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[2+1] Cycloaddition reaction of bis(iodozincio)methane with 1,2-diketones: face-to-face complex of bis(iodozincio)methane and 1,2-diketones as a reaction intermediate

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Abstract—A reaction of 1,2-diketone with bis(iodozincio)methane gave a cyclopropanediol derivative via [2+1] cycloaddition. The reaction proceeded via a sequential nucleophilic attack of the dizinc reagent to a couple of carbonyl group in the substrate. The reaction proceeded with high diastereoselectivity to give *cis*-isomer. Detailed mechanistic studies have been examined by ab initio calculation. © 2002 Elsevier Science Ltd. All rights reserved.

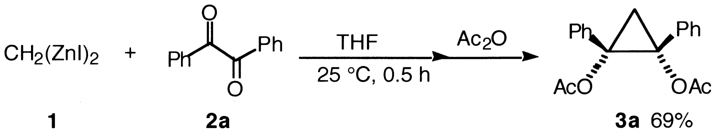
1. Introduction

Reaction of *gem*-dimetallic reagents has attracted considerable attention as versatile reagents in organic synthesis.[1] As doubly nucleophilic species, they have been treated with electrophiles to form a couple of new bonds on the same carbon. Although those are supposed to be highly reactive, the corresponding *gem*-dizinc reagents are relatively stable and have moderate reactivity compare to the other dimetal compounds such as dilithium and dimagnesium ones:[2] These features mean that *gem*-dizinc reagents have the possibility of the selective reaction combining an appropriate mediator, activator, or catalyst.[1c,3]

In the case of a reaction of hetero-atom substituted ketones such as α-alkoxy ketones with the *gem*-dizinc reagent, the activation of the reagent through the chelate type coordination can be expected.[4] This activation in Grignard reagents has been utilized for the diastereoselective addition, that is the well-known Cram's chelation control.[5] The explanation of Cram's chelation control is represented by five-membered transition state complex. However, a reaction of *gem*-dizinc compounds with the α-hetero-atom substituted ketones may be more complex, as this organometallic reagent has a double Lewis acidic sites[6] that connect to the same carbon. We examined the reaction of **1** with benzil (**2a**) as shown in Scheme 1, and found to give a derivative of [2+1] cycloaddition product **3a**.[7] The reaction proceeded with a high diastereoselectivity, and might be controlled under some special activation based on the coordination. The detailed mechanistic investigation by ab initio calculation may give us some information.

2. Reaction of bis(iodozincio)methane (1) with 1,2-diketone

Benzil (**2a**) was treated with bis(iodozincio)methane (**1**) at 25°C in THF for 0.5 h. Acetic anhydride was added to the reaction mixture, and the whole was stirred for another 30 min at 25°C. After aqueous work-up followed by purification with silica-gel column chromatography,



Scheme 1.

Keywords: zinc; cyclopropanation; [2+1]; diketone; dimetal; ab initio.

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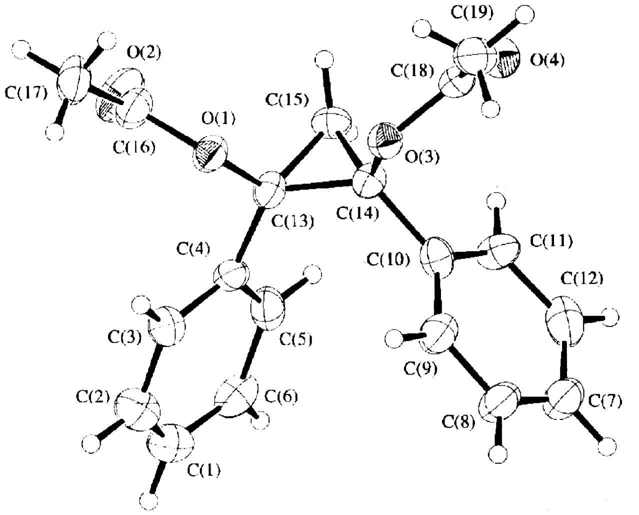


Figure 1. X-Ray analysis of *cis*-1,2-diacetoxy-1,2-diphenylcyclopropane (**3a**). Crystal data: M=310.35, monoclinic, $C2/c$, a=43.816(9), b=5.922(2), c=38.178(8) Å, β=100.53°, V=9739(3) Å^3, Z=24, ρ_{calc}=1.270 g/cm^3, λ (Mo Kα)=0.71069 Å, F(000)=3936.00, μ (Mo Kα)=0.88 cm^{-1}, T=296 K, 2θ_{max}=54.0°, R=0.130 for 4583 reflections (I>2σ(I)).

cis-1,2-diphenylcyclopropane-1,2-diol diacetate was obtained in 69% yield diastereoselectively. An X-ray analysis confirmed the structure and stereochemistry (Fig. 1). Other examples are summarized in Table 1.

