Ketene Recognizes 1,3-Dienes in Their s-Cis Forms through [4 + 2] (Diels−Alder) and [2 + 2] (Staudinger) Reactions. An Innovation of Ketene Chemistry

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Abstract: The mechanism of ketene−diene reactions has been studied both experimentally and theoretically. Careful experiments of the reactions of diphenylketene (**1**) with cyclic (s-cis) 1,3-dienes [cyclopentadiene (**2**) and cyclohexa-1,3-diene (**3**)] lead to the first direct detection of the Diels−Alder cycloadducts (**10** and **11**) by low-temperature NMR spectroscopy. The initially formed cycloadducts are converted to the final Staudinger products, cyclobutanones (**6** and **7**), by [3,3] sigmatropic (Claisen) rearrangements. In contrast, ketene **1** reacts with open-chain 1,3-dienes [2,3-dimethyl-1,3-butadiene (**4**) and 1-methoxy-1,3-butadiene (**5**)] to afford initially both the Staudinger-type (**8**, **9**) and Diels−Alder-type cycloadducts (**12**, **13**). The Staudinger cycloadducts (**8**, **9**) are converted eventually to Diels−Alder products (**12**, **13**) by the retro-Claisen rearrangement. Thus, ketene recognizes dienes in cycloadditions as ketenophiles different from olefins. [4 + 2] and [2 + 2] cycloadducts are generated and can be intermediates or products flexibly according to diene structures.

I. Introduction

In the first decades of this century, Staudinger discovered ketene[2−6] and its reactions[7] in the cycloaddition of diphenylketene[2] (**1**) and cyclopentadiene (**2**).[8−11] The pioneering studies on ketene [2 + 2] cycloadditions (Staudinger reactions) have been confirmed by a huge number of experiments.[12−14] They showed that *ketenes react with olefins across the C═C bond rather than the C═O one*. Ketenes are potentially useful

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(2) Staudinger first isolated a ketene, diphenylketene (**1**), generated from $Ph_2CCl-COCl$ with granulated zinc. Staudinger, H. *Chem. Ber*. **1905**, *38*, 1735−1739.

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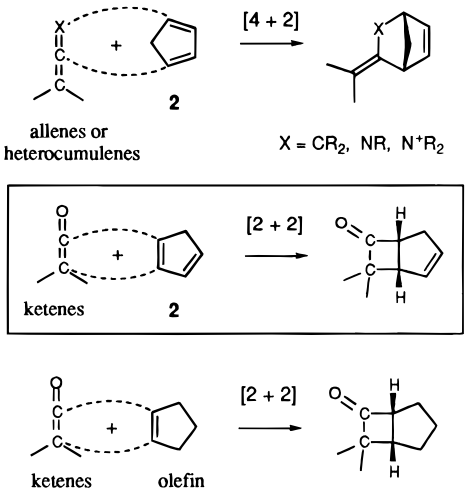
Scheme 1. The Anomaly of Ketene Cycloaddition

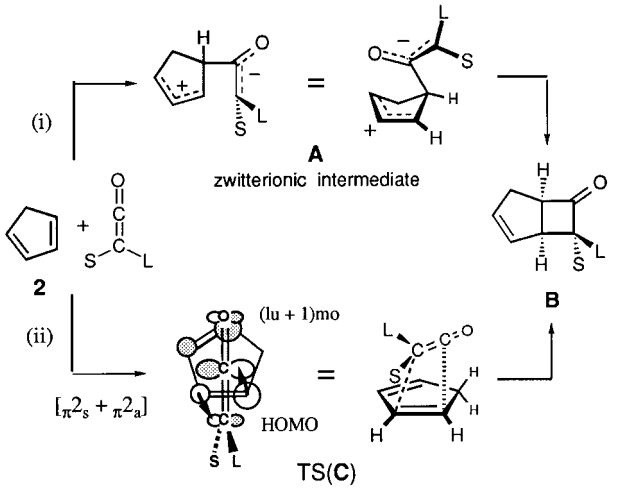


dienophiles but they do not appear to owe their reactivity toward dienes to Diels−Alder reactions. They react preferentially with 1,3-dienes to give four-membered rings, cyclobutanones,[13,14] rather than six-membered ones, cyclohexanones.[15] The unusual capability and the periselectivity of ketenes in 1,2-cycloadditions have been widely employed in organic syntheses[13,16] including those of natural products.[12,13] The most representative example is found in a key initial stage of the total synthesis of the natural primary prostaglandins.[17]

Scheme 1 shows that allenes[18] (>C=C=C<) and heterocumulenes[12] [such as ketenimines[19] (>C=C=N−) and keteniminium ions[20] (>C=C=N$^+$<)] participate in the Diels−Alder ([4 + 2] cycloadditions) reactions with conjugated dienes such as cyclopentadiene. Exceptionally, most ketenes (>C=C=O) do not appear to react by [4 + 2] cycloadditions.

It was difficult to rationalize the feature of ketene cycloadditions (Staudinger reaction), until the proposal of the Woodward−Hoffmann rule.[21] The rule explained the easy and exclusive formation of a four-membered ring by a nonphotochemical process even with 1,3-dienes. As a conventional result, it has been thought that ketenes do not add as dienophiles to the 1,4-positions of 1,3-dienes but rather yield cyclobutanones exclusively. Scheme 2 illustrates the traditional interpretation of the Staudinger reaction. Ketenes undergo cycloadditions toward 1,3-dienes through either (i) a nonconcerted two-step pathway via a zwitterionic intermediate **A** to give a [2 + 2] cycloadduct **B** or (ii) a concerted [$_\pi$2$_s$ + $_\pi$2$_a$] cycloaddition[22] via a transition state (TS) **C**. An excellent study of secondary deuterium kinetic isotope effect on the reaction between

Scheme 2. The Traditional Scheme for the Cycloaddition Reaction of Ketenes toward Conjugated 1,3-Dienes To Give a [2 + 2] Cycloadduct (B)[a−d]



[a] Upper: Two-step mechanism via a zwitterionic intermediate (**A**). Lower: Concerted [$_\pi$2$_s$ + $_\pi$2$_a$] pathway via a transition state **C**. [b]TS(**C**) shows the charge-transfer model from HOMO of **2** to (lu + 1)mo of ketene. [c]L and S stand for large and small substituents, respectively. See ref 27. [d]For experimental results, see refs 9−11. For mechanistic investigations, see refs 20 and 21.

diphenylketene and 5,5-dimethylcyclopenta-1,3-diene was reported.[23a] The result indicated that the reaction takes a nonconcerted two-step mechanism.[23b] Other evidence against the one-step pathway has been provided by both experimental[23−25] and theoretical studies.[26]

Open-chain (acyclic) 1,3-dienes undergo 1,2-cycloadditions similarly to cyclic 1,3-dienes with ketenes.[12−14] Huisgen[28] et al. reported the first kinetic measurement that diphenylketene (**1**) reacts with cyclopentadiene (**2**) 3.05×10^4 times faster than cyclopentene at 40 °C.[15b] The rate preference of **2** to cyclopentene has been explained by the secondary orbital interaction in TS(**C**) of Scheme 2.[12e,15b] But, Staudinger reactions of open-chain 1,3-dienes were found to be considerably slower than those of cyclic 1,3-dienes.[15] Introduction of an electron-donating substituent, methoxy group, at the 1-position of open-chain 1,3-butadiene increases the reactivity of the diene.[29] It is curious that the ethylene bond is more reactive than the vinyl ether double bond of the diene in this reaction.

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(22) Thermal [2π + 2π] cycloadditions are allowed generally as [$_\pi$2$_s$ + $_\pi$2$_a$] processes according to the Woodward−Hoffmann rule. But, the paths must involve the orthogonal approach of the reacting species. Such reactions are precluded for normal olefins due to the strain of the transition state. However, ketenes were regarded as especially good antarafacial components in [$_\pi$2$_s$ + $_\pi$2$_a$] cycloadditions. The next lowest unoccupied molecular orbital, (lu + 1)mo, of ketenes could overlap efficiently with the highest occupied molecular orbital (HOMO) of olefins orthogonally in Scheme 2.

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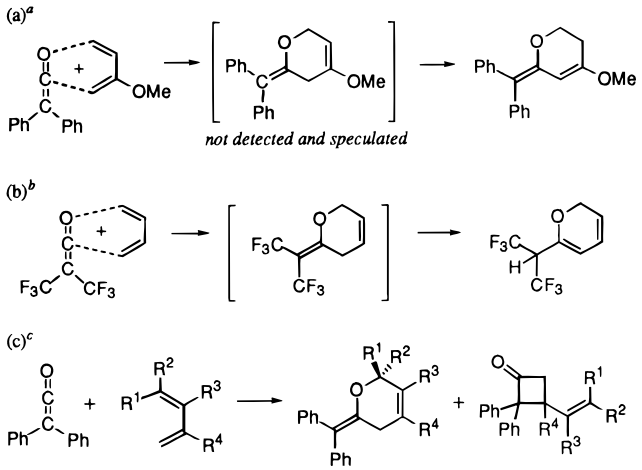
(27) Cycloadditions of ketenes with a large and a small substituents (L and S) to **2** give **B** regio- and stereoselectively: The predominance of the adduct **B** with the larger substituent in the *endo* position was regarded as evidence for the [$_\pi$2$_s$ + $_\pi$2$_a$] pathway in Scheme 2.

(28) For an autobiographic account, see ref 1.

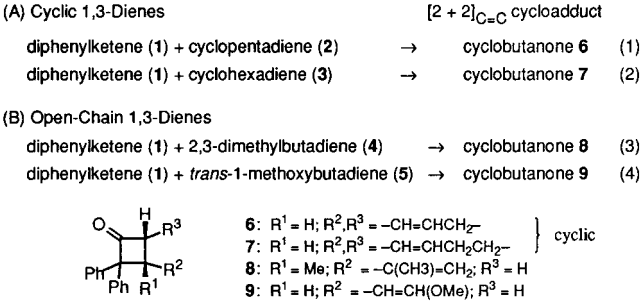
Scheme 3. The Exceptional Examples, 1,4-Cycloadditions, in Ketene−Diene Reactions



[a] The first sign of a 1,4-cycloaddition of a ketene (refs 29 and 30). [b]The first detection of a 1,4-cycloadduct (ref 32b). [c]Results of 1,4-addition of diphenylketene (**1**) to butadienes. For the formation of a mixture of [4 + 2] and [2 + 2] products, see ref 34 (*trans*-1-ethoxy- or *trans*-1-thioethylbutadiene). Exclusive formations of [4 + 2] adducts, see ref 34 (2-ethoxybutadiene, *trans*-1-ethoxy-2,3-dimethylbutadiene, etc.) and ref 33 (*trans*-1-*tert*-butoxybutadiene).

It is a primitive question why ketenes do not undergo [4 + 2] cycloadditions in most cases. There are various examples of those reactions across the C═O bond of ketene.[13,14] However, those Diels−Alder-type reactions ([4 + 2] in Scheme 1) are rare and have been regarded as exceptions. Scheme 3 illustrates the exceptions, i.e., the reactions of ketenes with conjugated dienes giving 1,4-cycloadducts or via [4 + 2] cycloadditions. The first symptom of the 1,4-addition of a ketene toward a diene was reported in 1965 (Scheme 3a).[29,30] An electron-deficient bis(trifluoromethyl)ketene[31] reacts with butadiene to form a 1,4-cycloadduct across the C═O bond of ketene (Scheme 3b).[32] When an electron-donating (alkoxy or trimethylsiloxy) group is introduced to 1,3-butadiene, 1,4-cycloadducts[33] are obtained exceptionally (Scheme 3c) in the mixture of [4 + 2] and [2 + 2] cycloadducts.[34] There also have been other examples of exceptional Diels−Alder reactions.[35−39]

Scheme 4. Four Cycloadditions Dealt with in This Work[a−c]



[a] Equations 1−3 are the known reactions, whereas eq 4 is an unknown reaction treated here for the first time. [b]For reaction 1, see refs 7, 9, 10, 11e, and 15. For reaction 2, see refs 9 and 39d. For reaction 3, see refs 9a, 15, and 41. [c]Reaction 4 is predicted to give cyclobutanone **9** judging from major examples of the conventional results from the reactions of a ketene with butadiene (see ref 42).

We have become aware that the above exceptions in Scheme 3 may reflect the general feature of the ketene reactions with 1,3-dienes. As a naive idea, the carbonyl group in the ketene should be a good dienophile (with the low-lying $\pi^*_{C=O}$ energy level) for the normal-electron demand in Diels−Alder reactions. Thus, *the conventional and traditional results (two-step mechanism via zwitterionic intermediate in i of Scheme 2) of the reaction between diphenylketene and cyclopentadiene has been revised to a two-step mixed reaction mechanism of a combination of a [4 + 2] addition and the subsequent [3,3] sigmatropic rearrangement in our preliminary report.*[40] In the first step, the frontier molecular orbital (FMO) theory has supported the Diels−Alder cycloaddition over the [2 + 2] addition. Second, ab initio calculations have confirmed the FMO prediction and have revealed that the [4 + 2] cycloadduct should be converted to the [2 + 2] adduct. The latter adduct is thermodynamically more stable than the former. Third, through low-temperature NMR monitoring, the α-methylenepyran-type [4 + 2] adduct has been detected successfully. Thus, a new stepwise mechanism ([4 + 2] cycloaddition → Claisen shift) has been proposed in the reaction between diphenylketene (**1**) and cyclopentadiene (**2**).[40]

But, there remain several problems in the new mechanism. First, cyclopentadiene has a small distance (2.363 Å) between two terminal (1 and 4) carbon atoms which is conveniently fit for the Diels−Alder reaction. Open-chain dienes have larger distances [e.g., 3.042 Å in 2,3-dimethyl-1,3-butadiene (**4**)] which are less fit for the reaction. In these acyclic dienes, [4 + 2] and [2 + 2] cycloadditions might be competitive. Second, one might criticize that our new stepwise route is minor and that the direct cyclobutanone formation is still major. Third, a parent ketene has been adopted in ab initio calculations, while low-temperature experiments have been carried out by the use of diphenylketene. To adjust the theoretical model to experimental reactants, diphenylketene must be employed in ab initio calculations. Phenyl groups might impose steric hindrance on reacting systems. To solve those problems and to get a decisive and general picture of the reaction mechanism, we would like to describe full accounts of ketene−diene reactions here. Four reactions (eq 1, 2, 3, and 4) in Scheme 4 will be examined both experimentally and theoretically. Historically ambiguous selectivities of ketene−diene reactions will be elucidated.

Reactions 1 and 2 have cyclic 1,3-dienes, and reactions 3 and 4 do open-chain 1,3-dienes. Is our new mechanism[40] specific only for reaction 1?

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(30) In Scheme 3a, the reaction of diphenylketene (**1**) with 2-methoxybutadiene leads to the isolation of an isomer of the real intermediate. The product is thought to be formed via a [4 + 2] cycloadduct and its isomerization, hydrogen 1,3-shift.

(31) Similarly, a 1,4-cycloadduct between bis(trifluoromethyl)ketene and 1,3-butadiene isomerizes easily to give a pyran (Scheme 3b). England, D. C.; Krespan, C. G. *J. Am. Chem. Soc.* **1965**, *87*, 4019−4020. England, D. C.; Krespan, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 5582−5587.

