring sizes of ethereal moiety was examined to demonstrate the scope of the cycloreversion reaction. Results in Table 1 indicate that diazoacetones bearing not only a tetrahydrofuryl moiety but also tetrahydropyranyl, oxepanyl, and furthermore oxocanyl moieties all reacted smoothly to afford the cycloreversion products under the Rh(II)-catalyzed reaction conditions. This indicates that the size of cyclic ethers is basically not a limiting factor of the cycloreversion, but a smaller ring size[7] seems to be better for facilitating the ring-cleavage process due to kinetic reason. In contrast, the size of transiently formed ylide ring that contains a carbonyl group is strictly limited to the five-membered furanone ring.

As the size of ethereal ring became larger, the yield of product decreased to some extent. One reason for this trend seems to be the gain of stability of bicyclic ylide due to a smaller strain than that of bicyclo[3.3.0] system. This is because the strain facilitates the two-bond cleavage process, the essential requisite of the cycloreversion, more than the central one-bond cleavage leading to the ring-enlargement.

In addition to the strain, the lifetime of oxonium ylide seems to be another key factor. In general, ethereal ylides are extremely short-living.[1e] Nevertheless, one can expect that substitution of an additional electron-withdrawing group on the diazomethyl carbon will elongate the lifetime of the ylides.[6] Indeed, as presumed, diazocarbonyl precursor **1f** bearing an ethoxycarbonyl group on the diazomethyl group improved the yield of cycloreversion products from 40 (**4b**) to 85% (**4f**) (Table 1).

As an alternative route to the ketene formation, [2 + 2] cycloreversion of bicyclo[4.2.0]octan-7-one (**6**),[6a] which can be formed by the 1,2-shift reaction of ylide **2**, was examined (Scheme 3). Treatment of **6** with $Rh_2(OAc)_4$ in methylene chloride under the same conditions, however, did not give the ester product nor ring-enlargement product at all, thus ruling out this possibility.

SCHEME 2. Preparation of Diazoketones 1, 7, and 8

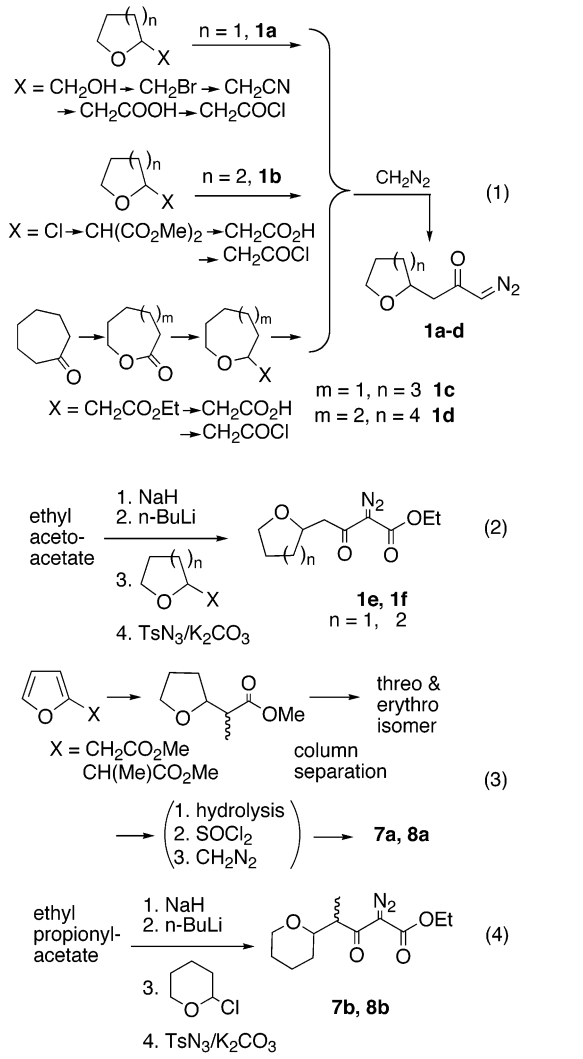
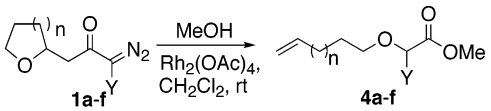