Instead of acetylation, an addition of chlorotrimethylsilane to the [2+1] reaction mixture gave the silyl ether (entries 1 and 4). Depending on the substrate, the formed 1,2-cyclopropanediol possesses reasonable stability that enables isolation by a silica-gel column chromatography (entry 2). In all cases, the [2+1] reaction proceeded stereoselectively to give *cis*-diol derivatives. In entry 6, α-ketoaldehyde and bis(iodozincio)methane also gave cyclopropanediol although methylenation of aldehyde proceeded to some extent.[3,4]

In these transformations, the following three points should be noted. The first point is that the cyclopropanation proceeds prior to the enolization of 1,2-diketones. The dizinc reagent **1** is not only nucleophilic but also basic,[8] and may work as deprotonation reagent to form a stable enolate. The second point is the diastereoslectivity of the product. The sterically unfavorable *cis*-1,2-diphenylcyclopropane-1,2-diol was obtained selectively without the formation of the *trans*-isomer. The third point is the cyclopropane formation itself. The dimetallic reagent is well known as an effective methylenation reagent.[1a,3,9] Even in the reaction with α-ketoaldehyde, the cyclopropanediol was a major product (Table 1, entry 6). These points were discussed through the following mechanistic studies.

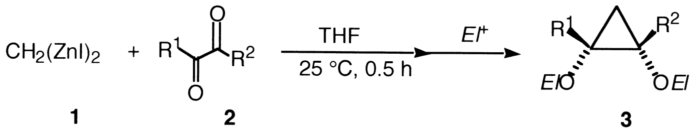
3. Mechanistic studies[10]

Computational details and reaction models will be documented in Section 5. As shown below (Scheme 2), we have assumed two different paths for this reaction, one which starts from a *face-to-face* complex (*path 1*), and the other which is initiated by the formation of a *chelation* complex (*path 2*).[11]

In path 1, bis(iodozincio)methane (**1**) and 2,3-butandione (**2e**) associate with each other to form a bidentate face-to-face complex CP1 (Fig. 2). It has the C_2 symmetry, the axis passing through the methylene carbon of **1** and the center of two carbon atoms in **2e**. Little deformation is seen in **1** while **2e** takes the conformation close to the unstable *s-cis* form to fit into the small space set by the two C–Zn–I lines. The dihedral angle formed by two C=O bonds with respect to the central C–C bond (O_{12}–C_8–C_9–O_{13}) is 47.7°. The reaction is initiated by the nucleophilic attack of the methylene carbon of **1** to one of two carbonyl groups in **2e** and proceeds via TS2 in which the bond-forming carbon atoms come to the distance of 2.322 Å and the ∠Zn–C–Zn is expanded from 101.4 to 147.6°. Estimated by energy difference between CP1 and TS2, the activation energy is 85.1 kJ/mol (117.9 kJ/mol by B3LYP/II//B3LYP/I).

The orbital interactions in TS2 are demonstrated by the interaction frontier orbital method. Fig. 3 is the primary pair of interaction orbitals between the occupied MO space of **1** and the unoccupied MO space of **2e**. It is seen that the pair of electrons at the C_1 center (ϕ_1) has effective overlap with the p-type lobe on C_8 of the π^* orbital of diketone (ψ_1). With