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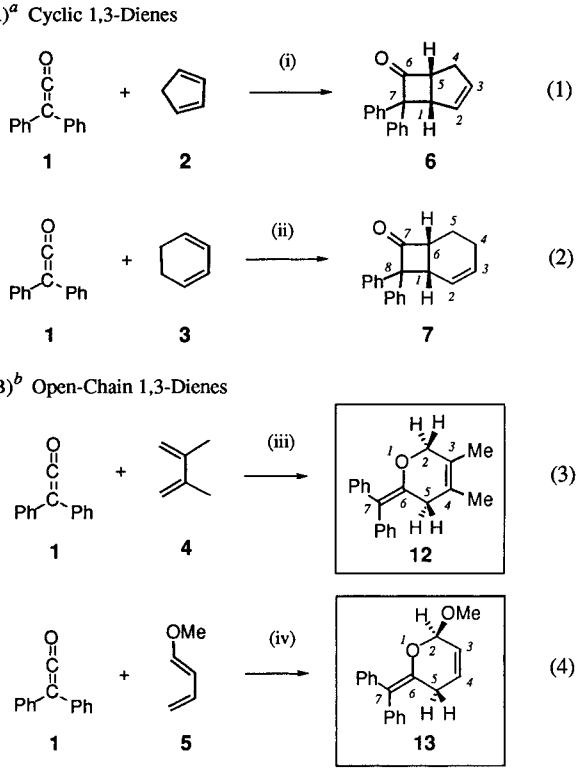
Scheme 5. Product Analyses for Diphenylketene-1,3-Diene Reactions (Reactions 1−4 in Scheme 4): Cyclic 1,3-Dienes Give Normal Staudinger-Type [2 + 2] Products, whereas Open-Chain 1,3-Dienes Give Diels−Alder-Type [4 + 2] Products[a,b]



[a] Conditions for isolation experiments of the final products, Staudinger-type [2 + 2] cycloadducts (**6** and **7**). (i) **1** + **2** → **6**: CH_2Cl_2, room temperature, 3 h, 98%; toluene, room temperature, 3 h, 98%. (ii) **1** + **3** → **7**: benzene, 80 °C, 2 days, 96%. [b]Conditions for isolation experiments of the final products, Diels−Alder-type [4 + 2] cycloadducts (**12** and **13**). (iii) **1** + **4** → **12**: $CHCl_3$, 40 °C, 32 days, 97%; no solvent, 40 °C, 40 days, 94%. (iv) **1** + **5** → **13**: $CHCl_3$, room temperature, 20 days, 98%; benzene, room temperature, 30 days, 96%.

II. Experimental Results

We have examined the four reactions (eqs 1−4) in Scheme 4. First in the experiments, we have analyzed four products precisely. Second, we have searched for reaction intermediates thoroughly to clarify the reaction mechanisms by ^{1}H NMR monitorings.

1. Analyses of Final Products. For cyclic 1,3-dienes [cyclopentadiene (**2**) and cyclohexa-1,3-diene (**3**)], we have traced reactions 1 and 2 in Scheme 4 at the traditional conditions. We have observed that reaction 1 proceeds in dichloromethane or benzene very readily even at room temperature and is completed within 3 h. Reactions 1 and 2 led to smooth and exclusive formation of the [2 + 2] products **6** and **7** in quantitative yields (i and ii in Scheme 5). We have confirmed that both reactions 1 and 2 give the Staudinger-type [2 + 2] cycloadducts, **6** and **7**, respectively, as Schemes 4A and 5A show. Their IR spectra of the products indicate the very strong C═O stretching vibrations for **6** (ν_{max} 1772 cm^{-1}) and **7** (ν_{max} 1770 cm^{-1}) of cyclobutanones, respectively.

For open-chain 1,3-dienes (**4** and **5**), we have carried out reactions 3 and 4 at 40 °C and room temperature, respectively. In contrast to the above conventional results of cyclic 1,3-dienes, we have newly found that both reactions 3 and 4 give EXCLUSIVE formation of the Diels−Alder-type [4 + 2] cycloadducts, **12** and **13**, respectively. *Staudinger-type [2 + 2] cycloadducts were not obtained as the final products*. Reaction 3 proceeds very slowly and takes a very long reaction time for complete consumption of diphenylketene **1**. Reaction 3 gave the [4 + 2] product **12** eventually (iii in Scheme 5). Similarly, we have found that reaction 4 affords the [4 + 2] product **13** exclusively (iv in Scheme 5). The IR spectra of the products (**12** and **13**) have revealed the strong C−O stretching vibrations for **12** (ν_{max} 1242 and 1028 cm^{-1}) and **13** (ν_{max} 1236 and 1012 cm^{-1}) and no C═O stretching vibrations due to cyclobutanone structures. ^{1}H and ^{13}C NMR spectroscopies have clarified that the new products, **12** and **13**, are not the traditional Staudinger-type [2 + 2] cycloadducts but the Diels−Alder-type [4 + 2] ones. For spectral detail, see the Supporting Information.

2. Reaction-Intermediate Search. To clarify the reaction mechanism, we have searched all the reactions (eqs 1−4 in Scheme 5) for the transient reaction intermediates by NMR spectroscopies. Choosing experimental conditions (Scheme 6) precisely, we have succeeded in detecting and isolating all the intermediates concerned with the elementary processes. All three experimental parameters—temperature, time, and concentrations—were strictly tested. (The NMR monitoring results in all the reactions are shown in the Supporting Information.)

3. Analyses of Elementary Processes and Intermediates of Cyclic 1,3-Dienes (A). For reactions 1 and 2, we have found that the reactions proceed in a *unique reaction pathway* (reactants → [4 + 2] intermediate → [2 + 2] product). Scheme 6A summarizes experimental results for cyclic 1,3-dienes. Two reactions 1 and 2 proceed initially by [4 + 2] (Diels−Alder) cycloadditions to form intermediates **10** and **11**. They are followed by [3,3] sigmatropic (Claisen) rearrangements to give [2 + 2]-type (Staudinger) products, cyclobutanones (**6** and **7**), eventually.

Figure 1 illustrates a low-temperature ^{1}H NMR and Fourier transform (FT) IR spectroscopic monitoring result of reaction 1. The figure shows that the reaction proceeds very readily even at low temperatures. Figure 2 shows that reaction 2 requires higher temperatures and longer reaction times than those in reaction 1. Both reactions give the [2 + 2] products (**6** and **7**) exclusively as the final form.

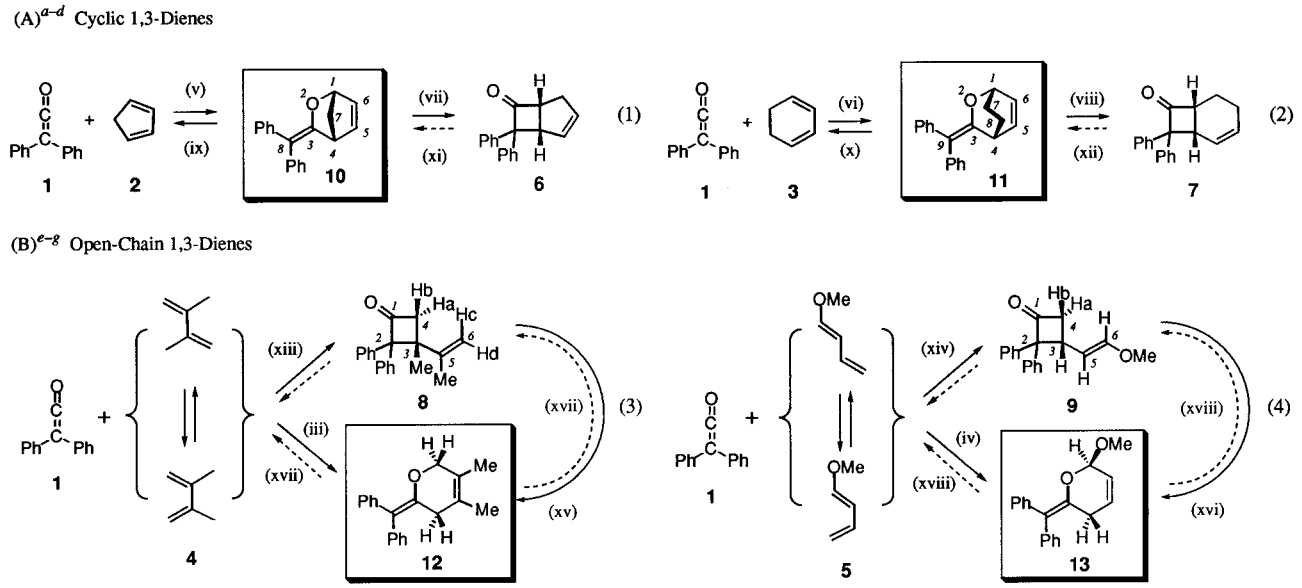
3.1. Diels−Alder Reaction, the First Step, and Isolation of [4 + 2] Cycloadducts. Figure 1a illustrates the low-temperature ^{1}H NMR monitoring result of reaction 1. This figure reveals the presence of a rapidly formed intermediate (**10**) of which the concentration exceeds surprisingly more than 40% of the reaction mixture at a stage (−20 °C, 3 h) of the reaction. Figure 3 illustrates the ^{1}H NMR for the reaction mixture at that stage. The spectra show that the transient intermediate **10** is a [4 + 2] cycloadduct between **1** and **2**. The reaction proceeds very smoothly at low temperatures (v in Scheme 6) and is completed within 3 h at 25 °C. FT-IR spectroscopic monitoring (Figure 1a, bottom) of reaction 1 has shown drastic changes of C═O stretching vibrations [ketene **1** → (a mixture of **1** + **10** + **6**) → cyclobutanone **6**].[43,44]

In reaction 1, we have made careful experiments with low-temperature column chromatography followed by recrystallization at −78 °C. The intermediate **10** could be isolated as a *labile crystalline material* [$t_{1/2}$(0 °C, solid) = ca. 6 h] with the melting point of 38 °C (v in Scheme 6). We have applied various

(41) Farooq, M. O.; Vahidy, T. H.; Husain, S. M. *Bull. Soc. Chim. Fr.* **1958**, 830−832.

(42) For example, the reaction of dimethylketene with *trans*-1-methoxybutadiene (**5**) gives the corresponding cyclobutanone, 2,2-dimethyl-3-(*trans*-2′-methoxyvinyl)cyclobutan-1-one.[29a] Also, reactions between diphenylketene (**1**) with butadienes (butadiene,[11d,41] *trans*-1-acetoxy-butadiene,[34] *cis*-1-cyanobutadiene,[15,34] *trans*-1-methylbutadiene,[9a,15,34] *cis*-1-methylbutadiene,[15,34b] and 2-methylbutadiene,[11d,15,34b] etc.) afford cyclobutanones.

Scheme 6. Low-Temperature Experimental Results for 1,3-Dienes (Reactions 1−4 in Scheme 4): (A) Cyclic 1,3-Dienes and (B) Open-Chain 1,3-Dienes



[a] Conditions for isolation experiments of [4 + 2] (Diels−Alder) intermediates (**10** and **11**). (v) **1** + **2** → **10**: CH_2Cl_2, −20 °C, 3 h, low temperature (−50 °C), column chromatography, 28%. (vi) **1** + **3** → **11**: $CHCl_3$, room temperature, 8 days, column chromatography, 31%. [b]Conditions for the Claisen rearrangements of the [4 + 2] cycloadducts, **10** and **11**: (vii) **10** → **6** (solution state): $CHCl_3$, 0 °C, 5 h, 98%; $CHCl_3$, −10 °C, 12 h, 96%. **10** → **6** (solid state): 0 °C, 2.5 days, 100%. Half-life times: $t_{1/2}$(−10 °C, CD_2Cl_2) = ca. 2 h; $t_{1/2}$ (0 °C, solid) = ca. 6 h. (viii) **11** → **7**: benzene, 80 °C, 2 days, 98%. Half-life time: $t_{1/2}$(80 °C, benzene-d_6) = 4.1 h. [c]Conditions for ^{1}H NMR detection of the retro-Diels−Alder reactions of the [4 + 2] adducts, **10** and **11**. (ix) **10** → **1** + **2**. Maximum dissociation: CD_2Cl_2, −10 °C, 4 h; **1** (8%) + **2** (8%) + **6** (53%) + **10** (14%). (x) **11** → **1** + **3**. Maximum dissociation: benzene-d_6, 80 °C, 10 h; **1** (2%) + **3** (2%) + **7** (78%) + **11** (18%). The adduct **11** remained unchanged in $CDCl_3$ (25 °C, 24 h; 40 °C, 24 h) or in benzene-d_6 at 60 °C for 24 h (no reaction occurred). [d]Conditions for nonoccurrence of retro-Claisen rearrangement. (Cyclobutanones **6** and **7** remained unchanged against the rearrangement.) (xi) **6** → **10**: No reaction occurred, CD_2Cl_2, $CDCl_3$, or benzene-d_6, 25 °C, 15 days. (xii) **7** → **11**: No reaction occurred, $CDCl_3$, 40 °C, 15 days; benzene-d_6, 80 °C, 2 days. [e]Conditions for isolation of [2 + 2] cycloadducts (**8** and **9**): (xiii) **1** + **4** → **8**: $CHCl_3$, 25 °C, 15 days, 28%; no solvent, 25 °C, 25 days, 25%. (xiv) **1** + **5** → **9**: $CHCl_3$, 0 °C, 5 days, 62%. [f]Conditions for retro-Claisen rearrangements of cyclobutanones (**8** and **9**): (xv) **8** → **12**: benzene, 40 °C, 17 days, 96%; $CHCl_3$, 40 °C, 12 days, 97%. Half-life times: $t_{1/2}$(40 °C, benzene-d_6) = ca. 4 days; $t_{1/2}$(25 °C, benzene-d_6) = ca. 20 days; $t_{1/2}$(40 °C, $CDCl_3$) = 1.7 days. (xvi) **9** → **13**: benzene, 25 °C, 24 days, 94%; $CHCl_3$, 25 °C, 16 days, 98%. Half-life times: $t_{1/2}$(25 °C, benzene-d_6) = 3.4 days; $t_{1/2}$(25 °C, $CDCl_3$) = 2.0 days. [g]Conditions for nonoccurrence of Claisen rearrangement as well as of retro-Diels−Alder dissociation in the [4 + 2] cycloadducts, **12** and **13**. (xvii) **12** → **8** and **12** → **1** + **4**: No reaction occurred and the cycloadduct **12** remained unchanged; benzene-d_6, 60 °C, 2 days; $CDCl_3$, 40 °C, 2 days. (xviii) **13** → **9** and **13** → **1** + **5**: No reaction occurred and the cycloadduct **13** remained unchanged; benzene-d_6, 60 °C, 2 days; $CDCl_3$, 40 °C, 2 days.

modern NMR techniques[45,46] to the intermediate **10**.[47] Those spectral data have given us satisfactory information to solve the spin networks of hydrogens of the structures as a [4 + 2]-type cycloadduct[48] (α-methylenedihydropyran). We have used the one-dimensional (1D) ^{1}H NMR enhanced with the sine-bell wind function (Figure 3, lower) and two-dimensional (2D) NMR (^{1}H and ^{13}C) spectra. By ^{13}C NMR measurements, the ^{13}C−^{1}H long-range spin network through J_{C-H} proved the

(43) The IR spectra of a reactant, diphenylketene (**1**), and the cyclobutanones (**6**−**9**) display very strong stretching vibrations of the carbonyl group at 2096 and around 1770 cm^{-1}, respectively. On the other hand, the [4 + 2]-type cycloadducts (**10**−**13**) indicate strong vibrations of C−O stretching at around 1240−1140 [ν_{as} (C−O)] and 1030−1010 [ν_s (C−O)] cm^{-1}. The FT-IR spectroscopy shows that the fragile intermediate **10** is an ether (ν_{C-O} 1138 and 1033 cm^{-1}). The ^{13}C NMR chemical shifts of the products (**6**−**9**) appear at around δ_C = 210 ppm, indicating that they are cyclobutanones. Those of the [4 + 2] adducts **10**−**13** appear downfield around δ_C = 150 and 70−90 ppm, indicating an enol carbon and methine (or methylene) ones, respectively.