TABLE 1. Effects of Ring Size and Substituent Y on the Cycloreversion

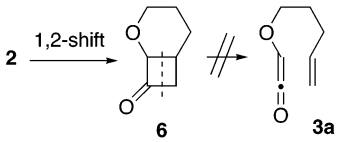


entry	substrate	*n*	Y	yield of **4** (%)
1	**1a**	1	H	**4a** (88)
2	**1b**	2	H	**4b** (40)
3	**1c**	3	H	**4c** (67)
4	**1d**	4	H	**4d** (51)
5	**1e**	1	COOEt	**4e** (82)
6	**1f**	2	COOEt	**4f** (85)
7[a]	**1f**	2	COOEt	**4g** (90)

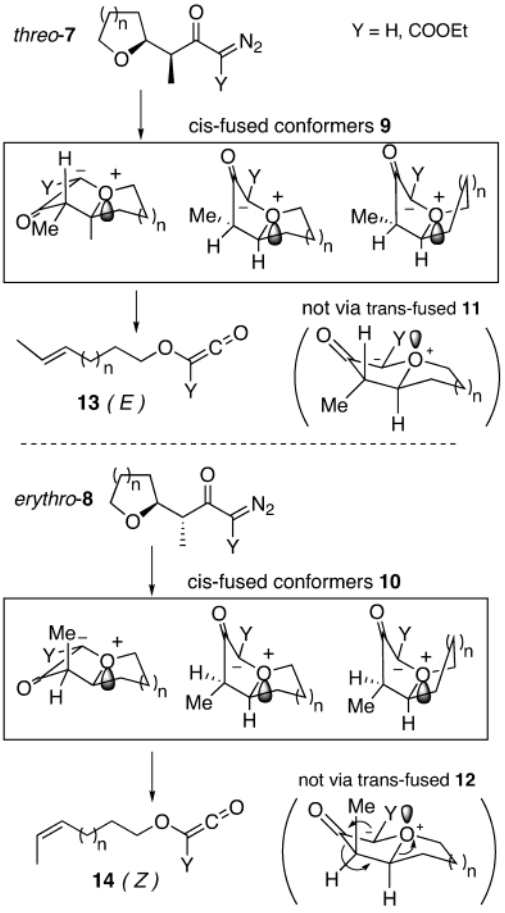
[a] PhOH was used instead of MeOH. Product **4g** was the corresponding Ph ester.

Cycloreversion of Diastereoisomeric α-Methyl-Substituted Diazoacetonyl Cyclic Ethers. One can assume from the mechanistic examination of the cycloreversion on prototype ylide **2a** that the cleavage of two rings may occur either in a single step or in a very fast

SCHEME 3. Exclusion of Possible [2 + 2] Cycloreversion of 6



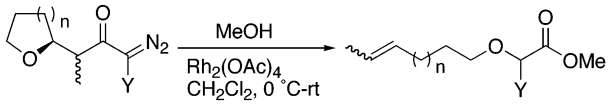
SCHEME 4. Stereospecific [3 + 2] Cycloreversion of Bicyclo[3.(*n* + 2).0]oxonium Ylide to Alkenyloxyketene



stepwise manner. If these are the only two possible cases, one can verify the mechanism by choosing a diastereoisomeric pair of methyl-substituted diazoketone **7** and **8** as the model, and the stereospecific outcome of the product structure will give the answer to this question.

