

Carbon–Carbon Bond Formation Reaction of Ethereal Oxonium Ylides via Metal–Enolate Intermediates

Yuichi Sawada, Takashi Mori, and Akira Oku*

Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

oku@ipc.kit.ac.jp

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First, the carbon–carbon (C–C) bond-forming reaction of aldehydes with bicyclo[m.n.0]-1-oxonium ylides was studied as the ylide was transiently formed in the Rh(II)-catalyzed reaction of a nonenolizable diazoketone, namely, 2-(3-diazo-1,1-dimethyl-2-oxopropyl)-2-methyldioxolane (**1**). The reaction of **1** with benzaldehyde in the presence of $\text{CITi}(\text{O}i\text{-Pr})_3$ gave the three-carbon, ring-enlarged, and C–C-bonded product **2a** (53%). Second, enolizable diazoketone **5** bearing no methyl substituents at the α -position was studied under similar catalytic conditions, and the ring-enlarged and C–C-bonded products **19a** and **20a** were also formed (87%) when titanium compound $\text{CITi}(\text{O}i\text{-Pr})_3$ or $\text{Ti}(\text{O}i\text{-Pr})_4$ was used. Similar reactions of diazoketones **27**, **29**, and **31** bearing a cyclic acetal ring and a longer tethering chain than **5** gave C–C-bonded products **28** (74%), **30** (8%), and **32** and **33** (overall 48%), respectively, albeit **28** and **30** possessed a spiro bisacetal structure. Thus, the hitherto unclarified C–C bond formation of ethereal oxonium ylides with carbonyl electrophiles was realized with the use of an appropriate Lewis acid, for example, $\text{CITi}(\text{O}i\text{-Pr})_3$.

Introduction

Carbenes or carbenoids react with heteroatoms to form onium ylides. A characteristic feature of onium ylides is the [1,*n*]-ambiphilicity that is inherited from the [1,1]-ambiphilicity of the carbenes or carbenoids. The onium ylides, for example, phosphorous,¹ sulfur,² and nitrogen³ ylides, have been utilized for synthesis.^{4a,5–8,10a} However, the use of ethereal oxonium ylides for synthesis has been limited in comparison with the widely acknowledged utility of carbonyl ylides.^{4,10a} This is probably due to the

extremely short lifetimes of the ylides as demonstrated by the impossibility of observing their spectra even at nanosecond time scales.⁹ Oxonium ylides are also known to be in equilibrium with carbenes, and therefore, it is generally difficult to shift the reactions selectively to either side.^{9–12,13} In the study of oxonium ylides, intramolecular rearrangements such as the [1,2]- and [2,3]-sigmatropic rearrangements have been widely studied¹⁰ but no results have been reported on carbon–carbon (C–C) bond formation. However, if the high reactivity of oxonium ylides can be properly controlled, C–C bond formation on the carbanion center of *O*-ylides will be realized. For example, the reaction with carbonyl compounds can afford β -hydroxyalkyl ethers, and this type

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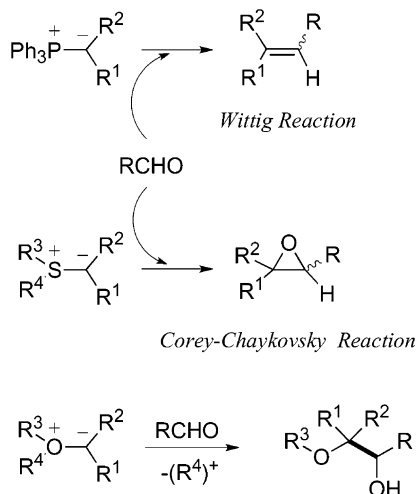
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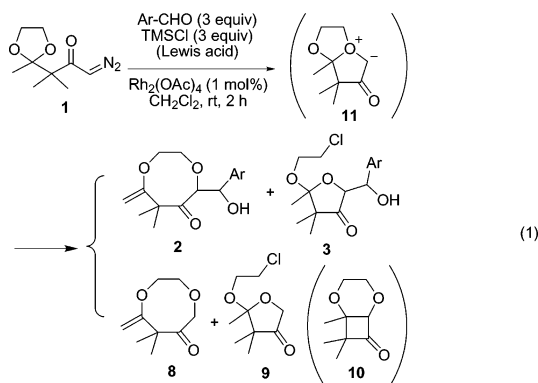
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of C–C bond formation is essentially unique in comparison with the widely known ones with phosphonium¹ and sulfonium¹⁴ ylides, because in those reactions, the onium moiety is eliminated in the last stage, but with *O*-ylides the ethereal oxygen atom remains in the product structure. Thus, appropriate molecular design of the substrates seems to enable the incorporation of the onium moiety in the product. If this type of C–C bond-forming reaction can be realized, it will become a novel member of onium ylide family that will provide potential tools for the construction of carbon frameworks (Scheme 1).

