New facets in the photochemistry and thermal reaction of 2,2-diphenylmethylenecyclopropane

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Abstract

Photochemistry and thermal reaction of 2,2-diphenylmethylenecyclopropane **1a** have been reinvestigated to make their mechanistic refinement. A new finding in the photochemistry of **1a** is the detection and isolation of cyclobutene **7**. While fragmentation and 1,3-carbon (C) shift is responsible for previously reported photoproducts, 1,1-diphenylethylene **3** and diphenylmethylenecyclopropane **2a**, respectively, a new pathway is required to explain the formation of cyclobutene **7**. A mechanism involving the 1,2-C shift (Scheme 3, arrow b) followed by 1,2-hydrogen (H) shift is proposed. In the thermal reaction of **1a**, on the other hand, a trimethylenemethane type of species is shown to be a common intermediate for degeneracy, rearrangement from **1a** to **2a**, and formation of indene **5**. In the photochemistry of **1a**, intervention of cyclobutylidene **8** is strongly supported by circumstantial evidences provided by steady-state and laser flash photolytic investigations. Further experiments designed to independently generate cyclobutylidene **8** showed the methylenecyclopropane/cyclobutene branching ratio (**1a/7**) to be in the range between 0 and 1.7, which is much lower than the value of 4.0 for parent cyclobutylidene. Nevertheless, the relative efficiency of 1,2-shift pathway to generate **8** is shown to be as high as 17–47% compared to 1,3-C shift to give **2a** at the early photochemical stage of **1a**.
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1. Introduction

Since the first discovery of the thermal structural isomerization of "Feist's ester" by Ullman [1], many other examples of methylenecyclopropane rearrangement have been found [2]. Trimethylenemethane intermediate is a matter of concern and numerous stereochemical and kinetic experiments have been designed to probe its mechanistic role. In contrast to abundant pyrolytic chemistry of methylenecyclopropanes, their photochemistry [3–6] has been investigated to a very limited extent. Even fewer reports can be found for their photochemistry by direct excitation [3], which hardly allow direct comparison between thermal and photochemical reactions with common methylenecyclopropanes. A most obvious reason may be that relatively simple methylenecyclopropanes without chromophores have been suited for thermolysis and subject to stereochemical and kinetic experiments to probe the mechanistic

detail. The other reason may be that direct photoexcitation of small ring compounds often results in complex mixtures with poor material balance owing to their fragmentations [7], which prevents quantitative stereochemical and kinetic analysis.

There are a few reports dealing with both photochemical and thermal reactions with common substrates. Phenyl-substituted methylenecyclopropanes appear to be among them. Gilbert and Butler [3b] studied the photochemistry of 2,2-diphenylmethylenecyclopropane **1a** with particular interest in the fragmentation and provided evidence for generation of elusive vinylidene **4**. Interestingly, they found the preceding degenerate 1,3-carbon (C) shift by observing the pairwise deuterium scrambling between **1b** and **1c** (Scheme 1, arrow a). They also briefly mentioned the occurrence of the photorearrangement from **1a** to **2a** (arrow b) without specifying the chemical yields or conversions. On the other hand, Kende et al. [3a] studied photochemistry of isomeric diphenylmethylenecyclopropane **2a** and found that not only fragmentations to **3** but also photoisomerization from **2a** to **1a** proceeded with sizable quantum yields (arrow c). These independent observations may be combined to indicate the photoreversibility between **1a** and **2a**.
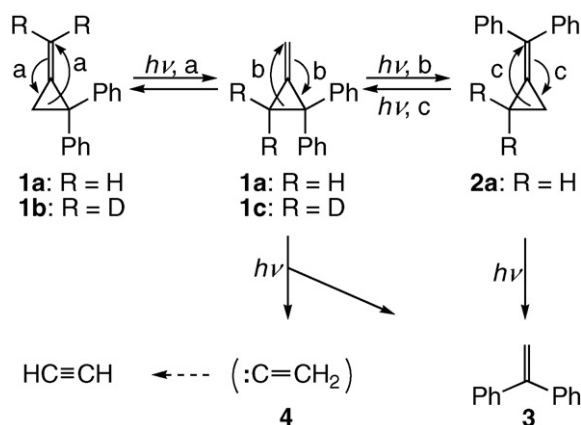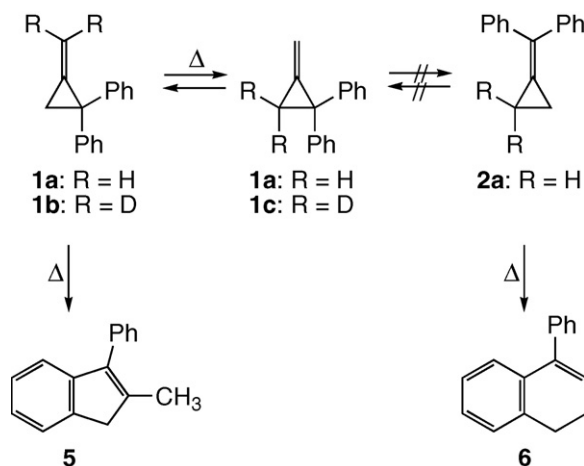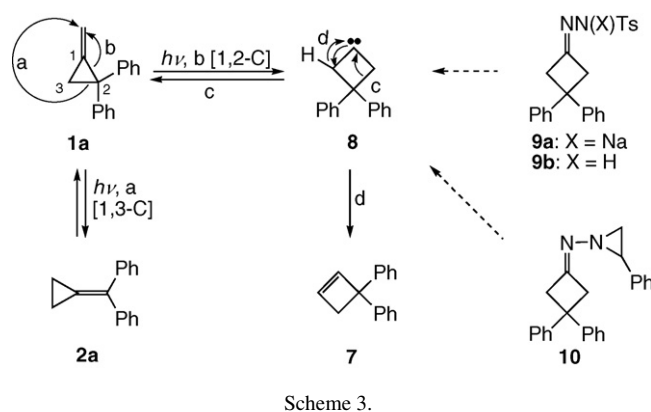
Scheme 1.