(44) At the initial stage of the reaction, i.e., immediately after mixing the reactants (**1** and **2**) at −80 °C, a strong C=O stretching vibration of the ketene appeared at 2096 cm^{-1} (Figure 1a, bottom left). At an intermediate stage (−20 °C, 3 h) of the reaction, the FT IR showed that the carbonyl absorption of ketene **1** was weakened and that new absorptions of the strong C−O stretching vibrations of **10** appeared at 1138 and 1033 cm^{-1} (Figure 1a, bottom center). At the final stage (0 °C, 5 h) of the reaction, the FT IR indicated a new absorption due to the strong C=O stretching vibration of cyclobutanone **6** at 1772 cm^{-1} (Figure 1a, bottom right). At the intermediate stage, the concentration of the Diels−Alder-type [4 + 2] cycloadduct **10** reached the maximum molar concentration of the total of the mixture by ^{1}H NMR monitoring.

(45) To accomplish a full assignment and accurate analysis we have used various modern techniques of the following NMR (^{1}H and ^{13}C) spectroscopies.[46] 1D NMR: Resolution-enhanced spectra with sine-bell wind function. 2D NMR: ^{1}H−^{1}H shift-correlation spectroscopy (COSY), ^{1}H−^{1}H shift-correlation spectroscopy by long-range couplings (COLOC), ^{13}C−^{1}H COSY, ^{13}C−^{1}H COLOC, with an aid of composite proton decoupling (CPD), gated decoupling, ^{13}C−^{1}H selective decoupling (SEL), and ^{13}C−^{1}H long-range selective decoupling (LSPD).

(46) (a) Derome, A. E. In *Modern NMR Techniques for Chemistry Research*; Baldwin, J. E., Ed.; Organic Chemistry Series 6; Pergamon: Oxford, 1987. (b) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy (English Translation)*, 2nd enlarged ed.; VCH: New York, 1993. (c) van de Ven, F. J. M. *Multidimensional NMR in Liquids: Basic Principles and Experimental Methods*; VCH: New York, 1995.

(47) The NMR (^{13}C and ^{1}H) spectral data show that the [4 + 2] cycloadduct **10** is formed by attack of diphenylketene to the terminal 1 and 4 positions of the diene **2**.

(48) In the ^{1}H NMR spectrum of **10**, two upfield resonances at δ 1.64 (dd) and 1.96 (dt) are assigned to aliphatic methylene protons (H-7*exo* and H-7*endo*, respectively) which couple each other with $J_{7,7}$ = 8.5 Hz and further with two methine signals at δ 3.62 (H-4) and δ 5.28 (H-1) with J = 1.5 Hz. The latter methine (H-1) signal shifts to downfield by influence of a linkage with the oxygen atom (O-2) directly attached to the methine carbon, C-1. The two methine signals of H-1 and H-4 are disposed in a W-type arrangement with a small coupling of $J_{1,4}$ = 1.5 Hz. They link further with two olefinic protons at δ 6.37 (H-6) and δ 6.58 (H-5) with vicinal couplings ($J_{1,6}$ = 2.5, $J_{4,5}$ = 3.0 Hz). These results indicate that the cycloadduct **10** is formed by attack at the C-1 position by the oxygen of the ketene **1** as well as at the C-4 position of **10** by the carbonyl carbon of **1**. 2D NMR ^{1}H−^{1}H COSY also demonstrates this proton spin network. Long-range interactions with small magnitudes between H-1 and H-4, H-1 and H-5, and H-4 and H-6 are observed in both the 2D NMR ^{1}H−^{1}H COLOC and homonuclear decoupling experiments. The ^{1}H−^{1}H relationship demonstrates that the structure of **10** has a norbornene moiety.

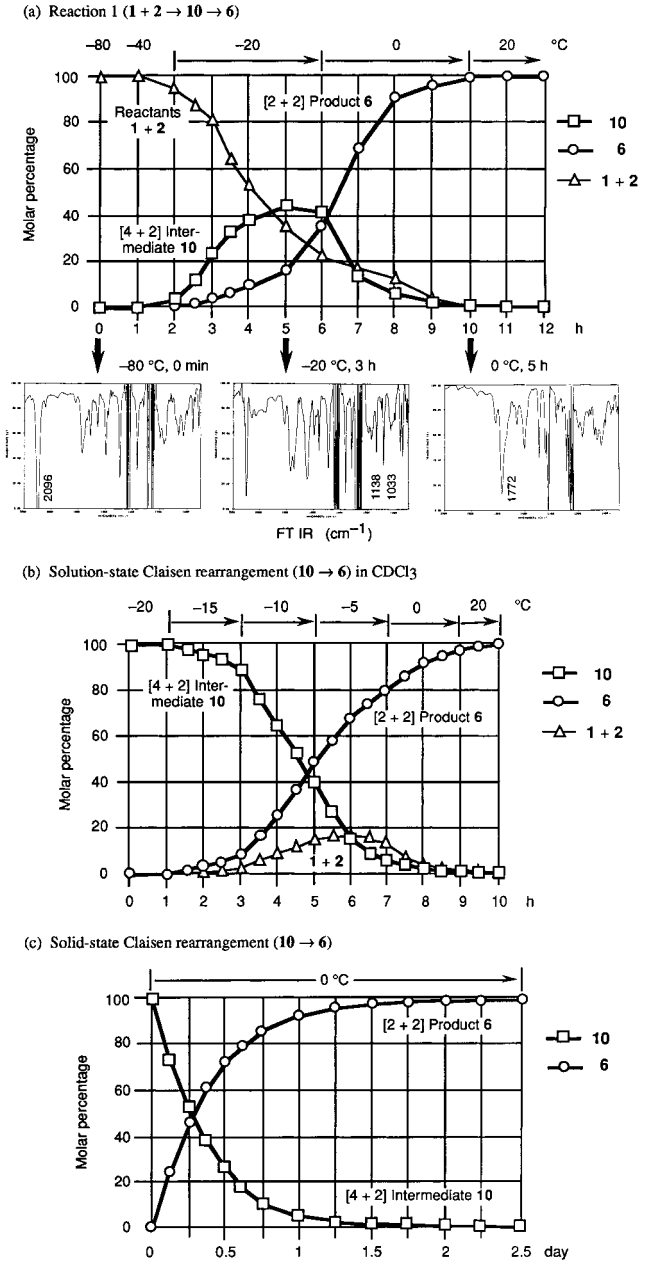


Figure 1. Spectroscopic monitoring of reaction 1. (a) Upper: ^{1}H NMR monitoring result of the reaction between diphenylketene (**1**) and cyclopentadiene (**2**) in CD_2Cl_2 by plots of molar ratio of the reaction components versus reaction times. The reaction was carried out in a sealed NMR tube. The reaction temperatures were regulated in an NMR probe. Lower: Selected FT-IR charts in the monitoring of the reaction [left, the initial stage (−80 °C) of the reaction immediately after mixing both reactants (**1** and **2**); center, a medium stage of the optimum concentration of **10** (−20 °C); right, the final stage (0 °C)]. (b) ^{1}H NMR monitoring result of the solution-state Claisen rearrangement (**10** → **6**) in $CDCl_3$ together with retro-Diels−Alder dissociation (**10** → **1** + **2**). The dissociation occurs above −15 °C. (c) ^{1}H NMR monitoring result of the solid-state Claisen rearrangement at 0 °C in the dark. The monitoring was performed by intermittent dissolution of the sample into $CDCl_3$. The measurements were made at the NMR probe temperature of −40 °C.

linkages between the ketene and diene frames in **10**.[49] (All the data as well as the selected NMR charts for all the products and intermediates are included in the Supporting Information.)

Reaction 2 gives exclusively [2 + 2] product **7** at conventional high-temperature conditions (ii in Scheme 5). Under mild conditions, it takes a long reaction time (8 days at 25 °C) for

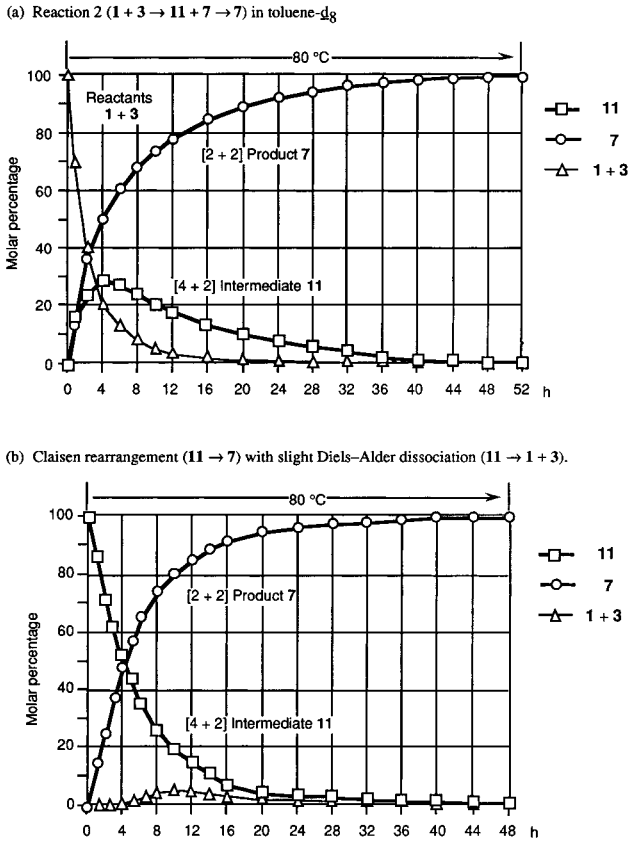


Figure 2. ^{1}H NMR spectroscopic monitoring of reaction 2. (a) Plots of molar ratio of the reaction components versus reaction times of the reaction between diphenylketene (**1**) and cyclohexa-1,3-diene (**3**) in toluene-d_8. The reaction was carried out in an NMR tube in the temperature range. (b) Monitoring result of the Claisen rearrangement (**11** → **7**) together with slight retro-Diels−Alder dissociation (**11** → **1** + **3**). A solution of pure isolated **11** in benzene-d_6 was heated in an NMR tube.

complete consumption of the reactants (**1** + **3**) and gives a mixture of [4 + 2] cycloadduct **11** (38%) and [2 + 2] product **7** (62%) in vi of Scheme 6. Figure 2a illustrates the ^{1}H NMR monitoring result and shows that reaction 2 is not so ready for completion as reaction 1. The low reactivity of the subsequent Claisen shift leads to the easy isolation of intermediate **11**.[50] We have isolated the [4 + 2] intermediate, **11**, as a *stable* crystalline compound. The initial [4 + 2] cycloadduct **11** is stable enough to be isolated and can be handled at room temperature.

3.2. Claisen Rearrangement of [4 + 2]-Type Intermediates, the Second Step. Figure 1b shows that isolated [4 + 2] intermediate **10** is unstable and that the Claisen rearrangement **10** → **6** takes place easily even at 0 °C to give [2 + 2] product

(49) In the ^{13}C NMR of **10**, an upfield signal at δ 53.80 (t) is assigned to the methylene carbon C-7 due to off-resonance experiment. Of the two methine−carbon signals at δ 49.78 (d) and 85.62 (d), the latter downfield-shifted signal is assigned to C-1 which directly links with the oxygen atom (O-1). The ^{13}C NMR confirms the existence of one exocyclic C(3)═C(8) bond, which linked with C-4, O-1, and two phenyl groups, whose chemical shifts appear at δ 150.85 (s, C-3) and 110.30 (s, C-8) (the atom numbering is shown in **10** of Scheme 6A). The C-3 and C-8 are connected with H-4 and *o*-phenyl protons, respectively, with long-range J_{CH} couplings [$^3J_{C(3)H(1)} = {}^3J_{C(3)H(7)} = 6.6$ Hz, $^3J_{C(8)H(4)} < 1.0$ Hz, $^4J_{C(8)H(o-Ph)} = 3.5$ Hz, $^4J_{C(8)H(o'-Ph)} = 3.5$ Hz]. The ^{13}C−^{1}H relationship of homonuclear long-range couplings builds up the carbon framework of compound **10** as an α-diphenylmethylene−dihydropyran structure. Both C-1 and H-1 are key atoms to decipher the ^{1}H and ^{13}C spectra, since the ^{13}C and ^{1}H signals shift to downfield prominently.

(50) Roberts and co-workers recently reported that the reaction gave an equilibrium mixture of **7** and **11**. See ref 39.

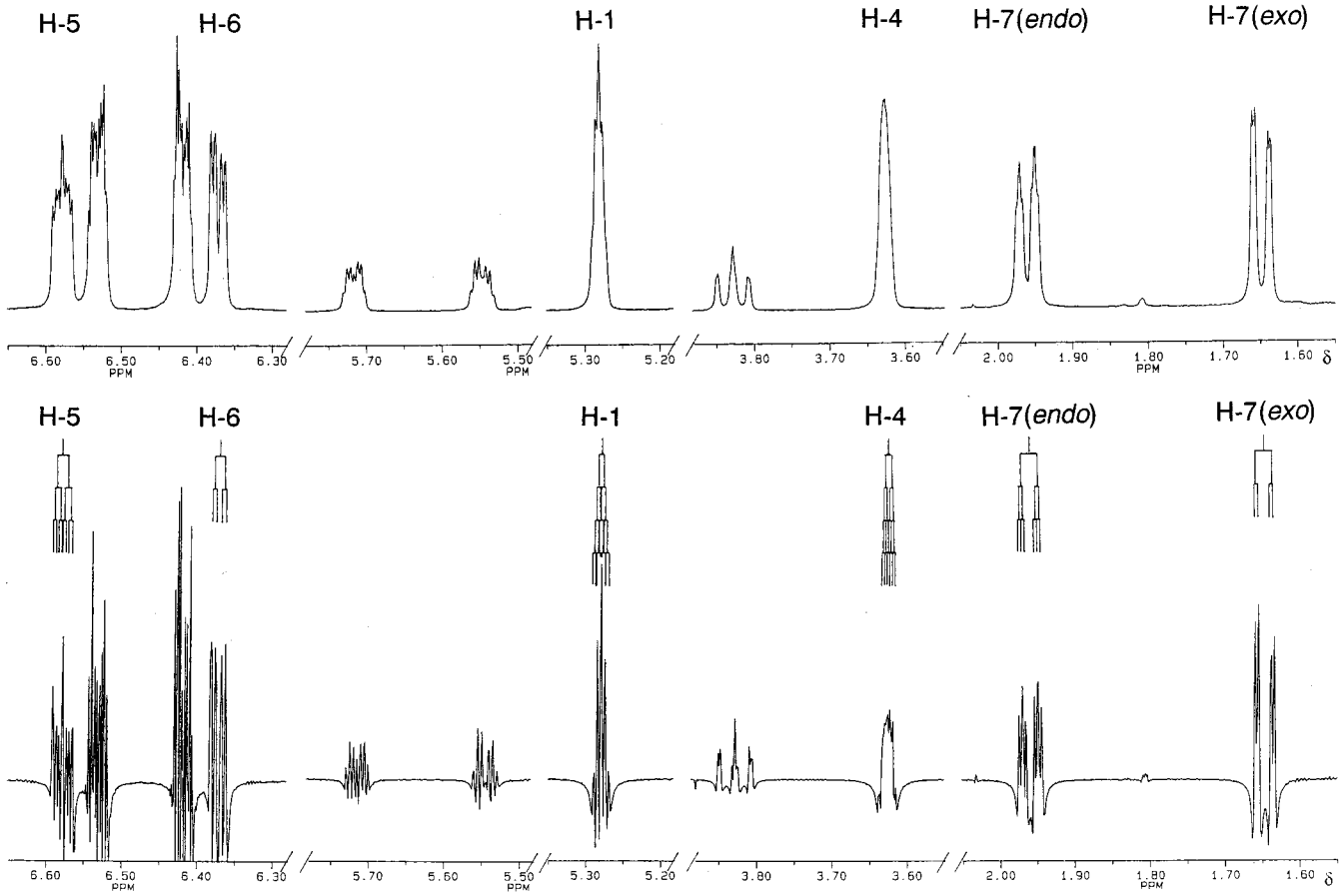


Figure 3. 400-MHz ^{1}H NMR (−20 °C, CD_2Cl_2) spectrum of the [4 + 2]-type transient intermediate **10** in the reaction between diphenylketene (**1**) and cyclopentadiene (**2**). Upper: Ordinary (Lorentz-transformed) spectrum. Lower: The spectrum resolution is enhanced with the sine-bell wind function. A molar concentration of the [4 + 2]-type intermediate **10** reaches 43% of the total reaction mixture (v in Scheme 6). For the selected 1D and 2D ^{1}H and ^{13}C NMR charts of pure isolated **10**, see the Supporting Information.