SCHEME 1. C–C Bond-Forming Reactions of Onium Ylides



As the model for this study, we chose the transition-metal-catalyzed reaction of diazoketones bearing a cyclic acetal ring. In our preceding communication¹⁵ where we reported the first example of a C–C bond-forming reaction of ethereal oxonium ylide with aromatic aldehydes, the bond formation was made possible by designing a specific structure of diazoketone **1** in which the α -position of the carbonyl group was protected by two methyl groups to endow it with an unenolizable nature (eq 1 and Table 1).



With this protection, proton transfer of the intermediately formed bicyclooxonium ylide was prevented thus suppressing the formation of unimolecular products **8** and **9** (eq 1). However, the protection limits the structural versatility of the substrates. An additional limitation of the reaction was the use of Me₃SiCl (TMSCl), which was needed to stabilize the ylide intermediate in the form of

TABLE 1. Rh(II)-Catalyzed Reaction of **1** with Aldehyde and Me₃SiCl in the Absence or Presence of a Lewis Acid

entry	aldehyde Ar	Lewis acid (mol %)	products (%)			
			2	3	8	9
1	C ₆ H ₅ (a)				18	14
2	<i>p</i> -MeOC ₆ H ₄ (b)				20	14
3	<i>p</i> -NO ₂ C ₆ H ₄ (c)		54	7		
4 ^a	<i>p</i> -NO ₂ C ₆ H ₄ (c)		27	8	4	6
5	<i>p</i> -CNC ₆ H ₄ (d)		38	3	4	6
6	<i>p</i> -MeOC ₆ H ₄ (d)	Ti(<i>O</i> <i>i</i> -Pr) ₄ (5)	25	56		
7	<i>p</i> -MeOC ₆ H ₄ (b)	Al(<i>O</i> <i>t</i> -Bu) ₃ (5)	11	17		4
8	C ₆ H ₅ (a)	Ti(<i>O</i> <i>i</i> -Pr) ₄ (5)	27	32		

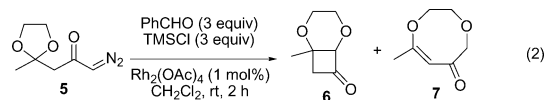
^a At –40 °C.

enol silyl ether¹⁶ to enable the aldol-type C–C bond formation. However, it caused undesirable side reactions because of the presence of the chloride ion. These limitations seemed to us to restrict the applicability of the C–C bond formation.

In the present report, we show that these limitations can be eliminated by the choice of an appropriate Lewis acid, and hence, the spectrum in the structural variation of carbene precursors as well as carbonyl compounds can be widened.

Results and Discussion

Reaction of Unenolizable Diazoketone **1 Bearing Two Methyl Substituents at the α -Position of the Carbonyl Group.** In our previous study¹³ the Rh(II)-catalyzed reaction of enolizable diazoketone **5**¹⁷ with benzaldehyde was investigated (eq 2)



in advance of the one with nonenolizable diazoketone **1**. The products were the [1,2]-rearrangement product **6** and the ring-enlarged enone **7**, but the expected C–C-bonded product was not obtained. To suppress those side reactions, an excess amount of TMSCl was added to trap the ylide effectively in the form of enol silyl ether before the side reactions could take place, but enone **7** was again formed exclusively. We presumed that TMSCl facilitates the proton transfer of the ylide to form **7**, and therefore, diazoketone **1** in which the α -position to the carbonyl was protected by two methyl groups was designed and its reaction examined. Indeed, the reactions with electron deficient aromatic aldehydes (Table 1, entries 3–5) produced the expected C–C-bonded products **2** and **3** (eq 1) but not with parent compounds benzaldehyde and anisaldehyde. We again presumed that in addition to the use of TMSCl which transiently stabilizes the ylide