Table 1. [2+1] Reaction of bis(iodozincio)methane with 1,2-dicarbonyl compounds

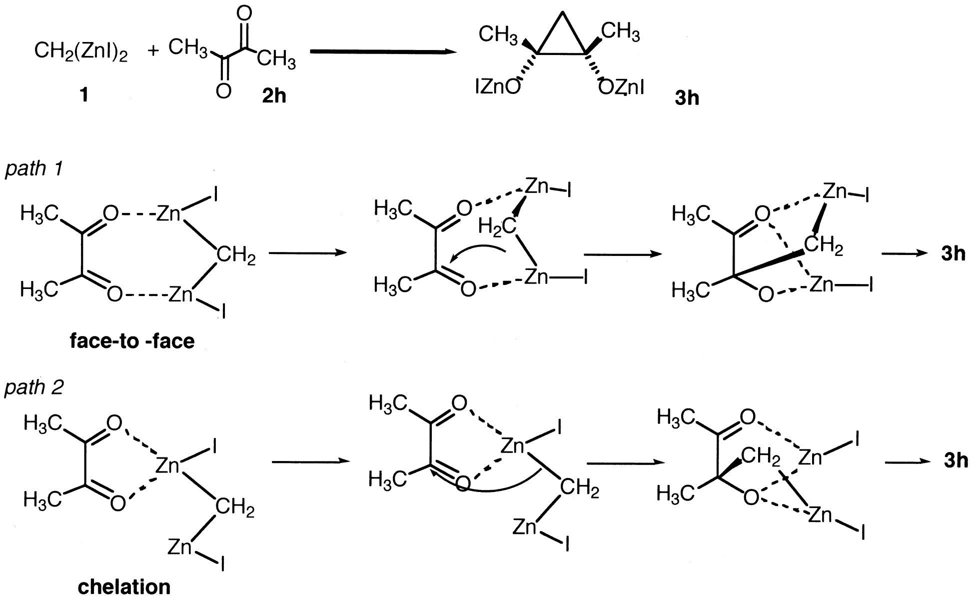


Entry	R^1	R^2		El^+ (El)	Yield of 3^a (%)	
1	Ph	Ph	**2a**	Me_3SiCl (Me_3Si)	78	**3b**
2	Ph	Me	**2b**	H_3O^+ (H)	80	**3c**
3	Ph	Me	**2b**	Ac_2O (Ac)	98	**3d**
4	Ph	Me	**2b**	Me_3SiCl (Me_3Si)	97	**3e**
5	CH_3CH_2	CH_3CH_2	**2c**	Ac_2O (Ac)	59	**3f**
6	Ph	H	**2d**	Ac_2O (Ac)	58[b]	**3g**
7	CH_3	CH_3	**2e**	Ac_2O (Ac)	31	**3h**

1,2-diketone (**2**, 1.0 mmol), *gem*-dizinc **1** (1.2 mmol) and El^+ (2.4 mmol) were used.

[a] Isolated yields. In each entry, only *cis*-isomer was formed diastereoselectively.

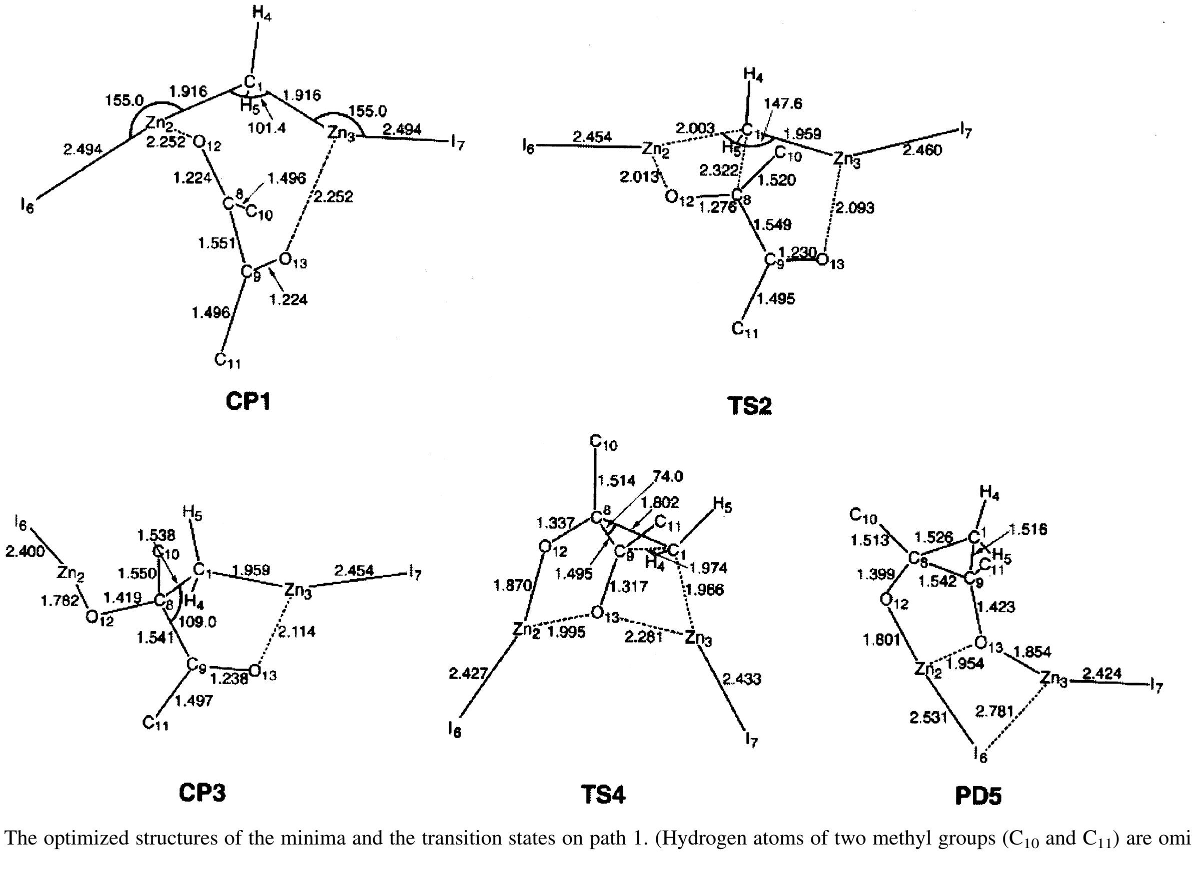
[b] The methylenated product (1-phenyl-2-propenone) was also isolated in 17% yield.



Scheme 2.

Mulliken overlap population analysis based on the transformed orbitals, the electronic charge shifted from **1** to **2e** through this paired orbital is calculated to be 0.413.