6 (vii in Scheme 6). Also, the dissociation, **10** → **1** + **2**, is induced by a retro-Diels−Alder reaction (ix in Scheme 6). Figure 1c shows that the Claisen rearrangement **10** → **6** occurs *even in the solid state* at 0 °C (below the melting temperature, 38 °C) without any sign of melting or retrogression[51] to the reactants (**1** + **2**) (vii in Scheme 6). The solid-state reaction of **10** gives the product **6** finally. Thus, the Claisen shift **10** → **6** in reaction 1 has been proved experimentally. In reaction 2, the Claisen shift **11** → **7** is very slow and requires higher temperatures (viii in Scheme 6 and Figure 2b) than those in reaction 1.

3.3. Retro-Diels−Alder Dissociation of [4 + 2]-Type Intermediates. Dissolution of the pure isolated **10** in toluene-d_6 or CD_2Cl_2 at the temperature above 0 °C causes a retrogression (retro-Diels−Alder reaction) to the reactants (**1** + **2**) (ix in Scheme 6 and Figure 1b). However, the smooth Claisen conversion **10** → **6** gives final [2 + 2] product **6** (i in Scheme 5). Figure 2b shows that the intermediate **11** in reaction 2 retrogresses slightly at temperatures higher than those in reaction 1 (x in Scheme 6).

3.4. Nonoccurrence of Retro-Claisen Rearrangement in [2 + 2]-Type Products. Two [2 + 2] products (**6** and **7**) of cyclic 1,3-dienes do not reveal any retro-Claisen rearrangement at room temperature. Although the [2 + 2] products, **6** and **7**, were subject to standing for a long time, the products were recovered unchanged (xi and xii in Scheme 6).

4. Analysis of Elementary Processes and Intermediates of Open-Chain 1,3-Dienes (B). In contrast to cyclic 1,3-dienes proceeding in a single reaction pathway, we have found that the open-chain 1,3-dienes react with diphenylketene in a *dual pathway* through both [2 + 2] (Staudinger) and [4 + 2] (Diels−Alder) reactions. Reactions 3 and 4 give finally and exclusively [4 + 2] cycloadducts (α-methylenedihydropyrans) according to ready retro-Claisen rearrangements (*[2 + 2] intermediates* → [4 + 2] products). Scheme 6B summarizes those experimental results.

4.1. Competition of [4 + 2] (Diels−Alder) and [2 + 2] (Staudinger) Reactions. Figure 4a shows the ^{1}H NMR monitoring result of reaction 3 at 40 °C in $CDCl_3$. The figure demonstrates that the reaction affords *simultaneously* both [2 + 2] **8** and [4 + 2] **12** cycloadducts. It also shows preferential [2 + 2] cycloaddition to [4 + 2] cycloaddition initially. It is shown explicitly that the formation of **8** is superior to that of **12** when the reaction was carried out at 25 °C (for details, see plotting of the reaction monitoring in the Supporting Information). At an initial stage (7 days) of the reaction at 25 °C, we have detected predominant formation of [2 + 2] cycloadduct **8** (33%) along with the minor formation of **12** (18%), while 49% of the reactants (**1** + **4**) remain unreacted. At 40 °C after 5 weeks, the reaction is completed by the consumption of the reactants and gives [4 + 2] cycloadduct **12** as the sole product. When the reactants (**1** + **4**) are mixed with no solvent at room

(51) The ^{1}H NMR monitoring has been carried out by intermittent dissolution of the crystals in $CDCl_3$. The measurements were performed at −60 °C. This conversion proceeds without any sign of melting as a crystal-to-crystal phase reaction. Cf.: Machiguchi, T.; Hasegawa, T.; Ito, S.; Mizuno, H. *J. Am. Chem. Soc.* **1989**, *111*, 1920−1921.

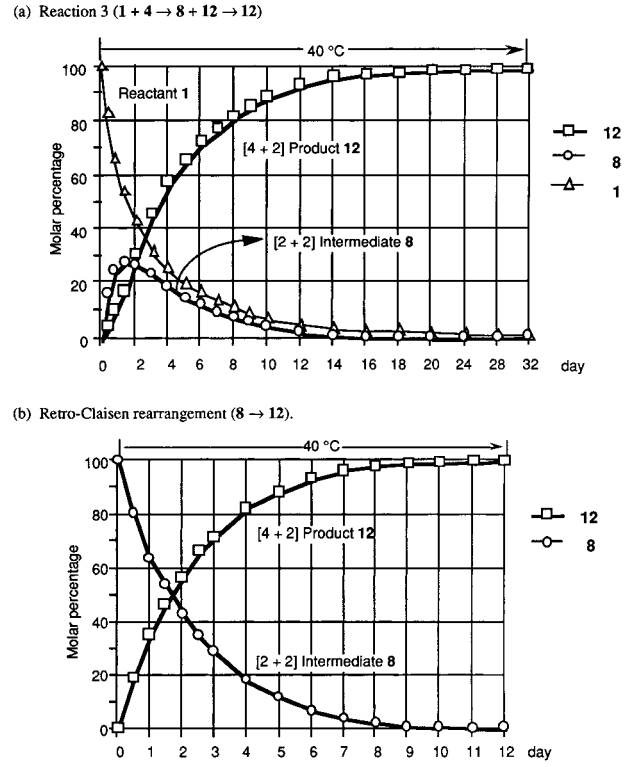


Figure 4. ^{1}H NMR spectroscopic monitoring of reaction 3. (a) Plots of molar ratio of the reaction components versus reaction times. The reaction was carried out in an NMR tube using diphenylketene (**1**) and 2,3-dimethylbutadiene (**4**) in $CDCl_3$ at 40 °C. (b) Monitoring result of the retro-Claisen rearrangement (**8** → **12**). A solution of pure isolated cyclobutanone **8** in $CDCl_3$ was heated at 40 °C in an NMR tube.

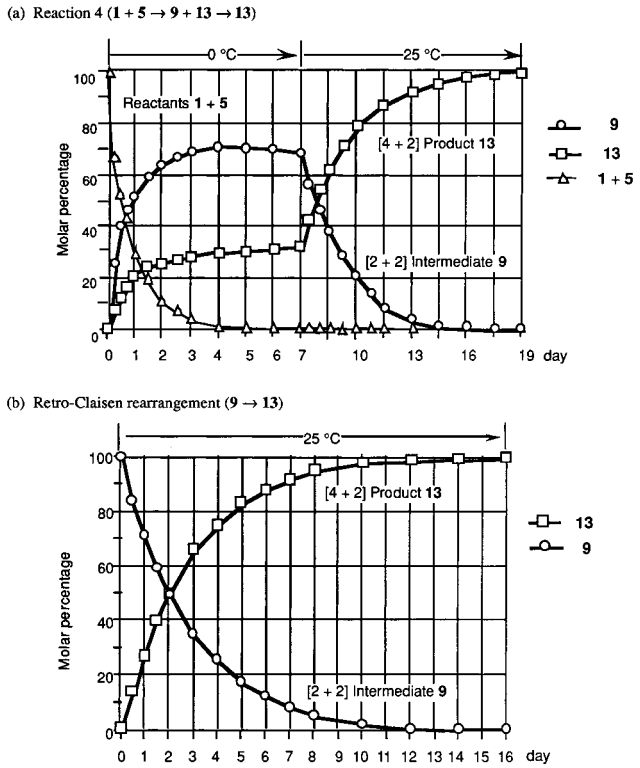


Figure 5. ^{1}H NMR spectroscopic monitoring of reaction 4. (a) Plots of molar ratio of the reaction components versus reaction times by ^{1}H NMR spectroscopic monitoring result of the reaction between diphenylketene (**1**) and *trans*-1-methoxybutadiene (**5**) in $CDCl_3$. The reaction was carried out in an NMR tube. (b) Monitoring result of the retro-Claisen rearrangement (**9** → **13**) of the [2 + 2] intermediate **9** to [4 + 2] product **13**. A solution of pure isolated cyclobutanone **9** in $CDCl_3$ was heated in an NMR tube.

temperature, the reaction proceeds very slowly (14 weeks[15b]) without solvent effect (vide infra).

Figure 5a shows that reaction 4 proceeds smoothly at low temperatures for complete consumption of the reactants (0 °C, 5 days, $CDCl_3$; 25 °C, 2 days, benzene-d_6). The reaction yields simultaneously [2 + 2] cycloadduct **9** and [4 + 2] product **13**, which is similar to reaction 3. Reaction 4 eventually affords [4 + 2] product **13** exclusively, when the reaction is carried out for long times (iv in Scheme 5).

4.2. Isolation of Reaction Intermediates. Reaction 3 gives a mixture of the [4 + 2] and [2 + 2] cycloadducts (**8** + **12**) in the approximate molar ratio of 38:19% (xiii in Scheme 6). Reaction 4 is terminated with the complete consumption of the reactants at intermediate conditions (0 °C, 5 days, $CHCl_3$). The reaction gives [2 + 2] cycloadduct **9** (70%) predominantly with a minor [4 + 2] product **13** (30%) (xiv in Scheme 6). We have isolated both the [2 + 2]-type intermediates, **8** and **9**, from the reaction mixtures (xiii and xiv in Scheme 6) in reactions 3 and 4, respectively, as *stable* compounds which can be handled at room temperature.

4.3. Resistance to Claisen Rearrangement and to Retrogression to the Reactants of [4 + 2]-Type Products. The pure isolated [4 + 2] products, **12** and **13**, were subject to heating. In contrast to the easy Claisen rearrangement in cyclic 1,3-dienes (reactions 1 and 2), we have found that [4 + 2] cycloadducts **12** and **13** resist the Claisen reactions (**12** → **8** and **13** → **9**) even at high-temperature conditions at 60 °C (xvii and xviii in Scheme 6). At this temperature, the [4 + 2] products do not retrogress at all to the reactants, and the products (**12** and **13**) were recovered unchanged. In reaction 4, neither the Claisen shift of the [4 + 2] product (**13** → **9**) nor the retro-Diels−Alder dissociation (**13** → **1** + **5**) takes place even at 60 °C (xviii in Scheme 6). In open-chain diene cases, thus, the [4 + 2] cycloadducts (**12**, **13**) do not show any sign of retrogression to the reactants (**1** and **4**−**5**) at room temperature. [4 + 2] products **12** and **13** are more stable than [2 + 2] cycloadducts **8** and **9**, respectively.

4.4. Ready Retro-Claisen Rearrangement of [2 + 2]-Type Intermediates. The pure isolated intermediates, **8** and **9**, were subject to warming. In contrast to the nonoccurrence of Claisen rearrangement in **12**, we have newly found that the retro-Claisen reaction of [2 + 2] cycloadduct **8** occurs gradually and gives a mixture of **8** + **12** after 15 days (25 °C, benzene-d_6). The Claisen step **12** → **8** does not occur at 25 °C and the reaction reaches an equilibrium mixture of **12** with **8** in the ratio of 71:29 at this temperature. At higher temperature (40 °C), the retro-Claisen rearrangement of **8** gives smoothly (Figure 4b) [4 + 2] product **12**, when the reaction of **8** was maintained at 40 °C for an additional 12 days (xv in Scheme 6). We have observed the similar retro-Claisen shift of [2 + 2] cycloadduct **9** to **13** in reaction 4 (xvi in Scheme 6). The **9** → **13** shift occurs smoothly at 25 °C to afford [4 + 2] product **13**.

5. Summary of the Experiments. The diphenylketene reacts with cyclic (i.e., s-cis) dienes to give [2 + 2] (Staudinger) products, cyclobutanones, exclusively under the traditional conditions at high temperatures and long reaction times. In contrast, we have found in this work that ketene reacts with open-chain (i.e., s-trans) dienes to give [4 + 2] (Diels−Alder) products, α-methylenedihydropyrans (not Staudinger products), under these conditions. ^{1}H NMR monitorings have clarified that ketene−*cyclic diene* reactions proceed in a *unique pathway* (initial Diels−Alder reaction followed by Claisen rearrangement)

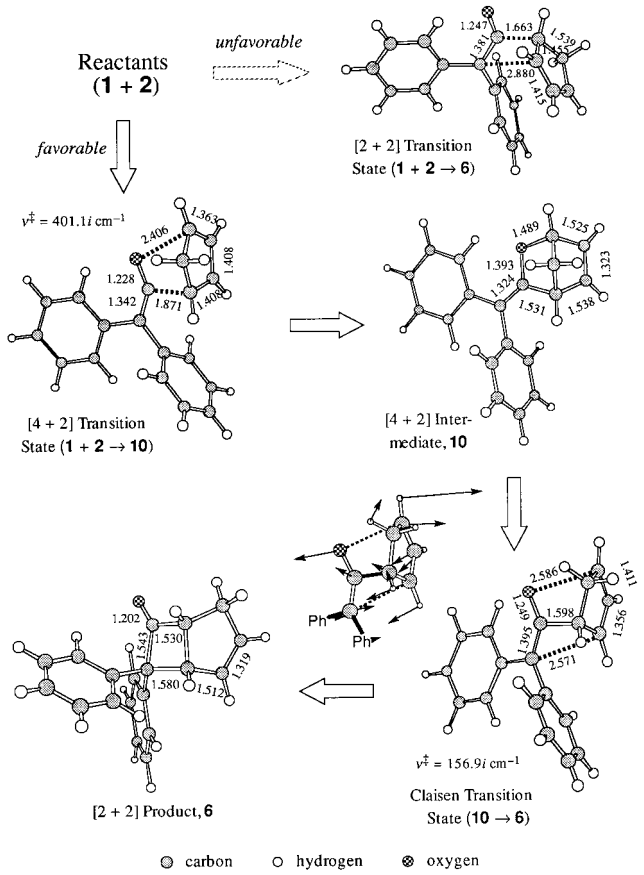


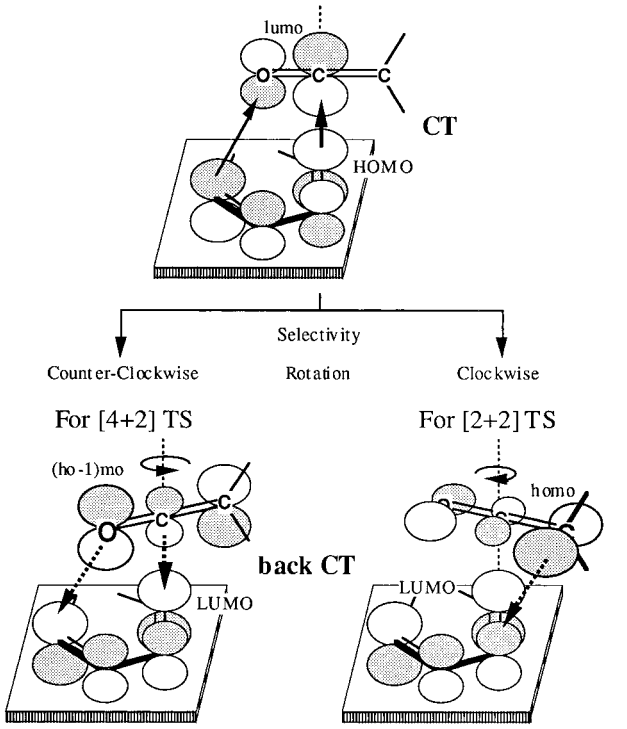
Figure 6. Geometries optimized with RHF/3-21G in the reaction between diphenylketene (**1**) and cyclopentadiene (**2**) (reaction 1). Distances are in Å. For transition states, sole imaginary frequencies in cm^{-1} are shown. Reaction-coordinate vectors of the Claisen (or retro-Claisen) transition state are also sketched.

as Scheme 6A shows. In contrast, we have newly found that ketene−*acyclic diene* reactions proceed in a *dual pathway*. It is a parallel reaction of Diels−Alder and Staudinger reactions. The latter is followed by retro-Claisen rearrangement of the [2 + 2] intermediate as Scheme 6B shows. In short, *ketene recognizes s-cis and s-trans 1,3-dienes distinctly*. Under mild conditions (0−30 °C) for short reaction times, all four reactions form mixtures of both [2 + 2] and [4 + 2] cycloadducts. Both the intermediates and products can often be isolated as stable compounds and can be handled at room temperature (except the labile intermediate **10** in reaction 1). At a glimpse, such formation of a mixture seems to be the common type of reaction. But, long reaction times transform such a mixture into the final product. They allow the exclusive formation of [2 + 2] products for cyclic 1,3-dienes by the Claisen rearrangement and the formation of [4 + 2] products for open-chain dienes by retro-Claisen rearrangement. The present experimental results may rationalize the conventional results (Scheme 2) and exceptions (Scheme 3) of ketene−diene reactions. Mixtures of [4 + 2] and [2 + 2] products reported so far most likely come from insufficient reaction times.