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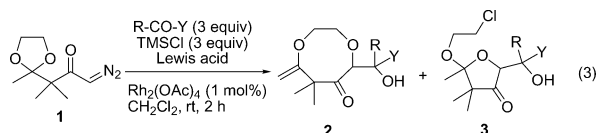
TABLE 2. Rh(II)-Catalyzed Reaction of **1** with Carbonyl Electrophiles in the Presence or Absence of TMSCl and with Ti(O*i*-Pr)₄ or ClTi(O*i*-Pr)₃^a

entry	carbon electrophile		Lewis acid (mol %)	TMSCl (mol %)	products % (dr) ^c	
	R	Y			2	3
1	styryl	H (e)	Ti(O <i>i</i> -Pr) ₄ (5)	300	29 (2:1)	40 (1:1)
2	isopropyl	H (f)	Ti(O <i>i</i> -Pr) ₄ (5)	300	35 (1.3:1)	20 (1.3:1)
3	phenyl	Me (g)	Ti(O <i>i</i> -Pr) ₄ (5)	300	21 (1.7:1)	33 (4.6:1)
4	phenyl	H (a)	ClTi(O <i>i</i> -Pr) ₃ (100)	0	29 (4.7:1)	24 (5.1:1)
5 ^b	phenyl	H (a)	ClTi(O <i>i</i> -Pr) ₃ (100)	0	53 (19:1)	32 (3.4:1)

^a At room temperature for 2 h. ^b At -40 °C. ^c For the determination of the dr of products in entries 1, 2, 4, and 5, see ref 15.

intermediate, activation of the carbonyl electrophile must be necessary. On the basis of this assumption, addition of Lewis acids such as Ti(O*i*-Pr)₄ and Al(O*t*-Bu)₃ in combination with TMSCl and Rh(II) was examined, and it was found that the use of Lewis acids is essential with other aldehydes (Table 1, entries 6–8). Those were the results reported.¹⁵

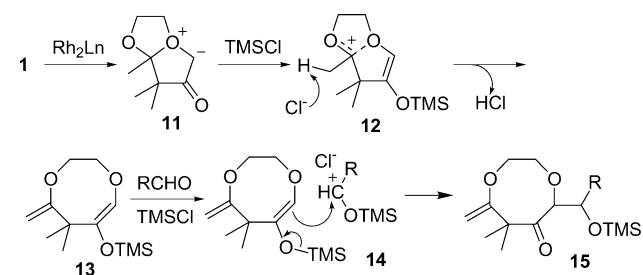
With this newly found triad catalyst system, that is, the combination of Rh(II), TMSCl, and a Lewis acid, the reaction was extended to other carbonyl compounds such as aliphatic aldehydes, α,β -unsaturated aldehydes, and ketones. In fact, these carbonyl electrophiles also afforded the C–C-bonded products **2** and **3** (eq 3 and Table 2, entries 1–3)



under the same reaction conditions. It should be noted that the formation of 1,2-rearrangement product **10** was suppressed in the reactions. Thus, the present reaction turned out to show essentially a general profile. However, a limitation still remains with regard to the protection of diazoketones at the α -position to the carbonyl group.

Use of a Lewis Acid without Trimethyl(chloro)silane. Mechanistic examination of the role of TMSCl suggests that it first transforms the ylide **11** to the corresponding enol silyl ether (Scheme 2). Then the

SCHEME 2. Plausible Mechanism for the C–C Bond Formation of **1**

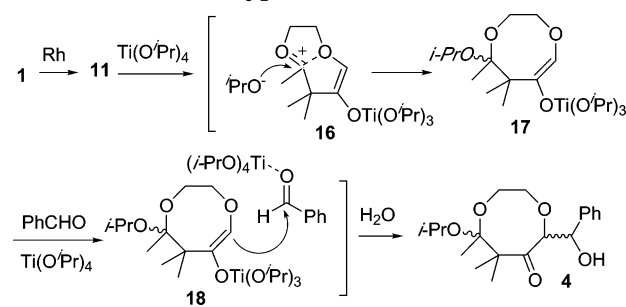


conjugate base Cl⁻ abstracts a proton from the vicinal position of the partially charged acetal carbon of **12** to afford ring-enlarged enol ether **13**. Thereafter, enol silyl ether **13** reacts with the aldehyde via transient intermediate **14** to give C–C-bonded product **15**. The steps from **13** to **15** are a typical aldol reaction¹⁵ that generally needs an acid catalyst¹⁸ such as a Lewis or Brønsted acid.