The next step of the reaction is induced by the strong electrophilicity of this zinc atom. As Zn_2 approaches O_{13}, the stable five-membered ring is transformed into TS4. In TS4, the carbonyl oxygen (O_{13}) is doubly coordinated by Zn_2 and Zn_3 and the ring is so distorted that the C_1 center and the carbonyl carbon atom (C_9) come close to the distance of 1.974 Å, ready to form the cyclopropane ring. Two methyl groups (denoted as C_{10} and C_{11}), which are staggered to each other with the dihedral angle of 90.7° in CP3, are eclipsed again and come on the same side of the forming cyclopropane ring. Despite such large distortion and the unfavorable steric interaction between two methyl


CP1

TS2

CP3

TS4

PD5

Figure 2. The optimized structures of the minima and the transition states on path 1. (Hydrogen atoms of two methyl groups (C_{10} and C_{11}) are omitted for clarity.)

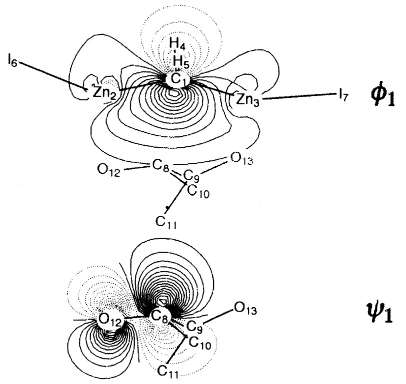


Figure 3. The paired interaction orbitals between the occupied MO space of **1** and the unoccupied MO space of **2e** in TS2.

groups in TS4, the barrier is only 48.4 kJ/mol (64.0 kJ/mol by B3LYP/II//B3LYP/I). This low reaction barrier may be rationalized by an intramolecular orbital interaction. As shown in Fig. 4, we applied the interaction frontier orbital method to TS4 and TS4′. TS4′ is an imaginary structure which has a methyl group instead of a Zn_2-I_6 bond with relative coordinates of the other atoms being fixed to those of TS4. At the left-hand side of Fig. 4, the primary pair of interaction orbitals for TS4 between the occupied MO space of $H_4-C_1-H_5$ and the unoccupied MO space of the remainder is shown. It is demonstrated that the formation of the three-membered ring is achieved by nucleophilic attack of the carbene $2a_1$ electron pair (ϕ_3) to the p-type lobe on C_9 being attacked (ψ_3). Similar orbitals (ϕ_4, ψ_4) are obtained for TS4′ as shown on the right-hand side in Fig. 4. There exists, however, a difference in the energy of the orbital on the unoccupied MO. The level of ψ_3 is 0.329 a.u., which is lower by 0.047 a.u. than that of ψ_4, 0.376 a.u. This difference is ascribed to the difference in the extent of the activation of the carbonyl group in TS4 and TS4′. As shown in Fig. 4, the carbonyl oxygen atom (O_{13}) of the former is doubly coordinated by the two zinc atoms (Zn_2, Zn_3) while in the latter only one zinc atom coordinates to the carbonyl oxygen atom. It is concluded that the cooperative action of two zinc atoms is a key factor for the formation of the cyclopropane ring. Then TS4 leads to PD5 that is stabilized by the two dative bonds, Zn_2-O_{13} and Zn_3-I_6. By the addition of an eliminator such as H_3O^+, PD5 is eventually transformed into *cis*-diol.

The initial complex of path 2 is the chelation complex CP6 as shown in Fig. 5. The zinc atom is coordinated by two carbonyl oxygen atoms in CP6, while Zn_3 remains divalent. The diketone **2e** takes a perfect *s-cis* conformation; the two methyl groups are completely eclipsed. The reaction proceeds via TS7, in which the C_1 center attacks one of the two carbonyl groups (C_8), accompanied by inversion of the arrangement of the substituent atoms or groups. The length of 2.487 Å for the incipient C_1-C_8 bond falls in a range of values obtained in the theoretical calculations for similar reactions in the Cram-type chelation complexes, such as between CH_3TiCl_3 and α-hydroxy ketone[12] or $Mg(CH_3)_2$ and α-methoxyketones.[13] Interaction frontier orbital analysis suggests that the orbital pair shown in Fig. 6, which is between the occupied MO space of the dizinc fragment and the unoccupied MO space of the diketone fragment, is liable for the formation of a new C–C bond. It is seen that the p orbital on C_1 (ϕ_5) effectively overlaps the p lobe on C_8 (ψ_5). In CP8, a five-membered ring (left) and a four-membered ring (right), both of which are supported by a Zn–O dative bond, are fused together with the C_8-O_{12} bond. The high stability brought about by the two Zn–O interactions is reflected in the large heat of formation of 103.3 kJ/mol (72.2 kJ/mol by B3LYP/II//B3LYP/I). In TS9, the distance between two bond-forming carbon atoms (C_1, C_9) is 1.673 Å, shorter by 0.301 Å compared to TS4 while longer only by 0.148 Å than PD10, the product. This means that the transition state emerges at a very late stage. Also, the bond angle at pivotal C_8 is 66.7°, very close to that in the cyclopropane ring of PD10. As expected from these features, the reaction barrier amounts to 100.1 kJ/mol (111.3 kJ/mol by B3LYP/II//B3LYP/I), larger by 51.7 kJ/mol (47.3 kJ/mol by B3LYP/II//B3LYP/I) for the second step of the path 1.