III. Computational Results

1. Structures. Four reactions are examined theoretically. Figure 6 exhibits geometries of five stationary points of reaction 1. The [4 + 2] transition state (TS) demonstrates that the carbonyl group of **1** works effectively as a dienophile. The bending and orientation of the ketene cumulene bond enhances the charge transfer (CT) interaction. The steric crowd between

Scheme 7. Orientations of Two Cycloadditions[a]



[a] Upward arrows indicate dominant charge-transfer (CT) interactions and broken downward arrows do minor (back CT) interactions.

one phenyl group and the cyclopentadiene ring is avoided by the parallel orientation. The other (remote) phenyl group is *conjugated* to the ketene fragment. The distance between the carbonyl oxygen and one diene carbon is large, 2.406 Å.

After the Diels−Alder TS, the transient intermediate, **10**, is attained. There is a ring strain in the bicyclo species (for structural details, see the Supporting Information). At two bridgehead carbon atoms, sp^3 bond angles are ca. 100°, which is smaller than 109.5°. The long C(1)−O(2) bond of **10** (1.489 Å) indicates their ready cleavage for [3,3] sigmatropic rearrangements. To escape from the ring strain of **10**, a [3,3] sigmatropic rearrangement takes place. In Figure 6, the TS geometry is shown. One may suspect that this TS is for [2 + 2] cycloaddition. However, the reaction-coordinate vector corresponding to $\nu^{\ddagger} = 156.9i\ cm^{-1}$ indicates clearly the motion of the Claisen shift.

The distance of the uncleaved C−C bond, 1.598 Å, in the Claisen TS (**10** → **6**) is slightly larger than the standard covalent-bond one, 1.52 Å. Phenyl groups do not give steric crowding during the rearrangement. After the Claisen TS, the cyclobutanone product, **6**, is obtained. There is a concerted [2 + 2] addition path shown in Figure 6. The path is also free from steric crowding due to phenyl groups. The crowd can be avoided because of the [2 + 2] TS one-center-like geometry.[52,53] The selectivity of [4 + 2] and [2 + 2] cycloadditions comes from orientations of ketene and diene planes (Scheme 7).

Figure 7 shows the process of reaction 2. The geometry of the [4 + 2] addition TS is similar to that in reaction 1. The C···C distance, 1.801 Å, of reaction 2 is slightly smaller than that, 1.871 Å, of reaction 1. On the contrary, the C···O distance of reaction 2 is larger. These distance differences demonstrate that the [4 + 2] TS of reaction 2 is more asynchronous due to the more distant terminal 1,4 carbon atoms in cyclohexadiene

(52) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1754−1756.
(53) Salzner, U.; Bachrach, S. M. *J. Org. Chem.* **1996**, *61*, 237−242.

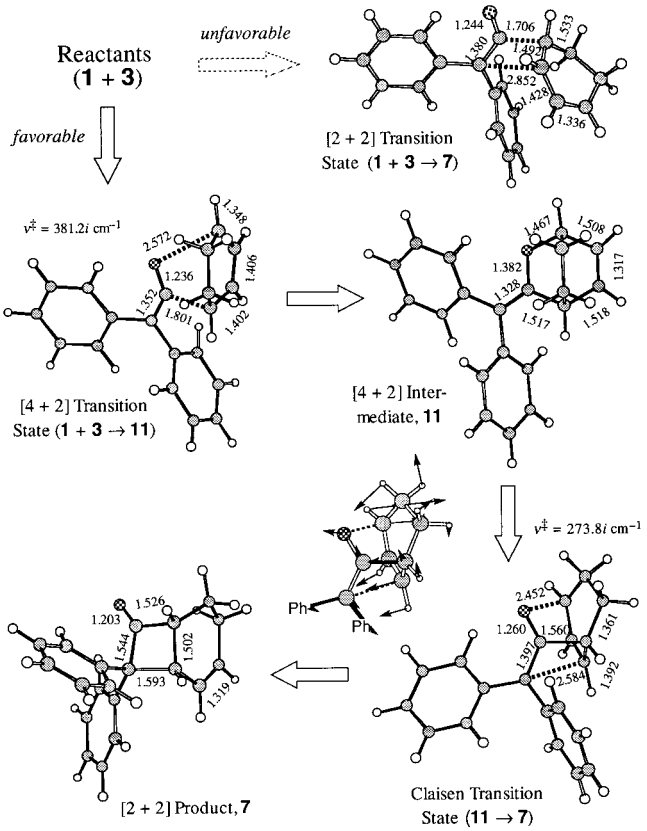


Figure 7. Geometries in the reaction between diphenylketene (**1**) and cyclohexadiene (**3**) (reaction 2).

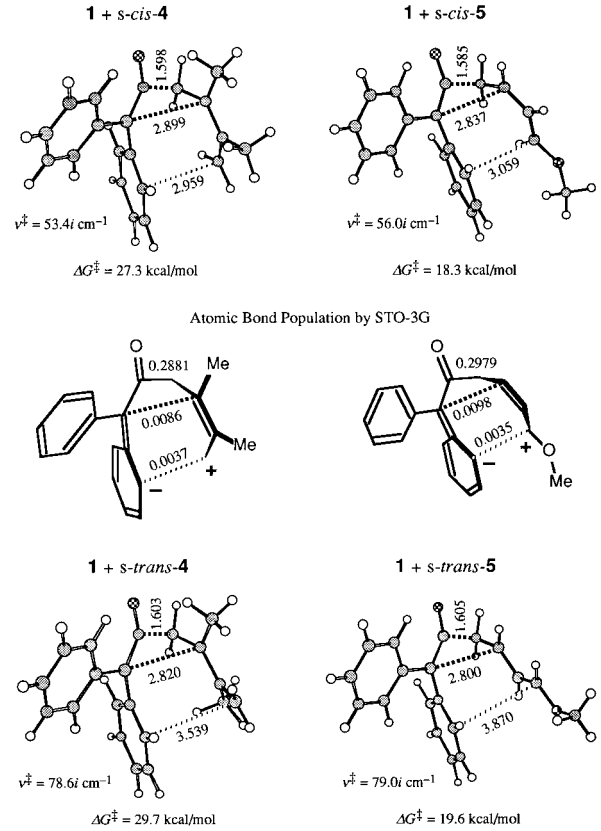
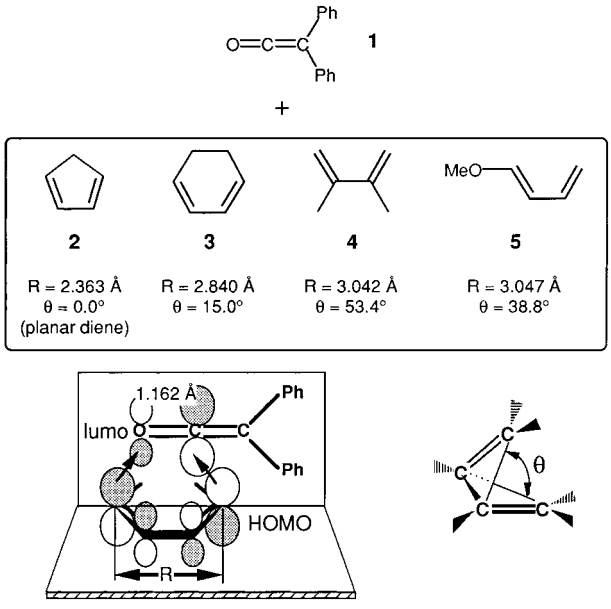


Figure 8. TS structures and changes of Gibbs free energies ($T = 298.15$ K) of [2 + 2] cycloadditions of diphenylketene (**1**) to s-cis- and s-trans open-chain dienes (**4** and **5**) (reactions 3 and 4). Atomic bond populations were calculated with RHF/STO-3G.

Scheme 8. Distances (R's) between 1- and 4-Carbon Atoms and Dihedral Angles (θ's) as Indices for [4 + 2] Cycloadditions



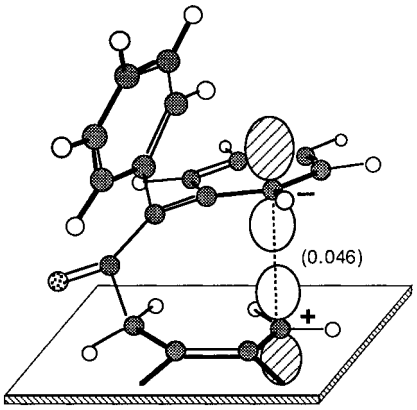
(**3**) (Scheme 8). In contrast to the difficulty in [4 + 2] cycloaddition, its resultant cycloadduct, **11**, does not suffer the ring strain as much as **10**. The bicyclo compound **11** suffers only eclipsed conformation in the ethylene group. In Figure 7, intermediate **11** is isomerized to the [2 + 2] cycloadduct, **7**, via the Claisen TS. This TS is somewhat earlier than that in reaction 1 due to the flexibility of the hexadiene ring.

Cyclic dienes (A) are restricted to cis geometrical isomers. But, open-chain dienes (B) prefer naturally trans forms, which are not fit to Diels−Alder reactions. The cis−trans energy differences in **4** and **5** are examined. Trans isomers of **4** and **5** are only more stable by 1.5 and 2.2 kcal/mol (MP2/6-31G*//RHF/3-21G) than cis ones, respectively. Rotational energy barrier heights are also small, $\Delta G^{\ddagger}$(trans → TS) = 2.9 (**4**) and 6.0 kcal/mol (**5**). Thus, dienes **4** and **5** undergo almost free rotations, and their cis and trans isomers are practically indistinguishable. Figure 8 exhibits TS structures of [2 + 2] cycloadditions. Surprisingly, those of cis dienes are more stable (with larger total energies) than those of trans dienes. A secondary interaction enhances the cis [2 + 2] addition (Scheme 9). Diphenylketene prefers cis dienes over trans dienes. Hereafter, only cis dienes are considered.

Figure 9 shows the process of reaction 3. In the [4 + 2] TS, clearly, the size of the ketene carbonyl group does not match that between two terminal methylene groups of **4** (Scheme 8). That is, the line of the incipient C···O bond deviates significantly from the direction of lumo ($\pi^*_{C=O}$). A large activation energy of the [4 + 2] TS of reaction 3 is predicted. But, the [4 + 2] adduct, **12**, has little ring strain and steric crowding (the ether bond ∠C−O−C = 115.2°). Figure 9 shows the other process of reaction 3, (**1** + **4**) → **8** → **12**. A steric repulsion between a phenyl group and a methyl group is noticed in **8**. Owing to this steric crowding, one C−C distance is 1.613 Å in the cyclobutanone ring. [2 + 2] adduct **8** is thought to be less stable than [4 + 2] adduct **12**. A retro-Claisen TS (**8** → **12**) has been found. The reaction-coordinate vector demonstrates the isomerization path. The steric congestion is somewhat relaxed by the shift, **8** → **12**.

Figure 10 exhibits the process of reaction 4. Diene **5** is nucleophilic at the C-4 methylene group. In accordance with

Scheme 9. An "Ortho Secondary Orbital Interaction" To Make the *cis*-Diene More Reactive than the *trans*-Diene for [2 + 2] Cycloadditions[a]



[a] The attractive interaction along the broken line is verified by the RHF/3-21G bonding population, 0.046.

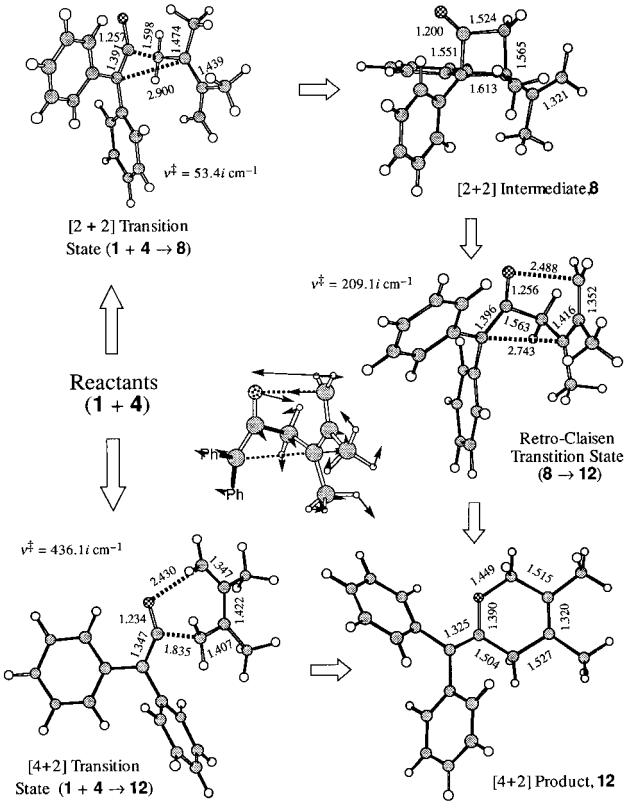


Figure 9. Geometries in the reaction between diphenylketene (**1**) and 2,3-dimethylbutadiene (**4**) (reaction 3).

this high reactivity of **5**, the [4 + 2] addition TS (**1** + **5** → **13**) is very early in the figure. A small activation energy of the Diels−Alder reaction is predicted. The [4 + 2] adduct, **13**, is of the small ring strain. Figure 10 shows the other process of reaction 4, (**1** + **5**) → **9** → **13**. The retro-Claisen TS is verified by reaction-coordinate vectors.