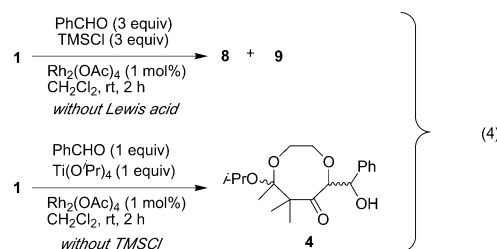
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Therefore, in the TMSCl-promoted reaction (Scheme 2), TMSCl, hydrogen chloride, or silyl ether seems to be the catalyst. In this respect, we expected that if a sufficiently active Lewis acid is used so that the acid converts the *O*-ylide to the corresponding metal enolate and/or activates the carbonyl electrophile, C–C bond formation will proceed without TMSCl through a transition state as shown in Scheme 3. To prove this assumption, several

SCHEME 3. Aldol-Type C–C Bond Formation



Lewis acid catalyzed reactions of **1** with benzaldehyde in the absence of TMSCl were investigated. Indeed, we found that the expected reaction took place with titanium catalysts, and among those examined,¹⁹ ClTi(O*i*-Pr)₃ used in equivalent amount gave the best yields of the C–C-bonded products **2a** and **3a** (53 and 32%, respectively, 85% overall) (Table 2, entry 5). When Ti(O*i*-Pr)₄ was used, C–C-bonded product **4**, that is, the analogue of **2**, was obtained exclusively in 70% yield (eq 4).



The superior effect of titanium catalysts over aluminum salts (see Table 1, entries 6–8) may be accounted for in terms of titanium's strong Lewis acidity and hypervalency with oxygen functionality (e.g. **18** in Scheme 3).

Plausible mechanistic pathways for the Ti-catalyzed C–C bond-forming reaction of **1** are shown in Scheme 3. When ylide **11** is generated, it is efficiently transformed to titanium enolate **17** which then reacts with an activated aldehyde via a linear transition state **18** known

(19) ClTi(O*i*-Pr)₃ was the best Lewis acid among those examined (ZnCl₂, MgBr₂, B(OEt)₃, and Al(O*t*-Bu)₃).

TABLE 3. Rh(II)-Catalyzed Reaction of **5** with Benzaldehyde in the Presence of a Lewis Acid^a

entry	Lewis acid	temp °C	products (%)			
			19a	20a	6	7
1	CITi(O <i>i</i> -Pr) ₃	rt	38			17
2	CITi(O <i>i</i> -Pr) ₃	-40	64	23		
3 ^b	CITi(O <i>i</i> -Pr) ₃	-15	52	24		
4	Ti(O <i>i</i> -Pr) ₄	rt	31	23	6	
5	Ti(O <i>i</i> -Pr) ₄	-40	17	26	37	

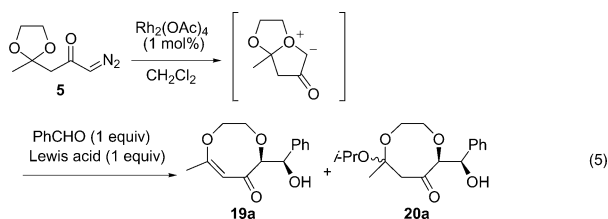
^a Reaction time, 2 h. ^b Using 0.5 equiv of CITi(O*i*-Pr)₃.

for the aldol reaction of Ti-enolate.²⁰ The formation of **17** from the ylide takes place faster than the [1,2]-rearrangement so that the 1,2-rearrangement of ylide **11** to **10** is suppressed.

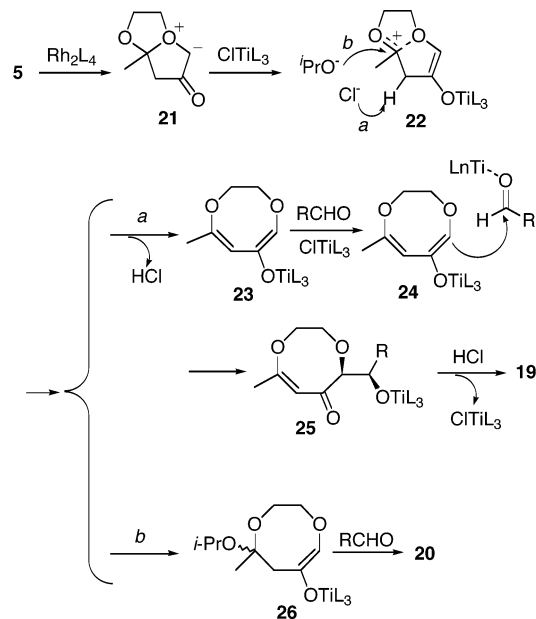
The experimental outcome of this C–C bond formation also provided us with an encouraging suggestion that the Ti-enolate formation with titanate salts will surpass the proton transfer path suppressing the formation of enones from enolizable diazoketone precursors. On the basis of this assumption, the reaction of enolizable diazoketone **5** with aldehyde was revisited.