The reaction profiles for paths 1 and 2 based on the B3LYP/I level calculations are shown in Fig. 7(1). Those based on B3LYP/II//B3LYP/I calculations are also shown in

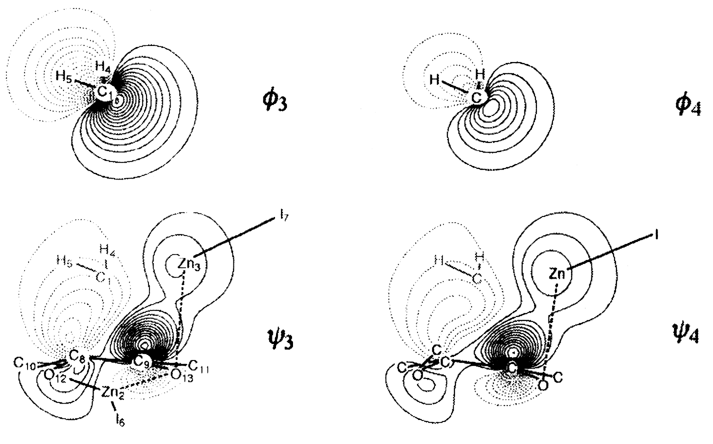
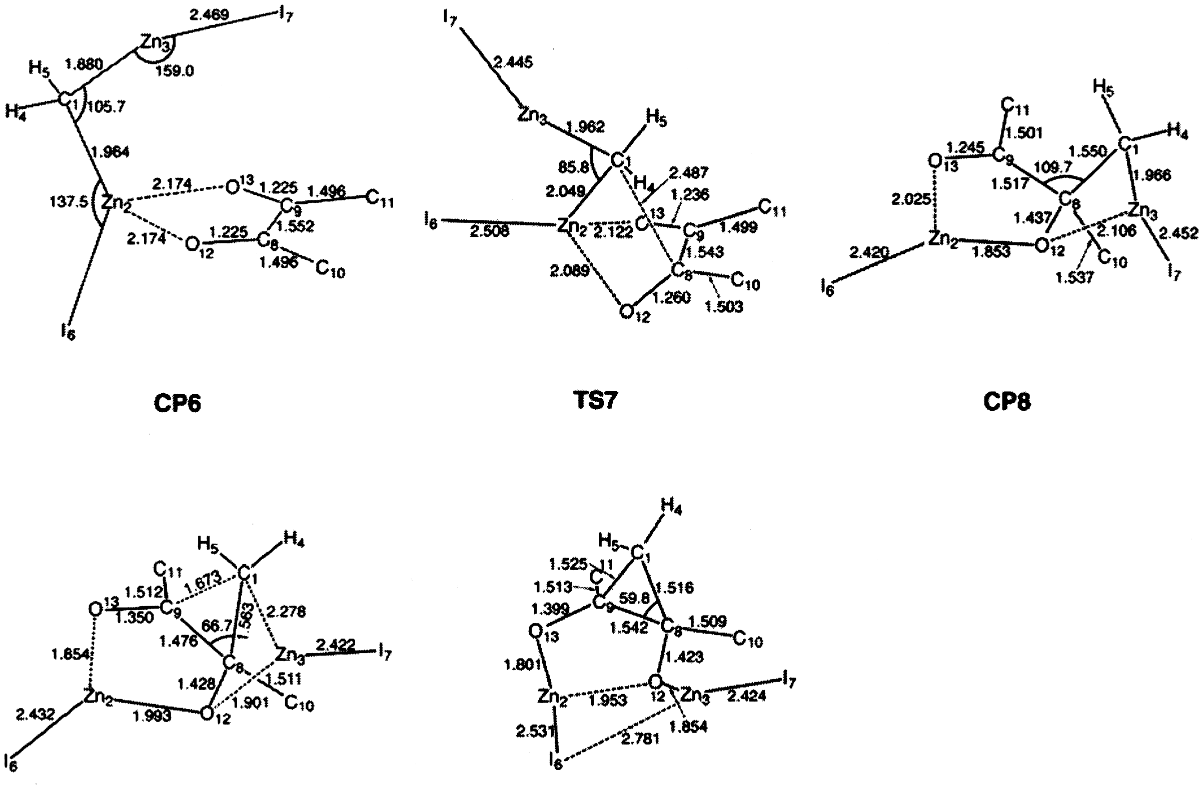


Figure 4. The paired interaction orbitals between the occupied MO space of carbene and the unoccupied MO space of the remainder in TS4 (on the left-hand side) and in TS4′ (on the right-hand side). The viewpoint is right below the $C_1C_8C_9$ triangle. (Hydrogen atoms of two methyl groups (C_{10} and C_{11}) are omitted for clarity.)