On the other hand, thermal reactions of **1a** and **2a** reportedly stand in marked contrast to their photochemistry (Scheme 2). While 2,2-diphenylmethylenecyclopropane **1a** underwent degenerate methylenecyclopropane rearrangement presumably via trimethylenemethane intermediate, no evidence was obtained for thermal interconversion between **1a** and **2a** [8]. The positional selectivity in the rearrangement is associated with the observation of negative entropy of activation and may be due to specific orientation in the trimethylenemethane type intermediate or transition state. At higher temperatures, these isomers **1a** and **2a** still did not interconvert but underwent independent structural isomerizations to indene **5** and dihydronaphthalene **6**, respectively [8b,c].

It seems obvious that in the excited state, the interaction between the phenyl chromophore and the adjacent σ-bonds play an important role in the photoreaction of 2,2-diphenlymethylenecyclopropane **1a**. As far as rearrangements are concerned, the interaction involving the C2–C3 σ-bond would cause structural isomerization of **1a** to **2a** (Scheme 3, arrow a) while the other interaction involving C1–C2 σ-bond would eventually induce 1,2-C shift of **1a** to produce cyclobutylidene **8** (arrow b). It may undergo 1,2-hydrogen (H) shift to give cyclobutene **7** (arrow d) competing with reversal 1,2-C shift reproducing **1a** (arrow c).

Scheme 2.

Scheme 3.

The present work is to address the possibility and relative importance of 1,2-C shift pathway (Scheme 3, arrow b) in the photochemistry of **1a**. We first sought to detect and identify cyclobutene **7** since it would be a strong support for intervention of cyclobutylidene **8**. Also carried out was a series of experiments designed to independently generate and understand the reactivity of cyclobutylidene **8**. Of particular importance is its branching ratio with respect to the formation of **1a** and **7**, which we newly determined by thermolysis and photolysis of two precursors, **9a** and **10**. Incidentally, the thermolytic experiments with **9a** and **10** required control experiments concerning with the thermal stability of **1a** under the comparable conditions. While assuring the thermal stability of **1a**, our thermolytic experiments with **1a** revealed the occurrence of new reactions.