Reaction of Enolizable Diazoketone **5 with Carbonyl Compounds.** In the preceding study,¹⁵ we reported that the Rh(II)-catalyzed decomposition of **5** in the presence of benzaldehyde but in the absence of either Ti(IV) salts or TMSCl preferentially afforded [1,2]-rearrangement product **6**. The analogous Rh(II)-catalyzed decomposition of **5** in the absence of aldehyde but in the presence of a titanium catalyst, for example, Ti(O*i*-Pr)₄ or CITi(O*i*-Pr)₃, afforded only the ring-enlargement product **7**. These observations indicate that the *O*-ylide derived from **5** can also be transformed to the titanium enolate by the use of titanium salts to stabilize the *O*-ylide, thus suppressing the [1,2]-shift reaction in a similar way as with TMSCl.

On the basis of this observation, the reaction of **5** with benzaldehyde was studied in the presence of an equimolar amount of CITi(O*i*-Pr)₃ or Ti(O*i*-Pr)₄ but without TMSCl. The result was remarkable, and ring-enlarged C–C-bonded products **19a** and **20a** were indeed obtained from enolizable diazoketone **5** (eq 5, Table 3).



Besides C–C-bonded products, some byproducts were formed in the reaction of **5**. For example, when Ti(O*i*-Pr)₄ was used as the catalyst in the reaction with benzaldehyde, [1,2]-rearrangement product **6** was formed in low yield at ambient temperature and in higher yield at lower temperature (compare entries 4 and 5 in Table 3). When CITi(O*i*-Pr)₃ was used in place of Ti(O*i*-Pr)₄, enone **7** was the byproduct (Table 3, entry 1) besides major product **19a**. The highest combined yields of C–C-bonded products (**19a** + **20a**, 87%) was attained with

SCHEME 4. Plausible Mechanism for the C–C Bond Formation of **5**

CITi(O*i*-Pr)₃ at a low temperature (–40 °C, Table 3, entry 2). It should be noted that when the amount of Lewis acid CITi(O*i*-Pr)₃ was reduced to one-half of the stoichiometric amount, the C–C-bonded products were still the solely obtained products with a combined yield of 76% (Table 3, entry 3). This indicates that CITi(O*i*-Pr)₃ plays the role of a catalyst more or less similarly to that of TMSCl in the reaction of **1** shown in Scheme 2.¹⁶ That is, with **5** (Scheme 4), the first intermediate *O*-ylide **21** is trapped by CITi(O*i*-Pr)₃ to form bicyclic titanium enolate **22**. In Scheme 4, two possible reaction pathways are shown. Route a shows the attack of conjugate base Cl[–] on **22** at the α-proton to the double bond to generate ring-enlarged Ti-enolate **23**, which undergoes the aldol reaction with an aldehyde to give aldol adduct titanate **25** reproducing CITi(O*i*-Pr)₃ to return it to the catalytic cycle. Another possible pathway is route b where *i*-PrO[–] attacks the oxonium carbon of bicyclic titanium enolate **22** to generate isopropoxy-substituted ring-enlarged Ti-enolate **26**, which also undergoes the aldol reaction with an aldehyde leading to the formation of adduct **20**.

The C–C-bonded products **19** were diastereomeric mixtures, and the ratios were about 3:1 for most of the reactions. The stereochemistry of the major isomer of **19a** is syn with regard to the OH group and vicinal ethereal C–O bond of the ring, and this is also supported by the X-ray crystallographic analysis (see the Supporting Information). The stereochemistry of the major isomer of **20a** was also analyzed by the X-ray analysis to prove that although the disposition between the two oxygenic groups was syn, the steric relation between the methyl group and the new C–C bond was anti.