CP6 **TS7** **CP8**

TS9 **PD10**

Figure 5. The optimized structures of the minima and the transition states on path 2. (Hydrogen atoms of two methyl groups (C_{10} and C_{11}) are omitted for clarity.)

Fig. 7(2). The energies given for the reaction species are relative from the energy of CP1. While the 15.3 kJ/mol (6.5 kJ/mol by B3LYP/II//B3LYP/I) preference of the chelation structure to the face-to-face structure for **2e**, the activation energies to the final product in path 1 are smaller than those in path 2. Moreover, in each initial complex, an interaction between C_{10} and C_{11} effects the stability as described above. When the phenyl group is chosen for the substituent (**2a**), the face-to-face structure is estimated to be favored by 7.5 kJ/mol (11.3 kJ/mol by B3LYP/II//B3LYP/I) compared to the chelation structure, due to the larger steric interaction of two phenyl groups in the latter than in the former. Accordingly, path 1 might be mainly taken and the cyclopropane formation is much more feasible compared to **2d**. Actually, the diketones with large substituents (**2a**,**b**) yields the *cis*-diols in good yields.

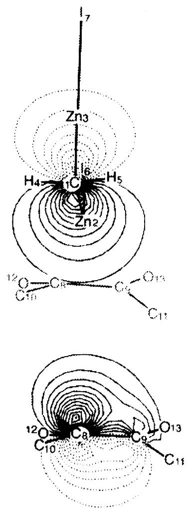


Figure 6. The paired interaction orbitals between the occupied MO space of carbene and the unoccupied MO space of the remainder in TS9. The viewpoint is right above the C_1–C_8–C_9 triangle.

The dihedral angle formed by two carbonyl groups of **2e** in face-to-face initial complex is 47.7° as described above. This may be the crucial point for preventing an enolization of the diketone. If the two carbonyl groups are placed in the same plane, the enolization to form the stable conjugated enol is much easier. And as shown in path 1, two zinc atoms cooperate to the reaction and form the sterically unfavored *cis*-cyclopropane diols.

4. Conclusions

The present study demonstrated that the presence of co-operative actions of two zinc atoms in the [2+1] cycloaddition of a *gem*-dizinc reagent with 1,2-diketones. Throughout the reaction, both zinc atoms in bis(iodozincio)methane interact to help the individual addition mutually. The results given in this study will serve not only for the sophistication of the *gem*-dizinc reagent but also for the development of new bimetallic reaction systems.

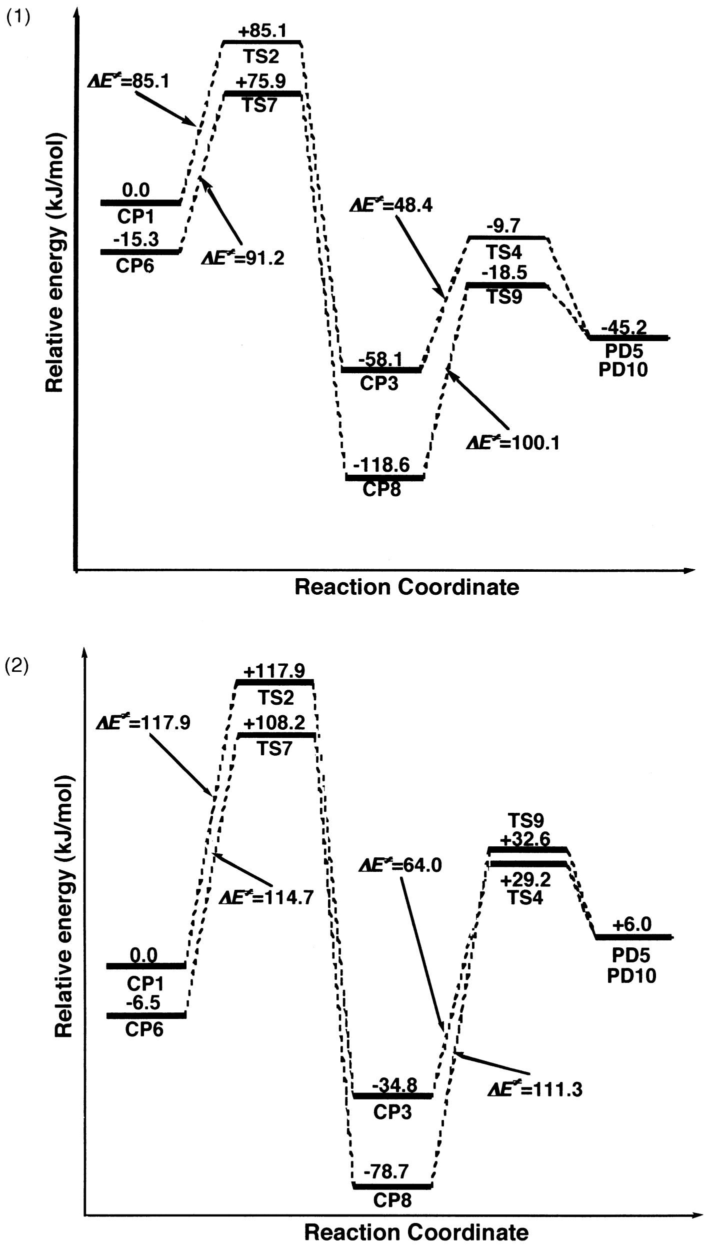


Figure 7. (1) The energy profiles of four pathways by the B3LYP/I level calculations. Relative energies (kJ/mol) are measured from CP1. (2) The energy profiles of two non-solvent pathways by the B3LYP/II/B3LYP/I calculations. Relative energies (kJ/mol) are measured from CP1.