2. Energy Diagrams. Figure 11 shows Gibbs free-free energy diagrams including the self-consistent-reaction-field (SCRF) solvent effect of reactions 1 and 2. First, energetics of reaction 1 are examined. The Diels−Alder activation free energy, $\Delta G^{\ddagger}$ = 19.7 kcal/mol (T = 300 K), is found to be small. The ketene carbonyl group is an excellent dienophile. For instance, the ethylene−cyclopentadiene Diels−Alder reaction has $\Delta G^{\ddagger}$ = 24.7 kcal/mol. The [4 + 2]-cycloadduct (**10**) intermediate has

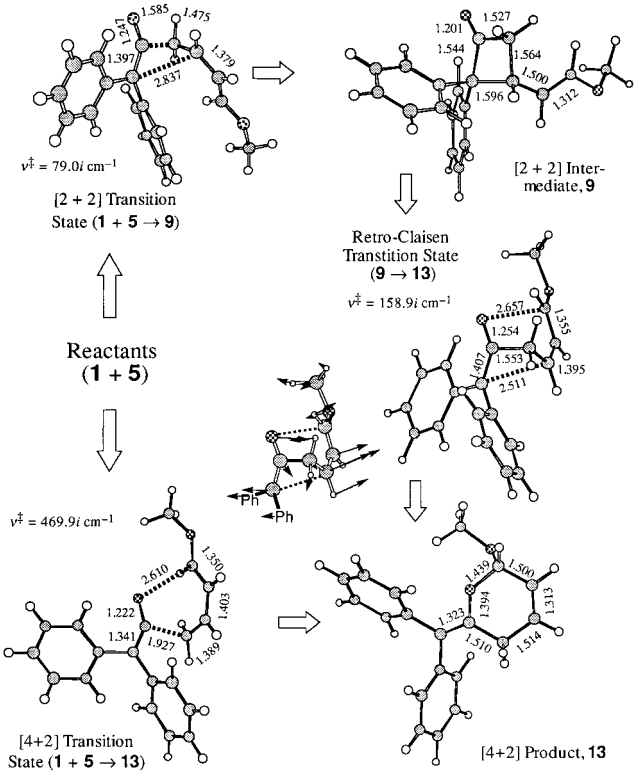


Figure 10. Geometries in the reaction between diphenylketene (**1**) and *trans*-1-methoxybutadiene (**5**) (reaction 4).

stability similar to that of reactants (**1** + **2**). If it were not for the Claisen shift, an equilibrium of similar molar concentrations between reactants and **10** would be attained. The second activation barrier ($\Delta G^{\ddagger}$ = 19.1 kcal/mol) is also small and similar to the first one. The Claisen shift should take place readily. The [2 + 2] product, **6**, is the most stable. It is clear that [4 + 2] intermediate **10** is eventually converted to **6**. The low-temperature experiment has been needed for us to trap the intermediate, **10** (see ΔG° = −0.6 kcal/mol at T = 300 K and ΔG° = −5.4 kcal/mol at T = 200 K). Owing to those small activation energies, it is understandable that reaction 1 has been thought to be of the concerted [2 + 2] process historically. Second, energetics of reaction 2 are examined in Figure 11. The value of $\Delta G^{\ddagger}$ of the [4 + 2] addition is larger than that of reaction 1. The reaction-center two-carbon atoms of cyclohexadiene (**3**) are more distant with each other and are less suitable for the Diels−Alder reaction than those of cyclopentadiene (**2**) (see Scheme 8). On the other hand, the [4 + 2] adduct (**11**) is more stable than the reactants (**1** + **3**). Adduct **11** has the small ring strain. The Claisen TS has a lower energy level than the Diels−Alder TS, and the [2 + 2] product (**7**) is most stable. Viewing the energy diagram of reaction 2, one may confirm that reaction 2 is slower than reaction 1 and that the [4 + 2] adduct intermediate **11** is trapped more easily than that (**10**) of reaction 1. Of course, the concerted [2 + 2] path (**1** + **3** → **7**, the broken curve) is ruled out energetically.

Figure 12 exhibits energy diagrams of reactions 3 and 4. The [4 + 2] TS of reaction 3 has the largest activation free energy, $\Delta G^{\ddagger}$ = 30.3 kcal/mol (T = 300 K). A very slow reaction is expected. Noteworthy is that [4 + 2] cycloadduct **12** is more stable than [2 + 2] adduct, **8**. *The exceptional examples* displayed in Scheme 3 and the present results in Scheme 6 are rationalized.

The mixture of **12** and **8** is the temporary product in reaction 3. Kinetically **8** is generated, and thermodynamically **12** is

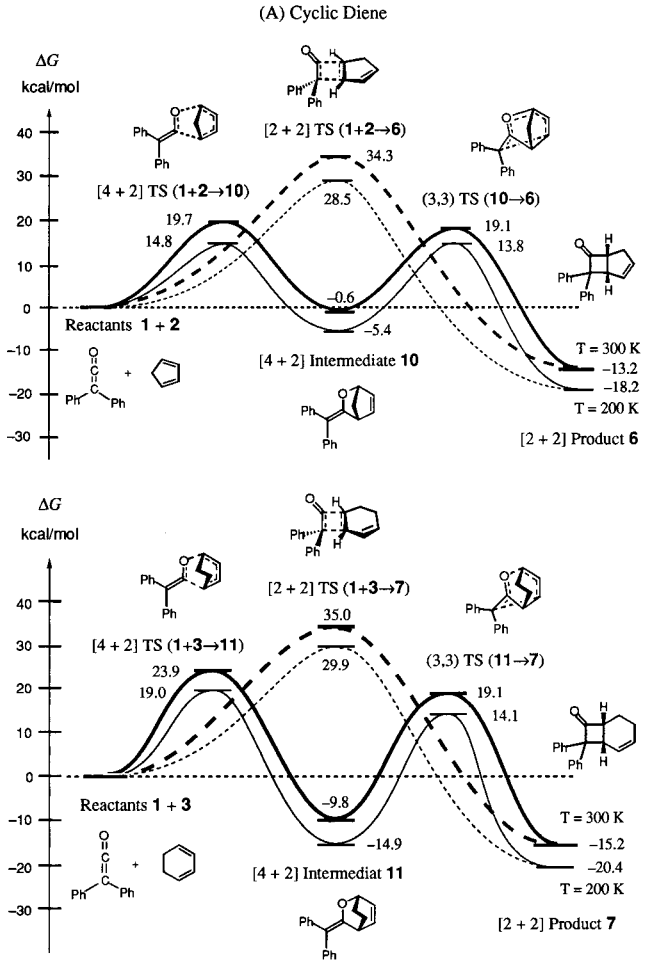


Figure 11. Gibbs free-energy diagrams of reactions 1 (upper) and 2 (lower) in kcal/mol. Electronic energies are obtained by MP2/6-31G* (frozen core) single-point calculations on the RHF/3-21G geometries in Figures 6 and 7 (MP2/6-31G*//RHF/3-21G). Thermal correction and entropies are evaluated via RHF/3-21G vibrational analyses ($T = 200$ and 300 K). The solvent effect is included as a RHF/3-21G SCRF correction to the MP2/6-31G* electronic energy. The dielectric constant ϵ is taken to be 6.0 for chloroform ($CHCl_3$).

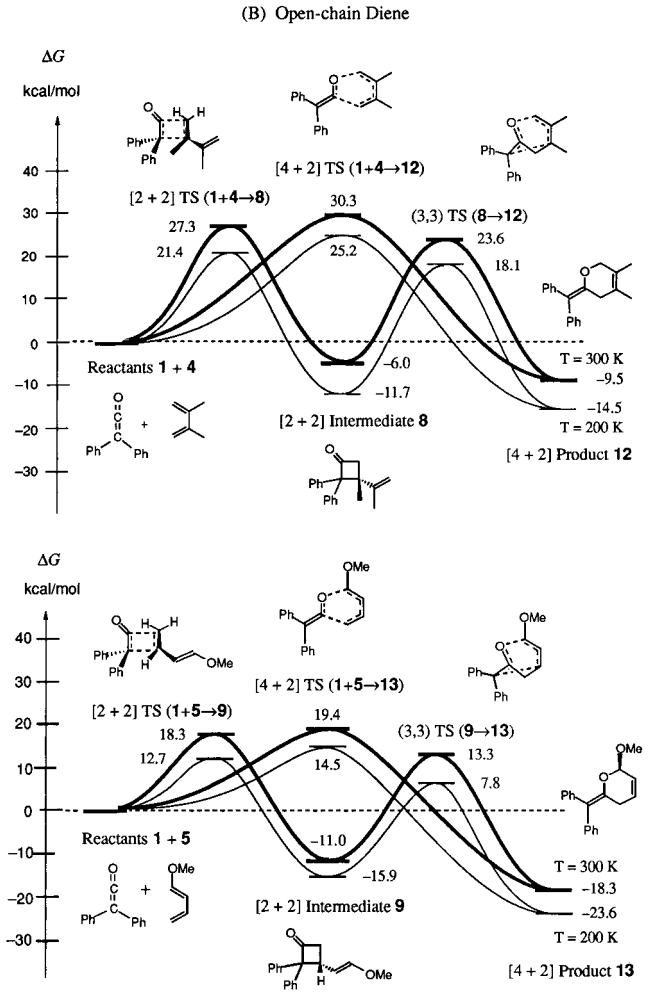


Figure 12. Gibbs free-energy diagrams of reactions 3 (upper) and 4 (lower).

produced. Reaction 4 will occur readily because of the small values of $\Delta G^{\ddagger} = 19.4$ kcal/mol ($T = 300$ K) for [4 + 2] and 18.3 kcal/mol for [2 + 2] in Figure 12. The [4 + 2] adduct (**13**) is much more stable than the [2 + 2] adduct (**9**), and **13** should not be exceptional but be dominant. Primarily, two adducts **9** and **13** are afforded. Eventually, **13** is obtained where **9** is isomerized to **13** by the retro-Claisen rearrangement.

Energetic results in Figures 11 and 12 are summarized. [4 + 2] cycloaddition and the subsequent Claisen shift are likely processes for cyclic dienes (A). The [2 + 2] products (**6** and **7**) are not generated via the concerted [2 + 2] cycloaddition. Contrary to the superiority or inferiority of [4 + 2] and [2 + 2] cycloadditions of cyclic dienes (A), the latter reaction is favored slightly for open-chain dienes (B). The [4 + 2] adducts **12** and **13** are final products. [2 + 2] adducts **8** and **9** are intermediates which are subject to facile retro-Claisen shifts.

IV. Concluding Remarks

In this work, four ketene−diene reactions have been investigated experimentally and theoretically. Precise and low-temperature experiments have been made to compare their results with computational data. Consistency between two independent approaches has been proved. The present experimental and theoretical verification of the new mechanism gives us a unified point of view as to the ketene−diene reaction. While the ketene carbonyl group (>C=*C*=*O*) has been regarded as an *inviolable substituent*, this work has demonstrated that the group is the reaction center and an excellent dienophile. Therefore, the primary cycloadditions between ketenes and dienes should be Diels−Alder reactions. However, when diene terminal carbon atoms are distant and two vinyl bonds are nonplaner, [2 + 2] cycloadditions are favored specifically. Cyclic dienes (A) have unique reaction channels, [4 + 2] cycloaddition → [3,3] Claisen rearrangement to [2 + 2] cycloadducts. Open-chain dienes (B) are reactive in their s-cis forms for [2 + 2] cycloadditions as well as for [4 + 2] cycloadditions. They have dual channels, direct [4 + 2] reaction, and [2 + 2] cycloaddition and subsequent retro-Claisen shift. Scheme 10 summarizes the present result, which seems to be an innovation in ketene history.

V. Experimental Section

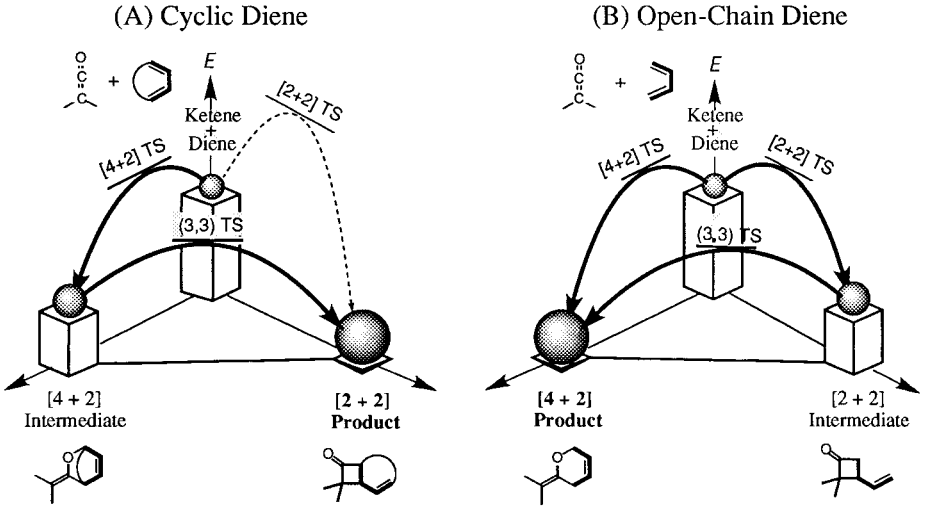
1. General. The starting materials, diphenylketene[54] (**1**), cyclopentadiene[55] (**2**), and cyclohexa-1,3-diene (**3**),[56] were prepared according to methods reported in the literature. Freshly distilled **1**−**3**, 2,3-

(54) Smith, L. I.; Hoehn, H. H. *Organic Synthesis*; Wiley: New York, 1955; Collect. Vol. 3, pp 356−358.

(55) Moffett, R. B. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. 4, pp 238−241.

(56) Schaefer, J. P.; Endres, L. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, pp 285−288.

Scheme 10. Summary of Ketene−Diene Reactions by Pictorial Energy Levels[a]



[a] Larger balls denote more stable species.

dimethylbutadiene (**4**) (Aldrich), and *trans*-1-methoxybutadiene (**5**) (Aldrich) were used for the reactions. The solvents used for the reactions were freshly distilled under nitrogen from appropriate drying agents, and all acids were removed carefully.[57] Methylene-d_2 chloride and chloroform-d_3 (Aldrich) were filtered through activity grade 1 basic alumina prior to use. For isolation of the intermediates and products, **6**−**13**, silica gel (0.063−0.200 mm) (Merck Kieselgel 60) was packed and eluted with pentane−ether (9:1). Preparative layer chromatography (PLC) was employed with Merck Kieselgel 60 (70−230 mesh). Thin layer chromatographic (TLC) analyses were performed on silica gel (Merck Kieselgel 60 GF_{254}) with a 0.2-mm-layer thickness. R_f values were measured on silica gel in pentane−ether (9:1) unless otherwise noted.

Melting points were determined on a Büchi 511 apparatus in open capillary tubes and are uncorrected. Ordinary IR spectra were recorded on a Hitachi 260-50 spectrometer using CH_2Cl_2 solution unless otherwise noted. Low-temperature FT-IR spectral monitoring was performed on a JEOL JIR-100 FT-IR instrument. Electron impact (EI) mass spectra (MS) were obtained with a JEOL DM-303 high-resolution (HR) spectrometer at 70 eV using direct inlet. The values of *m*/*z* of significant ions are reported with relative intensities in parentheses (percent for the base peak) for low-resolution analyses. NMR (^{13}C and ^1H) spectra were recorded on a Bruker AM-400 instrument (100.6 and 400 MHz for ^{13}C and ^1H nuclei, respectively) in $CDCl_3$, unless otherwise specified, with Me_4Si as the internal standard. The assignments of NMR spectra are based on $^1H\{^1H\}$ homonuclear decoupling and $^{13}C\{^1H\}$ heteronuclear 1D and 2D NMR ($^1H-^1H$ COSY, $^1H-^1H$ COLOC, $^{13}C-^1H$ COSY, and $^{13}C-^1H$ COLOC) experiments. (The experimental details for each type of 2D NMR spectroscopy are described on page 5 of the Supporting Information.)

2. Manipulations. All reactions and their NMR monitorings were performed using either an inert atmosphere or a high-vacuum line ($<10^{-4}$ Torr) technique and were degassed by three successive freeze−pump−thaw cycles to 10^{-4} mmHg. NMR tubes for sealed tube experiments were flame-dried under vacuum immediately prior to the experiments. Low-temperature chromatographies were carried out in a cooling glovebox (Suns Engineering L-131) under a cold nitrogen stream. All the reactions with solvents $CHCl_3$, $CDCl_3$, CH_2Cl_2, and CD_2Cl_2 were carried out in the dark to prevent generation of hydrochloric acid under exposure to light.

3. General Procedure for the Reactions of Diphenylketene (1) with 1,3-Dienes (2−5). (i) Under Preparative Conditions: In a typical case, into a solution of **1** (1.16 g, 6.0 mmol) in 5 mL of an organic solvent (benzene, $CHCl_3$, CH_2Cl_2, or toluene) was added dropwise at 0 °C a solution of a diene (6.6 mmol) in the same solvent (5 mL). The reaction mixture was stirred until the reaction was completed by TLC check. Solvent removal gave a residue which was purified (for the products, **6**−**7** and **12**−**13**) or separated into each component (for isolation of the intermediates, **10**−**11** and **8**−**9**) by chromatography. Analytical samples were obtained by recrystallization from cold pentane−ether (9:1) unless otherwise noted. The IR and ^1H NMR of the obtained samples of the known compounds **6**, **7**, **8**, and **11** were identical with those of authentic samples.[58,59]

(ii) ^1H NMR Monitoring of the Reactions. 1 (0.60 mmol), diene (**2**−**5**) (0.60 mmol), and 0.40 mL of a solvent (benzene-d_6, CD_2Cl_2, $CDCl_3$ or toluene-d_8) were vacuum transferred into an NMR tube. The temperatures of the mixture were regulated in an NMR probe within the range of ±1 °C. The monitoring of the reactions was carried out periodically at various temperatures. For long-time reactions, the samples stood at a desired temperature in a thermostated bath in the dark during intervals of the measurements. These analytical results are displayed in the Supporting Information.