According to the presumed one-step cycloreversion mechanism as depicted in Scheme 4, ring-cleavage of the bicyclo[3.(*n* + 2).0]-1-oxonium-4-methyl-3-oxo-2-ylide rings take place to afford either *E*- or *Z*-alkenyloxyketene depending on the threo and erythro diastereoisomerism of the starting diazoketone, respectively. Taking threo isomer **7** for example, the ylide will prefer cis-fused configuration **9** to the trans-fused one **11**. In this isomer **9**, the methyl group always keeps an anti (or trans) position to the vicinal C−C bond that once composed the ether ring. Here, if a concerted [two single-bond cleavage]-[two double-bond formation] takes place, it will result in the formation of *E*-configuration at the newly borne olefinic bond. If the ring-fission takes place slowly in a stepwise manner via a biradical or zwitterion, the stereospecificity will be lost. Similarly, with erythro isomer **8**, ylide **10** will also prefer cis-fused configuration to the trans, in which the methyl group keeps a syn (or cis) position to the vicinal C−C bond. Therefore, a synchronous bond-cleavage will lead to the formation of a *Z*-double bond.

TABLE 2. Stereospecificity of the Cycloreversion



entry	substrate	*n*	Y	product yield (%)
1	*threo*-**7a**	1	H	**15a** (*E*) (84)
2	*erythro*-**8a**	1	H	**16a** (*Z*) (88)
3	*threo*-**7b**	2	COOEt	**15b** (*E*) (87)
4	*erythro*-**8b**	2	COOEt	**16b** (*Z*) (80)

To verify a general profile of the above-predicted stereospecific cycloreversion by chemical means, we prepared two pairs of diastereoisomeric diazoketones **7a**, **8a** bearing a THF ring and **7b**, **8b** bearing a THP ring, all having a methyl group at the 3-position of diazoacetonyl side chain. Results of the Rh(II)-catalyzed decomposition of the pairs in the presence of methanol are summarized in Table 2.

Trapping of the primary product alkenyloxyketenes **13** and **14** ($n = 1, 2$) by MeOH proceeded smoothly to afford the corresponding methyl esters in good to high yields, i.e., **15a**, **16a**, **15b**, **16b** from **7a**, **8a**, **7b**, **8b** in 84, 88, 87, 80%, respectively. As expected from the molecular framework examination described above (Scheme 4), stereochemistry of the alkenyl groups in the product structures was stereospecifically controlled by the diastereoisomerism of starting diazoketones **7** and **8**. Thus, *E*-olefins **15** were exclusively formed from threo isomers **7** whereas *Z*-olefins **16** from erythro isomers **8**. The *Z*-configuration of **16a** was identified by the NOESY observable between two olefin protons[9] and, consequently, **15a** was assigned to the *E*-isomer. The stereochemistry of **15b** and **16b** was assigned on the basis of their *J* values, 15 and 11 Hz, respectively.[9] Diazoketones bearing much larger rings such as oxepane and oxocane rings are also assumed to react stereospecifically on the same basis.

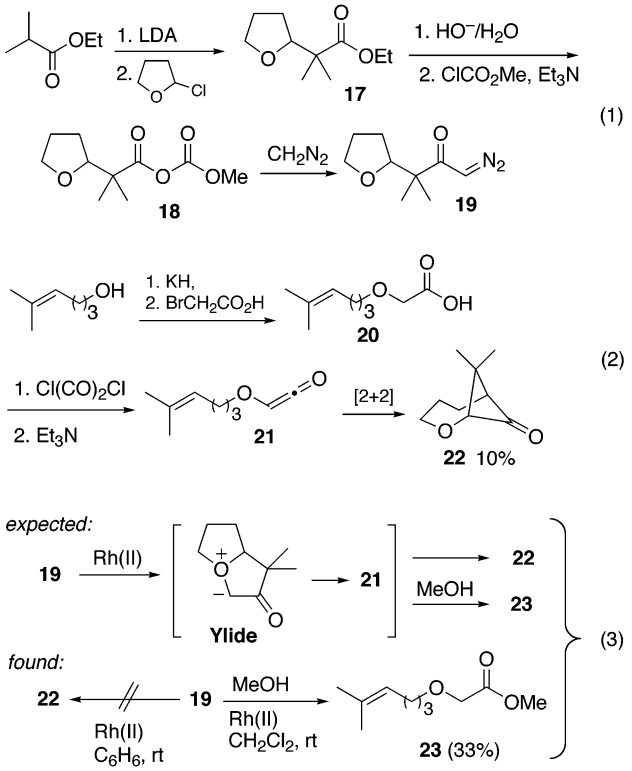
Diazoketones having a longer tethering chain than diazoacetonyl were found unsuccessful in cycloreversion because the corresponding ylide rings are larger than five so that one-step [3 + 2] cycloreversion mechanism cannot work.