5. Experimental

5.1. General information

All solvents except tetrahydrofuran were used as obtained from commercial suppliers. Tetrahydrofuran was distilled over benzophenone-ketyl. Zinc powder was used after washing with 10% HCl according to the reported procedure.[14] Chromatographic purification of products was accomplished using forced-flow chromatography on Kanto Chemical Co., INC. Silica gel 60 N (spherical, neutral).

^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini-2000 (300 and 75 MHz, respectively) instrument and are internally referenced to residual protio solvent signals. Data for ^{1}H NMR are reported as chemical shift (δ ppm), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported as chemical shift.

For the X-ray diffraction, a crystal was mounted on a glass fiber coated with epoxy resin. Measurements were made on a Rigaku Mercury charge-coupled device (CCD) system with graphite monochromated Mo Kα radiation.

5.2. Computational details and reaction models

The density functional theory (DFT) method has been employed with the B3LYP functional for the exchange correlation terms,[15] using Gaussian 98 program package.[16]

All the geometries have been determined with the basis set system referred to as basis I, which is composed of the 6-31G* basis set for the zinc, carbon, oxygen and hydrogen atoms and the (21|21|1) basis set[17] with a single set of d polarization for the iodo atom[18] whose core electrons up to 5d were replaced by the Los-Alamos effective core potentials.[17] Transition states and energy minima were verified to have one and a zero imaginary mode, respectively, by the normal-mode analysis, which at the same time gives the zero-point energy correction. For the structures without the THF molecule, the potential energies are refined by the single-point calculations at the B3LYP level of theory with another kind of basis set system referred to as basis II, which consists of the standard cc-pVTZ basis set for carbon, oxygen and hydrogen atoms[19] and the TZV basis set for zinc atoms[20] and the Saldej-pVTZ basis set for the iodo atom.[21] The total energies are given by the sum of the zero-point energy corrections and the potential energies, which are obtained by the B3LYP/I and B3LYP/II//B3LYP/I calculations. A brief explanation for the interaction frontier orbital method[22] is as follows. Consider the complex AB, reaction intermediate or transition state, in which the fragments A and B interact with each other. Suppose that the fragment A has m occupied MOs with $M-m$ unoccupied MOs and in the fragment B the lowest-level n of the N canonical MOs have electron pairs leaving the remainder $N-n$ vacant. The frontier orbital theory focuses attention only on the HOMO–LUMO interactions of $m(N-n)$ interactions between the occupied MOs of A and the unoccupied MOs of B and $(M-m)n$ interactions between the unoccupied MOs of A and the occupied MOs of B, based on the assumption that they are so strong that the contributions of others are relatively negligible. However, this assumption is ruled out for the orbital interactions of the molecules with moderate or large size in which the energy gaps between the frontier orbitals and other MOs are not so large. To solve this problem, it is necessary to take the contributions of all occupied and unoccupied MOs of the two fragments into account. For this purpose, we expand first the MOs of the complex AB in a linear combination of the MOs of fragments A and B. We carry out next the unitary transformations of the fragment orbitals simultaneously within the occupied MO space of one fragment and within the unoccupied MO space of the other fragment, referring to the strengths of the orbital interactions (density matrix) calculated from the wave function of the complex. By this treatment, electron delocalization is represented by a few pairs of the fragment interaction orbitals that include the contributions not only of the frontier orbitals but also of all the MOs of A and B. Over the past two decades, this method has been applied to the analysis of the orbital interaction in the reaction intermediates or the transition states and has been shown by us to afford an interpretation of some interesting features of the reactions such as regioselectivity, stereoselectivity and the unexpectedly high reactivity which are irrational or incomprehensible within the framework of the frontier orbital theory.

5.2.1. Bis(iodozincio)methane (1). A mixture of Zn (25 mmol), diiodomethane (1.0 mmol), and PbCl$_2$ (0.01 mmol) in THF (2.0 mL) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. To the mixture, diiodomethane (10 mmol) in THF (20 mL) was added dropwise over 15 min at 0°C with vigorous stirring. The mixture was stirred for 2 h at 0°C. After the stirring was stopped, the reaction vessel was stood undisturbed for several hours. Excess zinc was separated by sedimentation. ^{1}H NMR spectra of the obtained supernatant showed a broad singlet at −1.2 ppm at 0°C, which corresponded to the methylene proton of **1**. The supernatant was used for the further reaction as a solution of **1** in THF (0.5–0.6 M). Bis(iodozincio)methane in THF can be kept unchanged at least for a month in the sealed reaction vessel.