3.1. Reaction 1. (i) Under Room-Temperature Conditions To Give [2 + 2] Product 6. The general procedure was followed, using **1** (1.16 g) and **2** (436 mg) in CH_2Cl_2 or toluene at room temperature for 3 h to give 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (**6**) (1.53 g, 98%).[60]

(ii) Under Low-Temperature Conditions To Isolate [4 + 2] Intermediate 10. The general procedure was followed, using **1** (2.33 g) and **2** (0.88 g) in CH_2Cl_2 at −20 °C for 3 h. Volatile material was removed under reduced pressure (oil-pump vacuum) at −40 °C to leave colorless glassy solid including a mixture of **10** (ca. 43%) and **6** (ca. 11%). Low-temperature medium-pressure column chromatography (−60 °C) followed by PLC (−50 °C) separation gave each component which was collected to give 2-oxa-3,3-diphenylmethylidenebicyclo-[2.2.1]hept-5-ene (**10**)[61] (880 mg, 28%) and **6** (252 mg, 8%).

(57) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: Oxford, U.K., 1988.

(58) The authentic samples were obtained by the literature methods for **6**,[11d] **7**, and **11**.[39]

(59) During the reexamination to obtain an authentic sample of the cyclobutanone **8** in Scheme 4, **8** was not obtained according to the Farooq's experimental method[9b,41] (heating conditions at 100 °C, overnight, no solvent). Instead of the isolation of **8**, the reaction (100 °C, 4 h) brought us the predominant formation of an unknown α-methylenedihydropyran **12** (82%), which has been reported in the present paper. The reaction was completed to consume the ketene within 3 h under the conditions. In a short reaction time (10 min, 100 °C), the reaction led to the isolation of the cyclobutanone **8** [mp 79−80 °C (not 118−119 °C[9b,15b,41])] in low yield (21%) accompanied by the dihydropyran **12** (12%) and most of the unreacted ketene **1**. When reaction 3 was carried out under mild conditions [room temperature, 3 months, no solvent (see the Supporting Information); 40 °C, 40 days, no solvent (iii in Scheme 5)], the product obtained exclusively has been identified to be α-methylenedihydropyran **12**. Cyclobutanone **8** was isolated as the intermediate of the reaction (xiii in Scheme 6).

(60) Cyclobutanone **6**: colorless prisms (MeOH), mp 89−90 °C; R_f = 0.34; IR ν_{max} 1772 (vs) cm^{-1}; detailed NMR (^1H and ^{13}C) and MS data are in the Supporting Information.

10: colorless needles, mp 37−38 °C; R_f = 0.43 (−50 °C); FT-IR ν_{max} (−60 °C) 1138 (s), 1033 (s) cm^{-1}; ^{1}H NMR (CD_2Cl_2, −60 °C) δ 1.64 (dd, J = 8.5, 1.5 Hz, H-7*exo*), 1.96 (dt, J = 8.5, 1.5 Hz, H-7*endo*), 3.62 (dq, J = 3.0, 1.5 Hz, H-4), 5.28 (ddt, J = 2.5, 1.7, 1.5 Hz, H-1), 6.37 (dd, J = 5.3, 2.5 Hz, H-6), 6.58 (ddd, J = 5.3, 3.0, 1.7 Hz, H-5); ^{13}C NMR (CD_2Cl_2, −60 °C) δ 49.78 (d, C-4), 53.80 (t, C-7), 85.62 (d, C-1), 111.30 (s, C-8), 150.85 (s, C-3); EI-MS *m*/*z* 260 (M^+, 22), 194 ($M^+ - C_5H_6$, 100), 165 (92), 66 (26). HR-MS calcd mass for $C_{19}H_{16}O$ 260.1202, found 260.1198. Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.58; H, 6.34.

(iii) Low-Temperature Monitorings of Reaction 1. (a) NMR (^{1}H and ^{13}C) Spectroscopy. The general procedure was followed, using **1** and **2** in CD_2Cl_2 and toluene-d_8, separately. After 3 h at −20 °C, the reaction mixture was confirmed to consist of the highest concentration of [4 + 2] intermediate **10**. The ^{13}C NMR measurements were performed at a probe temperature of −60 °C.[62] The monitoring results exhibited similar changes in the following molar-% ratios (**10**:**6**). Run 1 (CD_2Cl_2): See Figure 1a. Run 2 (toluene-d_8): 4:1 (−20 °C, 0 h), 30:9 (−20 °C, 4 h), 42:18 (−20 °C, 8 h), and 90:3 (0 °C, 2 h). **(b) FT-IR Spectroscopy.** The above procedure was followed, using **1**[63a] (58 mg) and **2**[63b] (20 mg) in CH_2Cl_2 (0.4 mL). The measurements were performed at −60 °C by intermittent dissolution of a small amount of the reaction mixture in cold CH_2Cl_2 (selected charts are displayed in Figure 1a).

3.2. Reaction 2. (i) Under Heating Conditions To Give [2 + 2] Product 7. The general procedure was followed, using **1** (2.19 g) and **3** (1.00 g) in refluxing benzene (10 mL) at 80 °C for 2 days to give 8,8-diphenylbicyclo[4.2.0]oct-2-en-7-one (**7**) (2.98 g, 96%).[64]

(ii) Under Room-Temperature Conditions To Isolate [4 + 2] Intermediate 11. The general procedure was followed, using **1** (2.43 g) and **3** (1.10 g) in CH_2Cl_2 at room temperature for 8 days to give a mixture of 2-oxa-3,3-diphenylmethylidenebicyclo[2.2.2]oct-5-ene (**11**) and **7** in the ratio of 38:62. Column chromatography [benzene−hexane (9:1)] followed by PLC separation gave each component, **11**(1.06 g, 31%) and **7** (1.99 g, 58%).[65]

(iii) ^{1}H NMR Monitoring of Reaction 2. The general procedure was followed, using **1** (116 mg) and **3** (48 mg) in benzene-d_6 and $CDCl_3$, separately. The results exhibited changes in the following molar-% ratios (**11**:**7**). Run 1 (toluene-d_8, 80 °C, 52 h): see Figure 2a. Run 2 (benzene-d_6, 25 °C, 8 days): 14:32 (1 h), 23:48 (2 h), and 38:62 (8 h). Further heating of the mixture at 80 °C for an additional day exhibited a conversion to **7**. Run 3 ($CDCl_3$, 25 °C, 8 days): 14:32 (1 day), 23:48 (2 days), and 38:62 (8 days).

3.3. Reaction 3. (i) Under Conditions at 40 °C To Give [4 + 2] Product 12. The general procedure was followed, using **1** (2.07 g) and **4** (1.83 g) in $CHCl_3$ at 40 °C for 32 days in the dark.[66] Removal of volatile material under vacuum left viscous liquid. Chromatographic purification gave 3,4-dimethyl-6-diphenylmethylidene-5,6-dihydropyran (**12**) (2.87 g, 97%) as pale yellowish oil. A similar result was obtained using **1** and **4** without solvent at 40 °C for 40 days to give **12** (2.78 g, 94%).

12: colorless liquid [colorless cubes, mp 10−12 °C (cold pentane−ether)]; R_f = 0.44; IR ν_{max} (neat) 1242 (s), 1028 (s) cm^{-1}; ^{1}H NMR δ 1.60 (dt, 3 H, J = 1.6, 0.9 Hz, 4-CH_3), 1.63 (dt, 3 H, J = 1.3, 1.0 Hz, 3-CH_3), 2.87 (ddd, 1 H, J = 1.9, 1.3, 0.9 Hz, H-5b), 2.88 (dd, 1 H, J = 2.3, 0.9 Hz, H-5a), 4.35 (ddd, 1 H, J = 1.9, 1.6, 1.0 Hz, H-2b), 4.36 (dd, 1 H, J = 2.3, 1.0 Hz, H-2a); ^{13}C NMR δ 14.14 (q, 4-*C*H$_3$), 18.08 (q, 3-*C*H$_3$), 32.62 (t, C-5), 70.86 (t, C-2), 119.86 (s, C-7), 122.91 (s, C-4), 123.27 (s, C-3), 147.52 (s, C-6); EI-MS *m*/*z* 276 (M^+, 66), 274 ($M^+ - H_2$, 37), 194 ($M^+ - C_6H_{10}$, 81), 165 (100), 81 (18). HR-MS calcd mass for $C_{20}H_{20}O$ 276.1514, found 276.1506. Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.73; H, 7.27.

(ii) Under Room-Temperature Conditions To Isolate [2 + 2] Intermediate 8. The general procedure was followed, using **1** (2.50 g) and **4** (2.21 g) in $CHCl_3$ at 25 °C for 15 days to give a mixture of **12** (0.677 g, 19%) and 2,2-diphenyl-3-isopropenyl-3-methylcyclobutan-1-one (**8**) (1.35 g, 38%), with recovery of **4**. After removing volatile material under vacuum, column chromatography [benzene−hexane (9:1)] followed by PLC separation gave both component **12** (0.357 g, 10%) and **8** (0.998 g, 28%).[68]

(iii) ^{1}H NMR Monitoring of Reaction 3. The general procedure was followed, using **1** and **4** in $CDCl_3$ at 40 (run 1) and 25 °C (run 2). Monitorings of the reaction without solvent were also carried out at 40 (run 3) and 25 °C (run 4), separately. All the results demonstrated an initial formation of [2 + 2] intermediate **8** preferentially to that of [4 + 2] cycloadduct **12**. The results exhibited similar changes in the following molar-% ratios (**8**:**12**). Run 1 (40 °C, $CDCl_3$): see Figure 4a. Run 2 (25 °C, $CDCl_3$): 22:5 (5 days), 38:19 (15), 18:78 (40), and 0:100 (84). Run 3 (40 °C, no solvent): 22:12 (2 days), 18:38 (5), 2:81 (15), and 0:100 (40). Run 4 (25 °C, no solvent): 17:3 (5 days), 22:10 (10), 38:28 (25), 35:38 (30), 19:71 (50), and 4:96 (105).

3.4. Reaction 4. (i) Under Conditions for Long Reaction Time To Give [4 + 2] Product 13. The general procedure was followed, using **1** (1.18 g) and **5** (0.563 g) in CH_2Cl_2 or benzene at room

in a short reaction time (100 °C, 3 h) (see also ref 59). **14**: colorless needles, mp 78.5−79.5 °C [pentane−ether (9:1)]; R_f = 0.31 (CCl_4); IR ν_{max} 1635 (s), 1584 (vs), 1227 (vs), 760 (vs), 698 (vs) cm^{-1}; ^{1}H NMR δ 1.12 (d, 3 H, J = 7.1 Hz, 5-CH_3), 1.76 (t, 3 H, J = 1.6 Hz, 4-CH_3), 2.26 (qddqd, 1 H, J = 7.1, 4.7, 3.9, 1.2, 1.0 Hz, H-5), 3.84 (dd, 1 H, J = 10.4, 4.7 Hz, H-6), 4.07 (dd, 1 H, J = 10.4, 3.9 Hz, H-6), 5.89 (qd, 1 H, J = 1.2, 1.0 Hz, H-3); ^{13}C NMR δ 15.17 (q, 5-*C*H$_3$), 21.31 (q, 4-*C*H$_3$), 33.43 (d, C-5), 70.76 (t, C-6), 117.72 (d, C-3), 118.35 (s, C-7), 140.26 (s, C-4), 147.25 (s, C-2); EI-MS *m*/*z* 276 (M^+, 100%), 261 (17), 194 (13), 166 (23), 165 (30), 109 (14), 81 (12), 77 (10). Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.75; H, 7.29.

(61) Recrystallization from cold pentane−ether gave pure crystals with the melting point. The crystals thus obtained remained unchanged at least over half a year at −80 °C. On standing at 0 °C below the melting temperature, however, the crystals of **10** were converted spontaneously to a solid yielding exclusively a [2 + 2]-type cycloadduct **6** (vii in Scheme 6).

(62) No change of the reaction was confirmed by ^{1}H NMR spectroscopy before and after the ^{13}C NMR measurement.

(63) (a) **1**: IR (CH_2Cl_2) ν_{max} (C=O) 2096 (vs) cm^{-1}. (b) **2**: IR (CH_2Cl_2) ν_{max} (C=C) 1632 (vs), 1597 (vs) cm^{-1}.

(64) Cyclobutanone **7**: colorless prisms (MeOH), mp 132−133 °C; R_f = 0.38; IR ν_{max} 1770 (vs) cm^{-1}; detailed NMR (^{1}H and ^{13}C) and MS data are in the Supporting Information.

(65) Dihydropyran **11**: colorless prisms [MeOH−ether (5:1)], mp 115−116 °C; R_f = 0.42; IR ν_{max} (KBr) 1208 (vs), 1018 (vs) cm^{-1}; detailed NMR (^{1}H and ^{13}C) and MS data are in the Supporting Information. Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.47; H, 6.62.

(66) We have carried out reaction 3 under acidic conditions in $CDCl_3$ containing a small amount of hydrochloric acid or trifluoroacetic acid under room light (not in the dark). After a long reaction time (1 month, room temperature), we observed the predominant formation of the [4 + 2] cycloadduct **12** accompanied by a small amount of its isomeric product **14**.[67] A similar conversion of **8** to **14** has also been confirmed under the acidic conditions (isolated yield 92−96%). A thermal conversion of **12** → **14** has also been monitored under heating conditions (100 °C, 12 h) in a sealed NMR tube. However, the thermal conversion **12** → **14** did not occur

(67) Compound **14** is also obtained from the reaction of **1** with **4** under photoirradiation (Otto, P. Ph.D. Dissertation, University of Munich, 1970). We thank Prof. Rolf Huisgen for his kind information.

(68) Cyclobutanone **8**: colorless prisms (cold MeOH or ether−pentane), mp 81−82 °C (lit.[9b,41] mp 118−119 °C, lit.[15b] mp 117−118 °C); R_f = 0.32; IR ν_{max} (KBr) 1763 (vs) cm^{-1}; ^{1}H NMR δ 1.23 (d, 3 H, J = 1.0 Hz, 3-CH_3), 1.71 (d, 3 H, J = 1.6 Hz, =C−CH_3), 2.85 (d, J = 17.2 Hz, H-4b), 3.64 (dd, J = 17.2, 1.0 Hz, H-4a), 5.05 (br s, 1 H, H-6d), 5.06 (q, J = 1.6 Hz, H-6c); ^{13}C NMR δ 21.64 (q, =C−*C*H$_3$), 28.31 (q, 3-CH_3), 45.65 (s, C-3), 55.27 (t, C-4), 79.64 (s, C-2), 113.45 (t, C-6), 148.78 (s, C-5), 208.22 (s, C=O). The IR (KBr; see Table 5 in Supporting Information) and ^{1}H NMR data of the [2 + 2] cycloadduct **8** in the literature[15b] are identical with those obtained by the present work. However, the melting point data (82 °C, from cold MeOH or ether−pentane) from the present work are different from those (118 °C, from ether−petroleum ether) in the literature.[9b,15b,41] The reason is not clear. Regarding this discrepancy, we have repeatedly examined reaction 3 with special care in two research groups (Saitama University and Sagami Chemical Research Center) independently. The IR spectrum and the melting point data of cyclobutanone **8** (mp 82−83 °C, measured on a Yanako MP-3 micro-melting point apparatus) obtained at the latter group were identical with those at the former group. By our hands, crystals of cyclobutanone **8** were found to show neither polymorphism nor formation of any hydrates.

temperature for 20 or 30 days, respectively, to give 2-methoxy-6-diphenylmethylidene-2,5-dihydropyran (**13**) (1.66 g, 98%) as pale yellowish oil.