2. Experimental

2.1. General

Melting points were measured on a Yanagimoto MP-500D melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 NMR spectrometer operating at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C by using CDCl$_3$ as a solvent unless specified otherwise. ^{1}H NMR chemical shifts are reported in ppm downfield from a TMS internal standard and coupling constants *(J)* are in Hz. ^{13}C NMR chemical shifts in ppm are based on solvent CDCl$_3$ resonance (77.00 ppm). A JASCO FT/IR-410 spectrometer, JEOL JMS-600W mass spectrometer, and SHIMADZU MultiSpec-1500 diode array UV/vis spectrometer were used for IR, MS, and UV/vis measurements. GPC was carried out on a HPLC system consisting of JASCO PU-880 pump unit and UV-875 detector with Shodex GPCH-2001 column. Commercially available spectroscopic grade solvents were distilled over calcium hydride prior to use. MERCK Silica gel 60 PF$_{254}$ and Kanto Silica gel 60 (7734-5B) were used for preparative TLC and column chromatography, respectively.

Time-resolved difference absorption spectra were obtained with 17 ns pulses from a Lambda Physik LETRA 50 excimer laser (XeCl, 308 nm) or with the forth harmonic (266 nm), 7 ns pulses from a Continuum Powerlite Precision 8010 Nd:YAG laser. The monitoring beam from a 150 W xenon lamp was collimated and was perpendicular to the excitation pulse. A combi-

nation of a monochromator, a photomultiplier tube (Hamamatsu R2949), and a digital oscilloscope (SONY/TEKTRONIX TDS-360P) was used for measurement of the decay kinetics. An analogous flash photolysis system has been described elsewhere [9].

2.2. Materials

2,2-Diphenylmethylenecyclopropane **1a** [10] and diphenyl-methylenecyclopropane **2a** [11] were synthesized according to the reported method. 3,3-Diphenylcyclobutanone [12,13] was synthesized according to the reported method. Reaction of 3,3-diphenylcyclobutanone with tosylhydrazide afforded the corresponding tosylhydrazone **9b**, mp 197–198 °C (from methanol), ^{1}H NMR: δ 7.81 (2H, d, J = 8.5), 7.31–7.13 (12H, m), 3.65 (2H, s), 3.50 (1H, br. s), 3.39 (2H, s), 2.42 (3H, s). Cyclobutene **7** was independently synthesized from tosylhydrazone **9b** according to the reported method [14]. Cyclobutene 7: colorless viscous oil, ^{1}H NMR: δ 7.29–7.16 (10H, m), 6.72 (1H, d, J = 2.9), 6.38 (1H, dt, J = 2.9, 1.0), 3.16 (2H, t, J = 1.0). ^{13}C NMR: δ 145.9 (2C), 141.9 (1C, C2), 136.1 (1C, Cl), 128.1 (4C), 127.0 (4C), 125.9 (2C), 58.3 (1C, C3), 47.2 (1C, C4). IR (KBr, ν/cm^{-1}) 1562, 1032, 856, 712. MS (EI) m/z 205.7 (M$^+$, 100%).

2.2.1. Preparation of sodium salt 9a

To a mixture of tosylhydrazone **9b** (39.0 mg, 0.100 mmol) and dry methanol (1 ml) was added a 0.10 M solution of sodium methoxide in methanol (1.0 ml). The resulting solution was stirred for 10 min and the solvent was removed under vacuum.

2.2.2. Precursor 10

To a solution of 3,3-diphenylcyclobutanone (150 mg, 0.68 mmol) in dry benzene (10 ml) was added l-amino-2-phenylaziridine (100 mg, 0.68 mmol), which was synthesized according to the reported method [15]. The reaction mixture was stirred for 12 h. Then the solvent was removed on a rotary evaporator and the resulting mixture was subjected to chromatography on a short silica gel column. Elution with a 5:1 mixture of n-hexane and ether afforded practically pure **10** as pale yellow solid, which was further purified by GPC with chloroform as an eluent. Iminoaziridine **10**, colorless powder, mp 83.5–85.1 °C (dec). ^{1}H NMR: δ 7.16–7.33 (10H, m), 3.78 (1H, d, J = 9.4), 3.67 (1H, d, J = 9.4) 3.66 (2H, s), 2.92 (1H, dd, J = 7.7, 4.8, H-CPh), 2.42 (1H, d, J = 7.7), 2.29 (1H, d, J = 4.8).