Reaction of (3,3-Dimethyl-1-diazoaceton-3-yl)-Substituted Tetrahydrofuran. It has been well studied that alkoxyketenes[10] are labile, having lifetimes shorter than milliseconds. Alkenyloxyketene **3** which is assumed to be a key intermediate in the present cycloreversion is an analogue of this family and, therefore, was expected to be identifiable spectroscopically. How-

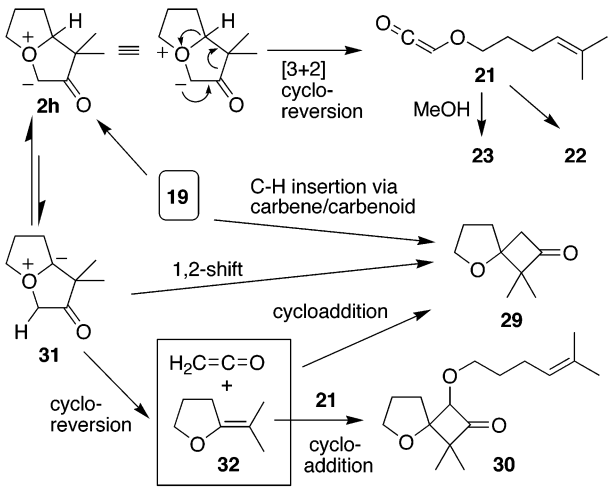
(9) Configuration of isomer **15a**, although its olefin protons had identical *d* values and it was impossible to measure its NOESY, was assumed to *E* after determining **16a** to *Z*. For **15b** and **16b**, although *d* values of two olefin protons in each isomer were almost identical again being impossible to measure NOESY, irradiation of allylic methylene protons showed a clear difference in the olefinic vicinal *J* values between two isomers.

(10) Tidwell, T. P. *Ketenes*; Wiley: New York, 1995.

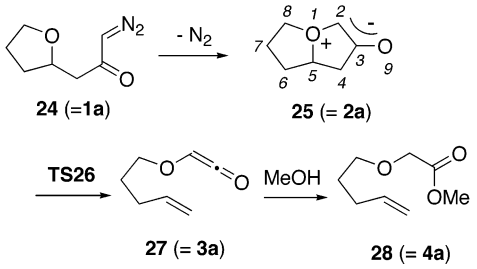
SCHEME 5. Preparation and Reaction of Diazoketone 19