When Ti(O*i*-Pr)₄ was used instead of CITi(O*i*-Pr)₃, [1,2]-rearrangement product **6** was obtained in addition to **19a** and **20a** (Table 3, entry 5). This difference in the behavior of Ti(O*i*-Pr)₄ compared to that of chlorotitanate can be ascribed to a slower rate of formation of the metal enolate of Ti(O*i*-Pr)₄ than that of CITi(O*i*-Pr)₃.

A plausible pathway for the C–C bond formation may also involve an intermediate of a Ti-enolate **22** analogous

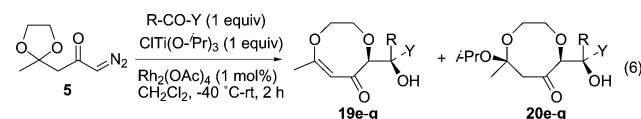
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TABLE 4. Rh(II)-Catalyzed Reaction of **5 with Other Carbon Electrophiles in the Presence of a Lewis Acid**

entry	carbon electrophile		products % (dr)	
	R	Y	19	20
1	styryl	H (e)	66 (5.6:1)	28
2	isopropyl	H (f)	35 (3.6:1)	20
3	phenyl	Me (g)	37 (4.2:1)	5

to **12** described in Scheme 2. As ylide **21** is generated, it reacts with $\text{CITi}(\text{O}i\text{-Pr})_3$ to form Ti-enolate **22** and subsequently **23** or **26**. To obtain more insight into the intervening Ti-enolates, diazoketone **5** was decomposed at -40°C in the presence of $\text{CITi}(\text{O}i\text{-Pr})_3$ but without benzaldehyde. Immediately after the disappearance of **5**, benzaldehyde was added to the reaction mixture, but enone **7** was the sole product.²¹ The result indicates that the *O*-ylide is consumed rapidly, in the absence of a carbon electrophile, to afford only **7**.²²

To extend further the scope of this reaction, reactions of **5** with other carbonyl electrophiles, for example, α,β -unsaturated aldehydes (**e**), aliphatic aldehydes (**f**), and ketones (**g**), in the presence of $\text{CITi}(\text{O}i\text{-Pr})_3$ were examined (eq 6 and Table 4).

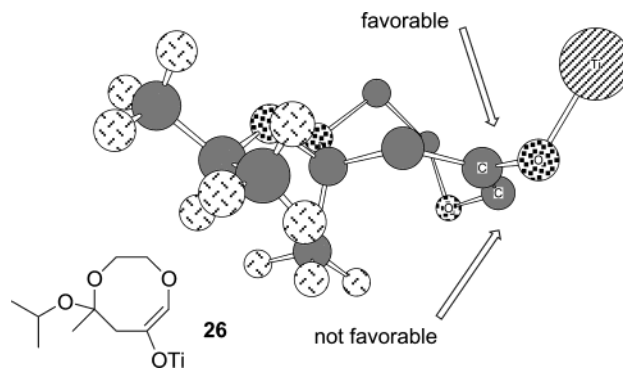


Indeed, as expected, ring-expansion C–C-bonded products **19e–g** and **20e–g** were obtained. Products **20e** and **20g** consisted preferentially of one diastereomer. The syn stereochemistry of **20e** is supported by the ^1H NMR analysis ($J_{\text{vicinal}} = 3.3$ Hz) in comparison with the major isomer of **20a** ($J = 2.7$ Hz) which was determined to be the syn isomer by X-ray crystallographic analysis (see the Supporting Information). However, when isobutylaldehyde was used as the electrophile, the product **20f** was composed of two diastereomers (dr = 3:1) in addition to the major product **19f**. The stereoselectivity in the formation of **20** can be explained as follows: the aldehyde normally approaches the carbanionic center of enolate **26** from the less-crowded surface of the ring avoiding a steric repulsion of the methyl group (Figure 1). However, with isobutylaldehyde the steric effect is smaller than with arylaldehydes, and therefore, the selectivity becomes low.

Effect of the Length of the Tethering Chain of the Diazoketone. One can expect that when equimolar amounts of aldehyde and Lewis acid are used, the reaction of *O*-ylide, once formed regardless of the ring strain, with aldehyde will proceed faster than the [1,2]-shift and β -elimination. On the basis of this assumption, we adopted a few diazoketones bearing a side chain elongated by one or two methylene units to see if the C–C bond-forming reaction would occur. Indeed, enolizable

(21) When an analogous reaction of **27** was studied, expected product **28** was not obtained, but a small amount of 1,2-rearrangement product was formed.