2.3. Steady-state photoreaction

2.3.1. Photoreaction of 2,2-diphenlymethylenecyclopropane 1a

A 3 ml solution of **1a** (0.20 mmol) in acetonitrile or cyclo-hexane was irradiated under nitrogen by using a low-pressure mercury lamp (Toshiba GL-20, 15 W) at 15 °C and the solvent was completely removed under vacuum. The resulting reaction mixture was analyzed by ^{1}H NMR with dibromomethane as an internal standard (4.91 ppm) with respect to the characteristic resonances **1a** (δ 1.89, 2H, dd, J = 2.6, 2.0), **2a** (δ 1.43, 4H, s), 3 (δ 5.45, 2H, s), and 7 (δ 3.16, 2H, t, J = 1.0). Repeated preparative TLC (silica gel, hexane) of the combined reaction mixture

afforded practically pure **2a** and **7**, whose ^{1}H NMR spectra show resonance signals identical with those of authentic samples.

2.3.2. Photolysis of tosylhydrazone sodium salt 9a and iminocyclobutane 10

Precursor **9a** (0.10 mmol) in a 5 ml solvent was irradiated under nitrogen by using a 300 W medium pressure mercury lamp equipped with an aqueous IR-filter λ > 370 nm at room temperature. After aqueous and ethereal workup, the solvent was removed and the resulting reaction mixture was analyzed by ^{1}H NMR as described above. Preparative TLC (silica gel, hexane-ether 5:4) of combined photolysates afforded azine **11** (R_f 0.4) as colorless powder, mp 114.2–116.7 °C (from n-hexane). ^{1}H NMR: δ 7.14–7.43 (20H, m), 3.76 (8H, s). ^{13}C NMR: δ 166.53 (2C, Cl,l′), 147.75 (4C, Ph-*ipso*), 128.48 (4C), 126.50 (4C), 126.20 (4C), 48.61 (2C, C2,2′ or C4,4′), 48.04 (2C, C4,4′ or C2,2′), 45.34 (2C, C3,3′). MS (El) m/z 440 (M$^+$, 52.7%), 349 (M$^+$–CH$_2$Ph, 100%), 220 (M$^+$/2, 13.3%), IR (NaCl, ν/cm^{-1}) 1696.

Precursor **10** (0.10 mmol) in cyclohexane was irradiated under nitrogen by using a low pressure mercury lamp (Toshiba GL-20, 15 W) at 15 °C. The solvent was completely removed under vacuum and the resulting residue was analyzed by ^{1}H NMR as described above. Similar photolysis of precursor **10** (0.10 mmol) in tetramethylethylene (TME) resulted in photoproducts as shown in Table 3. Preparative TLC (silica gel, hexane) of the photolysate afforded a crude product (3 mg, 3%) other than **1a**, **7**, and azine **11**. Further TLC purification of the crude product afforded a practically pure product as colorless viscous oil, which was tentatively assigned to be adduct **12** based on its ^{1}H NMR data: δ 7.10–7.41 (10H, m), 2.64 (4H, s), 0.87 (12H, s).

Photolysis of precursor **10** (0.10 mmol) in ethyl vinyl ether (EVE) afforded a mixture containing oligomeric material. After quick chromatographic workup followed by removal of solvent, the resulting mixture was analyzed by ^{1}H NMR. Preparative TLC (silica gel, hexane-ether, 10:1) of the mixture afforded EVE adduct **13**, as colorless viscous oil, ^{1}H NMR: δ 7.36–7.13 (10H, m), 3.30 (2H, m, –OEt), 3.07 (1H, dd, J = 6.3, 3.3, >CH–OEt), 3.06 (1H, d, J = 11.4), 2.89 (1H, d, J = 11.4), 2.87 (1H, d, J = 11.4), 2.75 (1H, d, J = 11.4), 1.13 (3H, dd, J = 7.0, 7.0, –OEt), 0.69 (1H, dd, J = 6.3, 6.3), 0.57 (1H, dd, J = 6.3, 3.3). ^{13}C NMR: 6 150.44 (1C, Ph-*ipso*), 149.66 (1C, Ph-*ipso*), 128.19 (2C, Ph-*m*), 128.17 (2C, Ph-*m*), 126.58 (1C, Ph-*o*), 126.38 (1C, Ph-*o*), 125.56 (2C, Ph-*p*), 125.51 (2C, Ph-*p*), 65.72 (1C, –OCH$_2$Me), 60.52 (1C, >CH–EEt), 47.88 (1C, >CPh$_2$), 43.62 (1C), 40.03 (1C), 19.52 (1C, spiro C), 17.83 (1C, Me), 15.17 (1C).MS (El) m/z 279.3 (M$^+$ + 1, 2.7%), 278.3 (M$^+$, 9.3%), 232.3 (M$^+$–OCH$_2$CH$_3$, 34.4%), 217.2 (32.2%), 205.2 (21.5%), 187.2 (20.0%), 167.2 (100%), 98.1 (77.7%), 91.1 (28.7%), 70.1 (24.0%). IR (NaCl, ν/cm^{-1}) 1122, 1027.