SCHEME 6. Plausible Route from 19 to Products 22, 23, 29, and 30



SCHEME 7. Basic Reaction Model for Calculation



ever, attempted FT-IR detection was unsuccessful. Snider reported[6a] that alkenyloxyketenes underwent intramolecular [2 + 2] cyclization reaction to form bicyclic ketones. Therefore, expecting that this type of reaction would afford a chemical proof for the intermediacy of alkenyloxyketene, we prepared both (3,3-dimethyl-1-diazoacetonyl-3-yl)-substituted tetrahydrofuran **19** and alkenyloxyacetic acid **20** as plausible precursors of alkenyloxyketene **21** (Scheme 5, eqs 1 and 2, respectively). Indeed, from **20**, bicyclo[4.1.1]-2-oxaoctan-7-one **22** was obtained though in 10%[6a,b] (eq 2). In parallel, the Rh(II)-catalyzed reaction of **19** that was carried out in methylene chloride in the presence of MeOH afforded mainly ester **23** (33%) besides minor amounts of **29** and **30** (5% each), indicating that the corresponding ylide **2h** was formed to some extent. In contrast, a similar reaction of **19** in benzene without MeOH gave **29** (9%) and **30** (52%) but expected **22** was not found (Scheme 6). Minor product **29** can be formed most plausibly by the intramolecular stepwise C−H insertion of the intermediate carbene or carbenoid. However, the formation of major product **30**, the structure of which was confirmed by HMBC spectral analysis, cannot be well accounted for yet. One of possible routes is hypothetically shown in Scheme 6 in which an intermolecular [2 + 2] cycloaddition of ketene and isopropylidenetetrahydrofuran **32** is proposed, the latter may be derivable from oxonium ylide **31**(Scheme 6).

Theoretical Calculations

Supportive information for the stereospecific nature of the present cycloreversion was also available from high-level theoretical calculations.

We have investigated the mechanism of the transformation of diazocarbonyl compound **1** to ketene **3** and ester **4** via the [3 + 2] cycloreversion of ylide **2** by means of theoretical calculations employing the hybrid density functional B3LYP[11] and the highly correlated quadratic configuration interaction QCISD method.[12,13] The B3LYP theory was employed to model the entire reaction path. The tetrahydrofuryl-substituted diazo compound **24** (see Scheme 7) was used as the model because it has less conformers compared with other compounds bearing larger cyclic substituents.

In **24** (= **1a**), the ethereal oxygen atom and the diazocarbon have a short interatomic distance of 3.322 Å (see Figure 1). The cyclization after loss of nitrogen leads to bicyclic oxonium ylide **25** (= **2a**), a process that is endothermic by 5.7 kcal·mol^{-1}. The formation of three different conformers of **25** (G_{rel} = +5.7, +6.4, +12.3[14]),

(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *96*, 5648.

(12) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**,*87*, 5968.

(13) Quantum calculations were carried out using the Gaussian98 package of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(14) All energies are from B3LYP/6-311+G(d,p) and given as Gibbs' free energies relative to [**1a** + N_2 + CH_3OH] in kcal·mol^{-1}