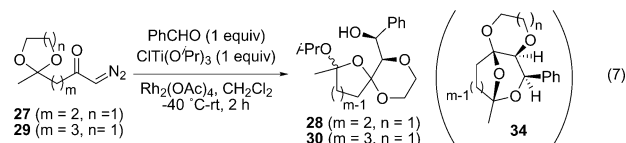
(22) The use of $\text{Ti}(\text{O}i\text{-Pr})_4$ was not attempted for this purpose because, as shown in Table 3 (entries 4 and 5), the use of $\text{Ti}(\text{O}i\text{-Pr})_4$ in the presence of PhCHO afforded a complex product mixture containing 1,2-shift product **6**. In addition, the analogous attempt to detect Ti-enolate in the reaction of **27** in the absence of PhCHO was again unsuccessful.

**FIGURE 1.** Energy-minimized Ti-enolate **26** (calculated by MM2).**TABLE 5. Rh(II)-Catalyzed Reaction of **27**, **29**, and **31** with Benzaldehyde in the Presence of $\text{CITi}(\text{O}i\text{-Pr})_3$**

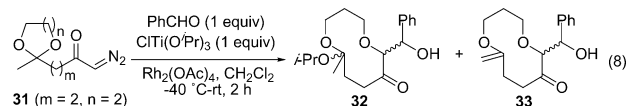
entry	substrate	product (%)
1	27 ($m = 2, n = 1$)	28 (74) ^a
2	29 ($m = 3, n = 1$)	30 (8) ^a
3	31 ($m = 2, n = 2$)	32 (25), 33 (23)

^a Single diastereomer.

diazoketones **27** ($m = 2, n = 1$), **29** ($m = 3, n = 1$), and **31** ($m = 2, n = 2$) possessing a diazocarbonyl side chain that is longer or an acetal ring that is larger than those of **5** ($m = 1, n = 1$) and a five-membered acetal ring were found to undergo the C–C bond-forming reaction with benzaldehyde. However, the products formed from both **27** and **29** were spiro compounds **28** (74%) and **30** (8%), respectively (eq 7).



In contrast, from **31** where both the side chain ($m = 2$) is longer and the ring-size ($n = 2$) is larger than those of **5**, the C–C-bonded ring-enlargement products **32** and **33** (overall 48%) were mainly formed together with a minor amount of spiro product (3%) (eq 8, Table 5).



The reaction was highly stereoselective and chemoselective because both **28** and **30** were composed of a single diastereomer (Table 5).

The bisacetal spiro structure of **28** was determined by ^1H NMR, ^{13}C NMR, COSY, heteronuclear multiple-quantum coherence (HMQC), heteronuclear multiple-bond correlation (HMBC), and IR analysis. Compound **28** was unstable and was easily transformed to bisacetal **34** (Scheme 5). The solid structure of **34** was elucidated by X-ray crystallographic analysis (Figure 2) showing that two ethereal oxygen atoms on its right side (one originates from benzaldehyde and the other from the acetal ring) are positioned syn to each other. This implies that the aldol reaction of the *O*-ylide (or its silyl enol

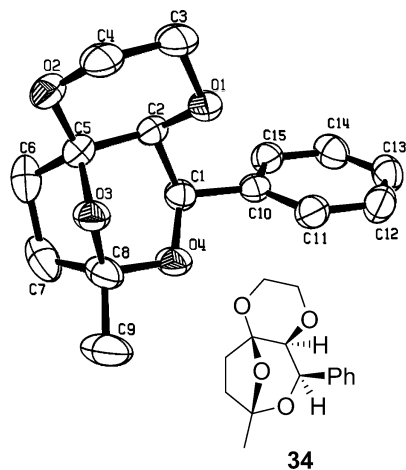
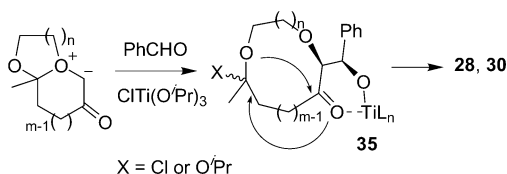
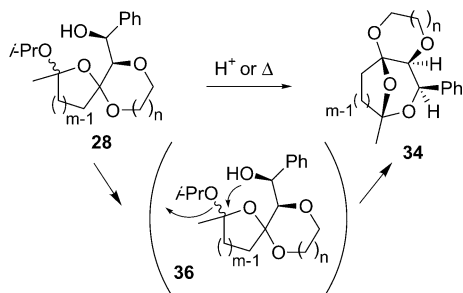


FIGURE 2. ORTEP structure of **34**.