2.4. Thermal reaction

2.4.1. Thermal reaction of 9 and 10

Precursor **9** or **10** (0.10 mmol) was heated under various conditions described in Table 3 and the resulting reaction mixture

Table 1

Photoreaction of 2,2-diphenlymethylenecyclopropane **1a**
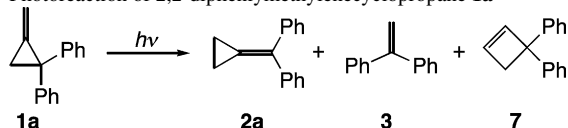
Entry	Solvent	Time (h)	Products (yield/%)	Recovery (%)
1	MeCN	5	**2a** (3), **3** (9), **7** (ca. 0.5)	87
2	MeCN	15	**2a** (4), **3** (16), **7** (ca. 1)	79
3	Cyclohexane	5	**2a** (5), **3** (8), **7** (ca. 0.5)	84
4	Cyclohexane	15	**2a** (7), **3** (16), **7** (ca. 0.5)	76

A 3 ml solution of **1a** (0.20 mmol) was irradiated ($\lambda = 254$ nm) under nitrogen and the resulting reaction mixture was analyzed by ^{1}H NMR (300 MHz).

was analyzed by ^{1}H NMR as described above. In the case of **9**, aqueous and ethereal workup of the reaction mixture preceded the ^{1}H NMR analysis.

2.4.2. Thermal stability of cyclobutene 7

Cyclobutene **7** (21 mg, 0.10 mmol) in 5 ml diglyme was heated to 150 °C for 10 min. After cooling and aqueous and ethereal workup, analysis of the resulting product mixture by ^{1}H NMR indicated complete disappearance of **7** and formation of butadiene **14** [16] in 91% yield. ^{1}H NMR data of **14**: δ 7.19–7.38 (10H, m), 6.71 (1H, d, $J = 11.0$), 6.43 (1H, ddd, $J = 16.8$, 11.0, 1.8), 5.38 (1H, dd, $J = 16.8$, 1.8), 5.12 (1H, dd, $J = 11.0$, 1.8). Similar thermal reaction at 100 °C for 10 min resulted in butadiene **14** in 16% yield with recovery of cyclobutene **7** (78%).

2.4.3. Thermal reaction of 2,2-diphenlymethylenecyclopropane 1a

Methylenecyclopropane **1a** (0.10 mmol) was heated under various conditions described in Table 4. After aqueous and ethereal workup if necessary, the resulting reaction mixture was analyzed by ^{1}H NMR. Preparative TLC (silica gel, hexane) of the combined reaction mixtures afforded **2a** (R_f 0.80), mdene **5** (R_f 0.75), and **15** (R_f 0.60). Indene **5** [3c,8b], colorless viscous oil, ^{1}H NMR: δ 7.00–7.42 (9H, m) 3.46 (2H, s) 2.15 (3H, s). Compound **15**, colorless blocks, mp 140.3–141.9 °C (from ether–methanol). ^{1}H NMR: δ 7.42–7.00 (18H, m), 3.28 (4H, s), 2.76 (4H, s). ^{13}C NMR: δ 146.23 (2C, Ph-*ipso*), 143.83 (2C, benzo), 142.44 (2C, benzo), 139.78 (2C, ≥CPh), 135.33 (2C, ≥C-ethano), 128.99 (4C, Ph-*m*), 128.41 (4C, Ph-*o*), 127.03 (2C), 126.16 (2C), 124.16 (2C), 123.49 (2C), 119.54 (2C), 40.38 (2C, >CH2), 29.31 (2C, –CH2CH2–). MS (EI) *m/z* 409.6 (M[+], 21.3%), 218.8 (5.6%), 204.8 (M[+]/2, 100%). Single crystals for X-ray analysis were grown from a mixture of ether and methanol.