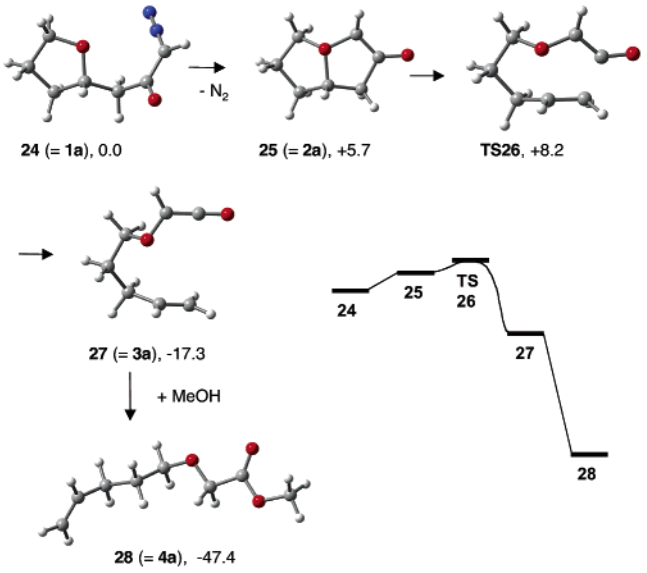


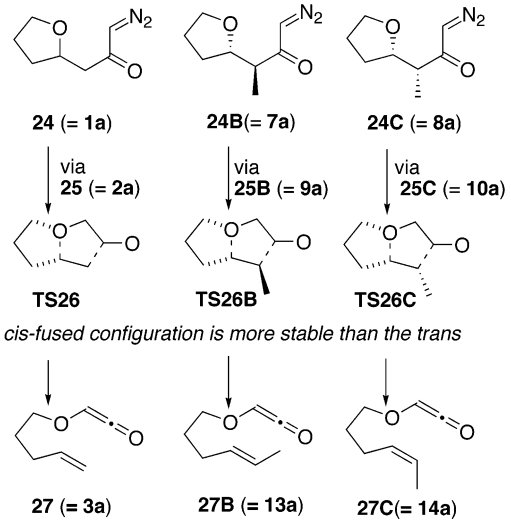
FIGURE 1. Conformations and relative energies of intermediates. All structures and Gibbs' energies are from the B3LYP/6-311-G(d,p) level.

ascribable to anti-anti, syn-anti, and syn-syn isomers, respectively, on the B3LYP[15] of **25** can be rationalized by a *syn*-attack of one of the lone-pairs of ethereal oxygen atom *O*(1) because an anti-attack seems disfavored because of the formation of highly strained trans-fused bicyclic ring.

As a result, atoms O(1) and C(5), which are incorporated in the cyclic ethereal substituent, become more positive by 0.2 and 0.3 e, respectively, whereas the oxygen O(9) of the carbonyl unit becomes more negative by 0.1 e. The two bond lengths of O(1)−C(5) (1.566 Å) and O(1)−C(8) (1.470 Å) are 6 to 8% longer than in **24a**. The tricoordinate carbanionic atom C(2) is less planar than expected (Σ bond angles: 348°) and possesses an electronic charge density of −0.2 e. The carbonyl oxygen O(9) is only slightly more negative than in **24** (3%) and C(3)−O(9) bond (1.230 Å) is a pure double bond. All these properties reveal that the C(2)−C(3)−O(9) unit is an α-keto carbanion rather than an enolate.

As suggested by the experiments, bicyclic ylide **25** can undergo a ring-opening reaction to form oxyketene **27** (= **3a**). The low-energy transition state[16] **TS26** (only ΔG = +2.5 kcal/mol above **25** at the B3LYP level) was found, which connects two minimum structures **25** and **27** directly. In **TS26**, the main interatomic distances are as follows: O(1)−C(5) = 2.024 Å, C(3)−C(4) = 1.720 Å, C(2)−C(3) = 1.370 Å, C(4)−C(5) = 1.420 Å and O(1)−C(2) = 1.400 Å, revealing that the reaction from **25** to **27** is a concerted process in which two bonds [C(1)−C(5) and C(3)−C(4)] are cleaved while two double-bonds are formed [C(2)═C(3) and C(4)═C(5)]. Additionally, the opening of five-membered ring shows almost perfect planarity with a maximum deviation from planarity of 0.008 Å and a sum of dihedral angles of 0.025°. Despite a careful search, neither a second transition state nor a stable intermediate linking **25** and **27** were found. Therefore, a two-step reaction seems to be unfavorable and, as a consequence, the present reaction is a one-step reaction passing through a planar transition state and can be defined as a pericyclic reaction, a novel example of a reverse [3 + 2] cycloaddition, namely a [3 + 2] cycloreversion.

SCHEME 8. Models to Show Stereospecificity of the Reaction



In the course of the reaction from **25** via **TS26** to **27**, O(1) loses its positive charge (−0.01 → −0.11→ −0.10 e) and C(2) its negative character (−0.42 → −0.35 → −0.21 e).[17] The formation of ketene **27** from **25** is exothermic by 23.0 kcal·mol^{-1} and the conformational conversion from "U"-shaped isomer **27** to a linear isomer releases further 1.5 kcal·mol^{-1}, rendering the reverse reaction cycloaddition unfavorable.

In the final step, the exothermic (ΔG = −30.1 kcal/mol) addition of one molecule of methanol to ketene **27** yields the unsaturated ester of type **28**. The overall loss of potential Gibbs' free energy from **24** to **28** is 47.4 kcal·mol^{-1}.