5.3. General procedure for the preparation of cyclopropanediol

To a solution of 1,2-diketone (1.0 mmol) in THF (3 mL), dizinc **1** (1.2 mmol) was added dropwise at 25°C. The mixture was stirred 30 min. Quenching reagent (2.4 mmol, water, acetic anhydride, and chlorotrimethylsilane) was added dropwise and the resulting mixture was stirred for another 30 min. The mixture was poured into sat. NH$_4$Cl (aq.) and extracted with ether. The combined ethereal phases were washed with brine and dried over Na$_2$SO$_4$. Purification on a neutral silica-gel column chromatography gave the corresponding product.

5.3.1. *cis*-1,2-Diacetoxy-1,2-diphenylcyclopropane (3a). ^{1}H NMR (CDCl$_3$) δ 7.28–7.20 (m, 4H), 7.18–7.10 (m, 6H), 2.51 (d, J=9.0 Hz, 1H), 2.11 (s, 6H), 1,83 (d, J=9.0 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 170.1, 135.3, 128.8, 127.8, 64.9, 23.8, 21.1. Calcd for C$_{19}$H$_{18}$O$_4$: C, 73.53; H, 5.85. Found: C, 73.25, H, 5.95.

5.3.2. *cis*-1,2-Bis(trimethylsiloxy)-1,2-diphenylcyclopropane (3b). ^{1}H NMR (CDCl$_3$) δ 7.17–6.90 (m, 10H), 2.18 (d, J=7.5 Hz, 1H), 1,48 (d, J=7.5 Hz, 1H), 0.08 (s, 18H); ^{13}C NMR (CDCl$_3$) δ 140.0, 127.9, 127.5, 126.5, 64.8, 23.1, 0.90. Calcd for C$_{21}$H$_{30}$O$_2$Si$_2$: C, 68.05; H, 8.16. Found: C, 67.80, H, 7.93.

5.3.3. *cis*-1,2-Dihydroxy-1-methyl-2-phenylcyclopropane (3c). ^{1}H NMR (CDCl$_3$) δ 7.60–7.20 (m, 5H), 3.85 (bs, 2H), 1.27 (d, J=7.5 Hz, 1H), 1.13 (s, 3H), 0.98 (d, J=7.5 Hz, 1H).

5.3.4. *cis*-1,2-Diacetoxy-1-methyl-2-phenylcyclopropane (3d). ^{1}H NMR (CDCl$_3$) δ 7.65–7.56 (m, 2H), 7.38–7.20 (m, 3H), 2.09 (s, 3H), 1.92 (s, 3H), 1.68 (d, J=9.0 Hz, 1H), 1,39 (d, J=9.0 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (CDCl$_3$) δ 170.6, 170.2, 135.6, 129.6, 128.3, 128.2, 125.9, 63.5, 60.5, 22.8, 21.0, 20.7, 18.3. Calcd for C$_{14}$H$_{16}$O$_4$: C, 67.73; H, 6.50. Found: C, 67.84, H, 6.59.

5.3.5. *cis*-1,2-Bis(trimethylsiloxy)-1-methyl-2-phenylcyclopropane (3e). ^{1}H NMR (CDCl$_3$) δ 7.41–7.15 (m, 5H), 1.34 (d, J=6.9 Hz, 1H), 1,06 (d, J=6.9 Hz, 1H), 1.05 (s, 3H), 0.23 (s, 9H), 0.03 (s, 9H); ^{13}C NMR (CDCl$_3$) δ 141.1, 128.0, 127.9, 126.9, 63.7, 59.7, 24.1, 22.2, 1.24, 0.82. Calcd for C$_{16}$H$_{28}$O$_2$Si$_2$: C, 62.28; H, 9.15. Found: C, 61.98, H, 9.27.

5.3.6. *cis*-1,2-Diacetoxy-1,2-diethylcyclopropane (3f). ^{1}H NMR (CDCl$_3$) δ 1.98 (s, 6H), 1.84 (ddq, J=15.0, 7.5, 0.9 Hz, 2H), 1.74 (dq, J=15.0, 7.5, Hz, 2H), 1.07 (dt, J=8.4, 0.9 Hz, 1H), 1.00 (t, J=7.5 Hz, 6H), 0.87 (d, J=8.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 170.4, 64.1, 24.2, 23.1, 20.9, 9.4.

5.3.7. *cis*-1,2-Diacetoxy-1-phenylcyclopropane (3g). ^{1}H NMR (CDCl$_3$) δ 7.51–7.40 (m, 2H), 7.41–7.28 (m, 3H), 4.26 (dd, J=8.1, 4.8 Hz, 1H), 2.13 (s, 3H), 2.04 (s, 3H), 1.80 (dd, J=8.4, 8.4 Hz, 1H), 1,49 (dd, J=8.4, 4.8 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 171.2, 170.2, 137.5, 128.4, 128.1, 127.7, 59.9, 55.0, 20.8, 20.4, 18.8.

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