2.4.4. X-ray crystal structure analysis of 15

A colorless block crystal of coupling product **15** (C32H26) having approximate dimensions of 0.25 mm × 0.20 mm × 0.12 mm was mounted on a glass fiber and the intensity data was collected on a Rigaku RAXIS-RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at 23 °C to a maximum 2θ value

of 54.8°. A total of 44 oscillation images were collected. The structure was solved by direct methods (SIR97) [17a] and expanded using Fourier techniques (DIRDIF99) [17b]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on *F* was based on 1186 observed reflections and 164 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.064$, $wR2 = 0.129$ with all reflections. All calculations were performed using the CrystalStructure [17c] crystallographic software package.

3. Results and discussion

3.1. Photochemistry of 2,2-diphenlymethylenecyclopropane 1a

Photoreaction of **1a** [3b] was revisited with particular attention to the formation of cyclobutene **7**. Although cyclobutene **7** has never been observed in the previous photochemical studies of **1a**, it would be an obvious product from cyclobutylidene **8** if it can be generated from **1a** via 1,2-C shift pathway (Scheme 3, arrow b). Photo irradiation ($\lambda = 254$ nm) of a 3 ml acetonitrile solution of **1a** (0.20 mmol) in a quartz tube under nitrogen for 5 h resulted in net chemical change (Table 1). Analysis of the resulting photolysate by ^{1}H NMR indicated the formation of 1,1-diphenylethylene **3** as a major product with recovery of **1a**, which is consistent with the previous report [3b].

Further inspection of the NMR spectrum indicated formation of two other products. The one showing characteristic singlet at 1.42 ppm was isolated by preparative TLC and unequivocally assigned to diphenylmethylenecyclopropane **2a** on the basis of spectral comparison with the authentic sample synthesized independently. Since no practical improvement in their yields was observed by longer time irradiation in acetonitrile or cyclohexane, multiple set of photolytic experiments were carried out to accumulate and isolate the third product. Repetitive preparative TLC afforded practically pure material, which was identified to be cyclobutene **7** in comparison of the spectroscopic data with those of the authentic sample synthesized independently. Cyclobutene **7** was confirmed to be stable under the photolytic conditions.

Table 2
Photolysis of **9a** and **10**

12: R = R' = Me
13: R = H, R' = OEt
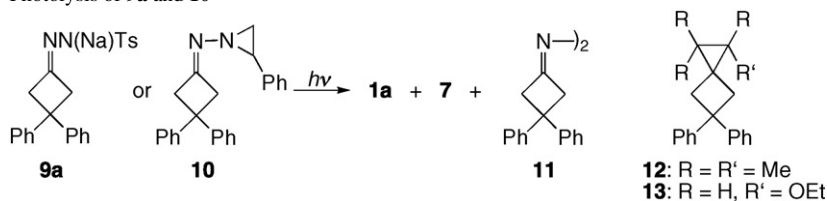
Entry	Precursor	Conditions	Conv. (%)	Products (yield/%)	1a/7
1	**9a**	λ > 300 nm, 18 h, DME	ca. 30	**1a** (5), **7** (6), **11** (10)	0.83
2	**9a**	λ > 300 nm, 17 h, THF	ca. 30	**1a** (4), **7** (5), **11** (9)	0.80
3	**10**	λ > 254 nm, 8 h, c-hex	100	**1a** (6), **7** (34), **11** (16)	0.18
4	**10**	λ > 254 nm, 8 h, MeCN	100	**1a** (7), **7** (41), **11** (12)	0.17
5	**10**	λ > 254 nm, 7 h, TME	100	**1a** (4), **7** (20), **11** (5), **12** (3)	0.20
6	**10**	λ > 254 nm, 6 h, EVE	100	**1a** (2), **7** (10), **11** (4), **13** (16)	0.20

Precursor (0.10 mmol) in a 5 ml solvent was irradiated under nitrogen and the resulting reaction mixture was analyzed by ^{1}H NMR (300 MHz). DME: dimethoxyethane, THF: tetrahydrofuran, c-hex: cyclohexane, TME: tetramethylethylene, EVE: ethyl vinyl ether.