13: colorless liquid [colorless prisms, mp 2−4 °C (cold pentane−ether)]; $R_f = 0.40$; IR ν_{max} (neat) 1236 (s), 1012 (s) cm^{-1}; ^1H NMR δ 2.89 (dddd, 1 H, $J = 21.0, 4.4, 2.4, 1.0$ Hz, H-5b), 2.96 (dddd, 1 H, $J = 21.0, 3.4, 2.4, 1.0$ Hz, H-5a), 3.23 (s, 3 H, OCH_3), 5.13 (dq, $J = 3.1, 1.0$ Hz, H-2), 5.76 (ddt, $J = 10.3, 3.1, 2.4$ Hz, H-3), 5.89 (dddd, $J = 10.3, 4.4, 3.4, 1.0$ Hz, H-4); ^{13}C NMR δ 26.95 (t, C-5), 56.14 (q, OCH_3), 98.03 (d, C-2), 123.29 (s, C-7), 124.12 (d, C-3), 127.54 (d, C-4), 143.46 (s, C-6); EI-MS *m*/*z* 278 (M^+, 18), 246 (M^+ − MeOH, 81), 194 ($M^+ - C_4H_5OMe$, 100), 165 (79), 84 (37); HR-MS calcd mass for $C_{19}H_{18}O_2$ 278.1307, found 278.1309. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.87; H, 6.68.

(ii) Under Conditions for Short Reaction Time To Isolate [2 + 2] Intermediate 9. The general procedure was followed, using **1** (1.22 g) and **5** (0.581 g) in $CHCl_3$ at 0 °C for 5 days to give a mixture of **13** (30%) and 2,2-diphenyl-3-(*trans*-2′-methoxyvinyl)cyclobutan-1-one (**9**) (70%). Column chromatography followed by PLC separation gave each component which was collected to give **13** (454 mg, 26%) and **9** (1.08 g, 62%) as colorless crystals.

9: colorless prisms, mp 75−76 °C (cold MeOH); $R_f = 0.34$; IR ν_{max} 1776 (vs) cm^{-1}; ^1H NMR δ 3.03 (dd, $J = 17.6, 9.0$ Hz, H-4a), 3.28 (dd, $J = 17.6, 9.0$ Hz, H-4b), 3.38 (s, 3 H, OCH_3), 3.78 (td, $J = 9.0, 8.4$ Hz, H-3), 4.36 (dd, $J = 11.3, 8.4$ Hz, H-5), 6.58 (d, $J = 11.3$ Hz, H-6); ^{13}C NMR δ 35.20 (d, C-3), 50.73 (t, C-4), 55.75 (q, OMe), 78.11 (s, C-2), 103.40 (d, C-5), 147.77 (d, C-6), 209.13 (s, C═O); EI-MS *m*/*z* 278 (M^+, 8), 246 (25), 194 (100), 165 (66), 84 (8), 77 (4), 69 (4). Quantitative difference NOE experiment: irr δ 3.79 (H-3), enhanced δ 3.28 (19%, H-4b); irr δ 6.68 (H-6), enhanced δ 3.08 (16%, H-4a); irr δ 7.45 (*o*-Ph), enhanced δ 4.30 (13%, H-5). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.81; H, 6.64.

(iii) ^1H NMR Monitoring of Reaction 4. The general procedure was followed, using **1** (102 mg) and **5** (44.2 mg) at 25 °C in benzene-d_6 (run 1) and at 0−25 °C in $CDCl_3$ (run 2), separately. The latter sample at 0 °C was then warmed to 25 °C for an additional 15 days until the completion of the reaction. The results exhibited the changes in the following molar-% ratios (**9**:**13**). Run 1 (25 °C, benzene-d_6): see Figure 5a. Run 2 (0−25 °C, $CDCl_3$): 22:3 (0 °C, 2 h), 52:21 (0 °C, 1 day), 30:70 (0 °C, 5 days, entire consumption of the reactants), 32:68 (0 °C, 7 days), 62:38 (25 °C, 1 day), 8:92 (25 °C, 4 days), 0:100 (25 °C, 8 days).

4. General Procedure for Claisen Rearrangement of the [4 + 2] Cycloadducts (10, 11) Originating from Cyclic 1,3-Dienes (2, 3) to Their [2 + 2] Products (6, 7). (i) Under Preparative Conditions. Crystalline sample or a solution of a [4 + 2] cycloadduct (1.0 mmol) in 10 mL of a solvent was allowed to stand in the dark or was heated until the ^1H NMR indicated disappearance of the signals of the [4 + 2] cycloadduct. Solvent removal gave a [2 + 2]-type cycloadduct. The samples obtained were identified by comparison of IR and ^1H NMR data with those of authentic samples.

(ii) ^1H NMR Monitoring of the Claisen Reaction with a Slight Retro-Diels−Alder Dissociation. A solution of 10 mg of the [4 + 2] intermediate (**10**, **11**) in 0.40 mL of solvent (benzene-d_6 or CD_2Cl_2) in an NMR tube was allowed to stand at various temperatures in the dark. The monitoring of the reactions was performed periodically at the desired temperature by ^1H NMR. These analytical results are exhibited in the Supporting Information.

4.1. In Reaction 1. (i) Under Preparative Conditions. (a) Solid-State Conversion. The general procedure was followed, using pure isolated crystals of **10** (65 mg) at 0 °C for 2.5 days to give cyclobutanone **6** quantitatively. The resulting solid samples were observed to be transformed completely to **6** by ^1H NMR. **(b) Solution-State Conversion.** The general procedure was followed, using **10** (130 mg) in $CHCl_3$ at 0 °C for 5 h to give **6** (127 mg, 98%). **(ii) ^1H NMR Monitorings. (a) Solid-State Conversion.** Pure isolated crystals of **10** were left at 0 °C in the dark. Periodical monitoring of the reaction with ^1H NMR (measured at −40 °C) by intermittent dissolution of the solid sample exhibited a complete conversion to cyclobutanone **6** without any sign of the retrogression to the reactants, **1** and **2** (Figure 1c) [$t_{1/2}$(0 °C) = ca. 6 h]. **(b) Solution-State Conversion with a Slight Retrogression.** A solution of pure isolated sample of **10** (ca. 4 mg) in 0.05 mL of CD_2Cl_2 was dissolved.[69] The reaction monitoring was performed at the temperature between −20 and 0 °C. The Claisen rearrangement was observed predominantly by a formation of [2 + 2] product **6** with a slight dissociation to the reactants, **1** and **2**, in the maximum molar concentration of 16% (0 °C, 2 h). The result is displayed in Figure 1b [$t_{1/2}$(0 °C, CD_2Cl_2) = 40 min].

4.2. In Reaction 2. (i) Under Preparative Conditions. The general procedure was followed, using **11** (274 mg) in 20 mL of benzene. The mixture was refluxed at 80 °C for 2 days until the TLC spot of **11** indicated complete disappearance. Solvent removal followed by short column chromatography gave [2 + 2] product **7** (263 mg, 96%). **(ii) ^1H NMR Monitoring with a Slight Retrogression.** The general procedure was followed, using **11** in $CDCl_3$ at 25 and 40 °C, separately, for 24 h or in benzene-d_6 (60 °C, 24 h). Any conversion was not observed by ^1H NMR monitoring. However, a solution of **11** in benzene-d_6 (80 °C, 10 h) in a sealed NMR tube indicated a slight retrogression (**11** → **1** + **3**) in the maximum concentration (4%) of the reactants, **1** + **3**, with a predominant formation of the Claisen-shift product **7** (78%) and **11** (18%) remained unchanged. Entire conversion of the mixture to the final product **7** was achieved at 80 °C for 2 days. The result is exhibited in Figure 2b [$t_{1/2}$(80 °C) = 4 h].

5. General Procedure for Nonoccurrence of Claisen Rearrangement as Well as of Retro-Diels−Alder Dissociation in the [4 + 2] Cycloadducts (12, 13) Originating from Open-Chain 1,3-Dienes (4, 5). (i) Under Preparative Conditions. A solution of a [4 + 2] cycloadduct (1.0 mmol) in 10 mL of a solvent was allowed to stand in the dark or was heated for 48 h. Solvent removal gave the cycloadducts recovered unchanged. **(ii) ^1H NMR Monitoring.** The monitoring was performed using a sample of [4 + 2] cycloadduct (4 mg) at desired temperatures in 0.4 mL of an organic solvent (benzene-d_6, $CDCl_3$ or toluene-d_8). These analytical results are displayed in the Supporting Information.

5.1. In Reaction 3. (i) Under Preparative Conditions. The general procedure was followed, using **12** at 40 °C for 2 days in $CHCl_3$ and at 60 °C for 2 days in benzene, separately. Each sample was recovered unchanged. **(ii) ^1H NMR Monitoring.** The general procedure was followed, using **12** under two conditions (40 °C, $CDCl_3$, 2 days; 60 °C, benzene-d_6, 2 days). Any conversions of **12** were not observed throughout the monitorings.

5.2. In Reaction 4. (i) Under Preparative Conditions. The general procedure was followed, using **13** in $CHCl_3$ (40 °C) and benzene (60 °C), separately, for 2 days. Each sample was recovered unchanged. **(ii) ^1H NMR Monitoring.** The general procedure was followed, using **13** under the above conditions (40 °C, $CDCl_3$, 2 days; 60 °C, benzene-d_6, 2 days). No conversions were observed throughout the monitorings.

6. General Procedure for Retro-Claisen Rearrangement of the [2 + 2] Intermediates (8, 9) Originating from Open-Chain 1,3-Dienes. (i) Under Preparative Conditions. A solution of the [2 + 2] cycloadduct (100 mg) in 5 mL of a solvent was left to stand at room temperature or was heated at 40 °C until the TLC indicated complete disappearance of the starting material. Solvent removal gave the [4 + 2] cycloadducts, **12** and **13**, quantitatively. The samples obtained were identified by comparison of their ^1H NMR data with those of authentic samples. **(ii) ^1H NMR Monitoring.** A solution of 4 mg of the [2 + 2] intermediate (**8**, **9**) in 0.40 mL of a solvent (CD_2Cl_2 or benzene-d_6) in an NMR tube was allowed to stand at 25 ± 1 °C in 0.4 mL of $CDCl_3$ and benzene-d_6, separately, in the dark. The monitorings of the reactions were performed periodically at this temperature by ^1H NMR. These analytical results are exhibited in the Supporting Information.

6.1. In Reaction 3. (i) Under Preparative Conditions. The general procedure was followed, using **8** in benzene at 40 °C for 17 days to give **12** in 96% yield. A similar experiment in $CHCl_3$ at 40 °C for 12 days gave **12** quantitatively. **(ii) ^1H NMR Monitoring.** The NMR monitoring confirmed that cyclobutanone **8** was converted to an equilibrium mixture of **8** and **12** after 15 days at 25 °C in the ratio of

(69) The measurements were performed using a 2.0-mm (i.d.) capillary (Japan Precision Instrument, N-502A), which was loaded inside of a 5ϕ-NMR tube (N-5P), to keep a concentration similar to that under preparative conditions.

71:29. Heating of the sample at 40 °C for an additional 12 days indicated the complete conversion to **12**.

6.2. In Reaction 4. (i) Under Preparative Conditions. The general procedure was followed, using **9** (60 mg) in $CHCl_3$ for 16 days or in benzene at room temperature for 24 days to give **13** in 98 and 94% yield, respectively. **(ii) ^{1}H NMR Monitoring.** The ^{1}H NMR monitoring result (25 °C, $CDCl_3$ or benzene-d_6) indicated the retro-Claisen rearrangement to the [4 + 2] adduct **13** in the ratios of 81:19 (17 h), 74:26 (24 h), 46:54 (2 days), 14:86 (6 days), and 0:100 (16 days). Likewise, a monitoring in benzene-d_6 demonstrated the conversion in the ratio of 82:18 (1 day), 23:77 (6 days), 6:94 (14 days), and 0:100 (24 days).

7. General Procedure for Nonoccurrence of Retro-Claisen Rearrangement of [2 + 2] Cycloadducts (6, 7) Originating from Cyclic 1,3-Dienes (2, 3). (i) Under Preparative Conditions. A solution of [2 + 2] cycloadduct (100 mg) in 5 mL of a solvent was heated at the desired temperature. Solvent removal left solid which was identified to remain unchanged by ^{1}H NMR with those of authentic samples. **(ii) ^{1}H NMR Monitoring.** A solution of 4 mg of [2 + 2] intermediate (**6**, **7**) in 0.40 mL of a solvent (CD_2Cl_2 or benzene-d_6) in an NMR tube was heated in 0.4 mL of $CDCl_3$ and benzene-d_6, separately, in the dark. The monitorings of the reactions were performed periodically. These analytical results and the representative charts are exhibited in the Supporting Information.

7.1. In Reaction 1. (i) Under Preparative Conditions. The general procedure was followed, using **6** (100 mg) in $CHCl_3$ and benzene, separately, at 25 °C for 15 days. Each sample used was recovered unchanged quantitatively. **(ii) ^{1}H NMR Monitoring.** The general procedure was followed, using **6** (100 mg) in $CDCl_3$ or benzene-d_6. No conversion was observed throughout the monitorings.

7.2. In Reaction 2. (i) Under Preparative Conditions. The general procedure was followed, using **7** (100 mg) in $CHCl_3$ (40 °C, 15 days) and benzene (80 °C, 2 days), separately. Each sample used was recovered unchanged. **(ii) ^{1}H NMR Monitoring.** The general procedure was followed, using **7** (100 mg) under the above conditions (40 °C, $CDCl_3$, 15 days, 80 °C, benzene-d_6, 2 days). No conversion was observed throughout the monitorings.

8. Computational Methods. Geometries of reactants (**1**−**5**), intermediates and products (**6**−**13**), and transition states were optimized with the RHF/3-21G method. RHF/3-21G vibrational analyses were made to judge whether the optimized geometries were at stable points or at saddle points. Electronic energies were obtained with single-point calculations of the MP2/6-31G* (frozen core) method on the RHF/3-21G geometries, MP2/6-31G*//RHF/3-21G. The solvent (chloroform, $CHCl_3$) effect is included by the self-consistent reaction field (SCRF) method of the Onsager reaction field model.[70] The SCRF correction was added to the MP2/6-31G* electronic energy. The dielectric constant ϵ of $CHCl_3$ was taken to be 6.0. Thermal corrections and entropies were evaluated at two temperatures, T = 200 and 300 K. These temperatures follow nearly the experimental conditions (the monitoring of reactions between −80 and 20 °C). Gibbs free-energy (G) diagrams were drawn at those two temperature. Thus, the energy G is composed of the MP2/6-31G* electronic energy, RHF/3-21G SCRF and thermal corrections, and RHF/3-21G entropies. All the calculations were carried out, using the GAUSSIAN94 (G94)[71] program. G94 was installed both at CONVEX spp1200/XA (the Information Processing Center, Nara University of Education) and at CONVEX spp1600/XA (Computer Center, Nara University).

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Supporting Information Available: List of experiments, tables of full spectral data [IR, MS, and NMR (^{13}C and ^{1}H)], selected NMR spectral charts [400-MHz 1D ^{1}H NMR (ordinary Lorentz-transformed spectra and those resolution-enhanced with sine-bell wind function), 2D NMR ^{1}H−^{1}H COSY and ^{1}H−^{1}H COLOC, 100.6-MHz 1D ^{13}C NMR with CPD, gated decoupling, and 2D NMR ^{13}C−^{1}H COSY and ^{13}C−^{1}H COLOC spectra] for the reported compounds **6**−**13**, plots of reaction monitoring experiments, Cartesian coordinates (Chem3D drawing input data) of optimized TS geometries shown in Figures 6−10, and tables of energetics (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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