To understand more easily the selective formation of either *Z* or *E* double-bond in the esters **4** as found in the experiment (see above), we carried out calculations on the transformation of diastereoisomeric methyl-substituted derivatives, i.e., from **25B** (= **9a**) to **27B** (= **13a**) and **25C** (= **10a**) to **27C** (= **14a**) (Scheme 8). Concerning the energy profile for the reaction of ylides (**25B** and **25C**) to the oxyketenes (**27B** and **27C**), no great deviations in comparison with the unsubstituted derivatives (**25** to **27**) were found. Only the formation of **27B** is less exothermic due to its higher stability in that the substituents are in anti positions.

The molecular structures **27B** and **27C** (see Scheme 8) clearly indicate that due to the concerted nature of the reaction (**TS26B** and **TS26C**) the stereochemical information is retained (stereospecific) and, thus, a *E* C(4)−C(5) alkenyl double bond (eventually coincides the C(4), C(5) numbers of **25** in Scheme 7) of **27B** is formed from *threo*-**25B** (= **9a**) and a *Z* double bond in **27C** is formed from *erythro*-**25C** (= **9a**). A two-step process,

(15) Calculations on the B3LYP -level were performed with the 6-311+G(d,p) basis set.

(16) An IRC calculation (implemented in Gaussian98) proved that **2a** and **4a** are connected via **TS26**.

(17) All charges are carbon-centered Mulliken charges.

TABLE 3. Calculated Energies for the Transformation of Oxonium Ylides 25, 25B, and 25C to Oxyketenes 27, 27B, and 27C (Gibbs' Free Energy (Hartrees) and Relative Energies (kcal/mol) Below)[a]

diazoketone	oxonium ylide **25**	**TS26**	oxyketene **27**
unsubst. **24**:			
B3LYP	−423.093804	−423.089883	−423.130503
	±0.0	**+2.46**	**−23.03**
QCISD	−421.722315	−421.707273	−421.7501544
	±0.0	**+9.44**	**−17.47**
***threo*-24B**:			
B3LYP	−462.394323	−462.389003	−462.434218
	±0.0	**+3.34**	**−25.03**
QCISD	−460.880082	−460.863491	−460.908203
	±0.0	**+10.41**	**17.65**
***erythro*-24C**:			
B3LYP	−462.390848	−462.386653	−462.432014
	±0.0	**+2.63**	**−25.83**
QCISD	−460.876384	−460.861308	−460.905480
	±0.0	**+9.46**	**−18.26**

[a] B3LYP = B3LYP/6-311+G(d,p); QCISD = QCISD/6-31+G(d)//B3LYP/6-311+G(d,p).

which would allow a rotation around C(4)−C(5) bond can thus be clearly excluded.

Employing the more sophisticated but time-expensive QCISD method, we found (see Table 3) that our calculations on the B3LYP level are valid for mainly all structures but underestimate the stability of oxonium ylide structures **25**, **25B**, and **25C**. The more precise activation barrier (on the QCISD/6-31+G(d) level) is about 7 kcal·mol^{-1} higher and the reaction is less exothermic by 5−6 kcal·mol^{-1}. Apparently, highly correlated calculation theories have to be employed to describe the sensitive oxonium ylide structure correctly.

Conclusion

Both studies on (1) experimental verification of stereochemical profile and (2) theoretical calculations have proven that the ring-cleavage rearrangement reaction reported here is a hitherto unknown concerted [3 + 2] cycloreversion process and, hence, realizing a highly stereospecific formation of *Z*- or *E*-double bond in the alkenyloxyesters **15** and **16**.

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Supporting Information Available: General methods; detailed experimental procedures for products **1a**−**d** and **19**; spectroscopic data for **1a**−**f**, **4c**−**g**, **5c**,**d**, **7a**,**b**, **8a**,**b**, **15b**, **16a**,**b**, **19**, **23**, **29**, and **30**. This material is available free of charge via the Internet at http://pubs.acs.org.

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