Formation of diphenylmethylenecyclopropane **2a** and diphenylethylene **3** is in line with Gilbert's observation that photochemical version of methylenecyclopropane rearrangement and photofragmentation occur with 2,2-diphenylmethylenecyclopropane **1a** [3b]. Very significant in the present case is the detection and isolation of cyclobutene **7** though the yields are low (Table 1). It is obvious that production of cyclobutene **7** requires adequate mechanism for its formation because no mechanistic connection can be made between **1a** and **7** by either 1,3-C shift or trimethylenemethane type intermediate. As mentioned at the beginning, the most reasonable pathway for production of cyclobutene **7** is to involve the photoinduced 1,2-C shift of **1a** followed by 1,2-H shift of the resulting cyclobutylidene intermediate **8** (Scheme 3, b and d).

We note that there have been several comparable precedents for photochemical generation of carbenes by 1,2-C migration of alkenes [18]. For example, Kropp and Fields [18a] have reported evidence for carbene intermediates in the photochemistry of tetraalkyl alkenes. Generation of cyclohexylcarbene intermediate is reported by Inoue et al. [18b] in the photorearrangement of cycloheptene to give methylenecyclohexane and bicyclo[4.1.0]heptane. A most relevant type of 1,2-C shift is suggested in our previous work dealing with photoreversal from **2a** to **1a** [19].

It is important to note that the chemical yield of cyclobutene **7** by itself is not a simple measure for degree of contribution of cyclobutylidene **8** in the photoprocess of **1a**. Also important is the branching ratio, **1a/7** for the formation of methylenecyclopropane **1a** and cyclobutene **7** from **8**. For parent cyclobutylidene, the corresponding ratio is found to be ca. 8:2 (methylenecyclopropane:cyclobutene) by decomposition of nitrogenous precursors [20a]. If this ratio is simply applied to the present case, formation of cyclobutene **7** in 0.5% would require generation of cyclobutylidene **8** in 2.5%, which is comparable to the yield of **2a** (3–5%) at the early stage of photoreaction of **1a** (Table 1, entry 1 and 3). Thus, we made additional experiments for evaluation of the branching ratio (**1a/7**) based on independent generation of cyclobutylidene **8** by photolysis and thermolysis of precursors **9a** and **10**.

3.2. Photolysis of precursors **9a** and **10**

Sodium salts of tosylhydrazones and aziridinylimino compounds rank among typical precursors for carbenes [20a,21,22]. Their photolyses and thermolyses generate diazo compounds and they undergo sequential photolytic or thermal extrusion of nitrogen to generate carbenes. Accordingly, tosylhydrazone sodium salt **9a** and aziridinyliminocyclobutane **10** were prepared as straightforward precursors to cyclobutylidene **8**.

As summarized in Table 2, they underwent photochemical decomposition to produce the expected hydrocarbons **1a** and **7** with concurrent formation of azine **11**. In the case of sodium salt **9a**, a suspension in 1,2-dimethoxyethane (DME) was irradiated because of its limited solubility. Prolonged irradiation resulted in analyzable amount of products, methylenecyclopropane **1a** (5%), cyclobutene **7** (6%), and azine **11** (10%) (entry 1). Similar photolysis in tetrahydrofuran (THF) afforded practically the same result (entry 2). In these cases, formation of cyclobutene **7** is only slightly favored over methylenecyclopropane **1a**, resulting in the **1a/7** ratio of ca. 0.8. For parent cyclobutylidene, methylenecyclopropane is produced in significant preference to cyclobutene and the corresponding ratio is found to be 4.0 by decomposition of nitrogenous precursors [20a].

Iminocyclobutane **10** is soluble in most organic solvents but it turned out that it is practically unreactive toward longer wavelength light (λ > 300 nm). Low pressure mercury lamp was found to be quite effective for photolysis to produce methylenecyclopropane **1a**, cyclobutene **7**, and azine **11** together with small amount of unidentified product(s). It is interesting to note that cyclobutene **7** is formed from iminocyclobutane **10** in significant preference to methylenecyclopropane **1a** (Table 2, entry 3–6). Indeed, the **1a/7** ratios of around 0.2 are four times smaller than those for the photolyses of **9a**. It is highly unlikely that the secondary photoreaction of methylenecyclopropane **1a** caused its partial loss and formation of cyclobutene **7** because photolysis of **1a** proceeds less efficiently and it should have resulted in the formation of **2a**, which was not observed.