SCHEME 5. Possible Mechanism for the Formation of **28 and **30****



SCHEME 6. Acid-Catalyzed Transformation of **28**



ether), formed from **27**, proceeds in a syn-selective manner (see **26** in Scheme 4) first to form nine-membered titanate **35** where two oxygen groups around the new C–C bond hold a syn disposition and then to undergo ring-reassembling of this primary product to the spiro-[4,5] compound **28** (Scheme 5). Further transformation of **28** to tricyclic bisacetal **34** is assumed to proceed by an acid catalysis (Scheme 6) showing that **34** is more stable than **28**. This assumption is based on the observation that (1) **28** was gradually transformed to **34** in CDCl_3 during its NMR measurement and (2) even the crystal of **28** was transformed to a crystal of **34** after standing for weeks at room temperature.

The formation of **33** from **31** was highly stereoselective affording one stereoisomer, whereas **32** was formed as a mixture of two diastereomers (dr = 2:1) suggesting that its isomerism arose only from the epimerism of the acetal carbon.

More mechanistic insight into this C–C bond formation reaction is possible. With diazoketones bearing a longer side chain than that of **5** ($m = 1$), equilibrium between the carbenoid and bicyclic *O*-ylide is shifted toward the carbenoid to a greater extent because the formation of six-membered ylides is kinetically and thermodynamically less favored than the formation of five-membered ylides. Therefore, to capture the short-lived six-membered ylide, strong electrophiles such as the proton of AcOH ($\text{p}K_a = 4.8$) must be used.¹³ In the above-mentioned reactions of **27**, **29**, and **31**, the aldehyde activated by Lewis acid $\text{ClTi}(\text{O}i\text{-Pr})_3$ can capture the short-lived *O*-ylide as fast as the protonation in conjunction with the stabilization of the ylide by $\text{ClTi}(\text{O}i\text{-Pr})_3$ in the form of the metal enolate.

Conclusion

Albeit our study, at the present stage, is limited to the in situ and intramolecular generation of ethereal oxonium ylide as a nucleophile in C–C bond-forming reactions, the hitherto unknown C–C bond-forming reaction of ethereal oxonium ylides and its profile obviously have been unveiled providing a new synthetic methodology. The structural factors that favor the formation of *O*-ylides, the methods needed to stabilize and tentatively protect these short-lived ylides, and the way to activate carbon electrophiles by acid catalysis are now clear. That more needs to be investigated to expand the scope of the reaction is obvious, such as formation of trimolecular C–C bonds based on the intermolecular formation of *O*-ylides and application of the reaction to the synthesis of useful molecules.

Experimental Section

General Experimental Procedure. A CH_2Cl_2 solution (2 mL) of diazoketone (1.0 mmol) was added by means of a syringe pump over 2 h to a mixed solution of $\text{Rh}_2(\text{OAc})_4$ (1.0 mol % to diazoketone) dissolved in CH_2Cl_2 (8 mL), carbonyl compound, and TMSCl and/or titanium compound, under a N_2 atmosphere. After the mixture was stirred for 15 min, an excess amount (vs TMSCl and/or titanium compound) of triethylamine was added and the reaction mixture was washed with 20 mL of saturated aqueous NaHCO_3 . The aqueous phase was extracted with 20 mL of CH_2Cl_2 (3 \times), and the combined organic phase was dried over anhydrous MgSO_4 . After filtration, the solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel flash column to isolate the products.

Acknowledgment. We thank Mrs. Ikuko Kamada for the X-ray crystallographic analysis.

Supporting Information Available: General methods and detailed experimental procedures for the reactions of diazoketones; ^1H NMR, ^{13}C NMR, and HRMS (FAB) data for products **2e–g**, **3e–g**, **4**, **19a,e–g**, **20a,e–g**, **28**, **30**, **32–34**; elemental analysis of **3f**, **4**, **19a**, **19f**, and **34**; IR spectra of **4**, **19a,e–g**, **20a,e,f**, **28**, and **34**; crystallographic solid structures of products **19a**, **20a**, and **34**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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