Pezacki et al. [23] investigated the photochemical decomposition of diazocyclobutane in solution and succeeded in trap-

ping parent cyclobutylidene with tetramethylethylene. Quenching studies with TME establish that free singlet cyclobutylidene rearranges almost exclusively to methylenecyclopropane whereas a significant fraction of the excited-state diazo compound rearranges directly to methylenecyclopropane and cyclobutene without intervention of cyclobutylidene.

We also carried out photolytic experiments with iminocyclobutane **10** in the presence of TME to gain insight into intermediacy of cyclobutylidene **8** and a direct pathway of excited-state diazo compound (Table 2, entry 5). Analysis of the photolysate showed formation of **1a** and **7** in the ratio of 0.2 together with azine **11** and a small amount of unknown product(s). Repetitive TLC separation afforded a product showing two singlets at 2.64 and 0.87 ppm by ^{1}H NMR, which was tentatively assigned to be adduct **12**. However, further purification and spectroscopic measurements have not been made owing to its limited stability.

Photolysis of precursor **10** in ethyl vinyl ether also proceeded to completion but afforded a mixture containing oligomeric material, which required preceding quick chromatographic workup prior to ^{1}H NMR analysis, which showed the formation of **1a** and **7** in the ratio of 0.2 together with azine **11** and a new product (entry 6). Repetitive TLC separation afforded a product showing signals due to ethoxy by ^{1}H NMR. The structure was determined to be **13** on the basis of the spectroscopic data. The yield of adduct **13** is higher than that of adduct **12** presumably because EVE is a better donor and is less hindered than TME.

These results indicate that **8** is a species with a trappable lifetime. However, TME or EVE resulted in no practical effect on the ratio of **1a/7**. It is likely that in the present case both carbene **8** and excited-state diazocyclobutane afford methylenecyclopropane **1a** and cyclobutene **7** in similar ratios, around 0.20 each, or the excited-state diazo cyclobutane does not play a role for production of **1a** or **7**.

3.3. Laser flash photolysis of methylenecyclopropane 1a and precursor 10

In order to gain evidence for intervention of cyclobutylidene **8**, nano-second laser flash photolysis (LFP) of methylenecyclopropane **1a** and iminocyclobutane precursor **10** was examined. Since cyclobutylidene **8** is expected to be spectroscopically invisible, a probe technique [24] with pyridine [25] was used. Many alkyl carbenes are known to form ylides with pyridine [25d,e] and the resulting ylide absorptions appear in UV–vis region (typically between 300 and 400 nm) [25]. Cyclobutylidene **8** may also be trapped with pyridine if they have trappable lifetime.

As shown in Fig. 1(a), LFP (XeCl, 308 nm) of a cyclohexane solution containing iminocyclobutane **10** resulted in broad and weaker absorption around 420 nm. It was found to be insensitive to pyridine concentration and no formation of pyridine ylide was detected. Instead, it was quenched by oxygen and ferrocene ($k_q = 1 \times 10^9$ and 7.0×10^9 M^{-1} s^{-1}, respectively) and it was assigned as being due to triplet excited state of **10**. On the other hand, LFP (Nd: YAG, 266 nm) of a similar solution of **10** in cyclohexane containing pyridine resulted in
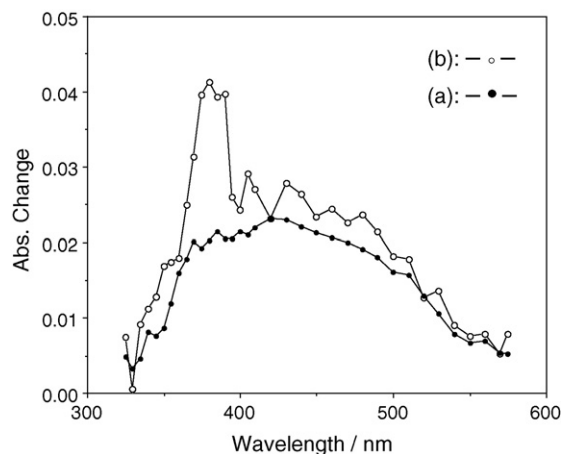

Fig. 1. (a) Transient absorption spectrum observed 500 ns after LFP (XeCl, 308 nm) of a cyclohexane solution containing precursor **10** (2×10^{-3} M). (b) Transient absorption spectra observed 500 ns after LFP (NdYAG, 266 nm) of a cyclohexane solution containing precursor **10** (2×10^{-3} M) and pyridine (0.01 M). The intensity of spectrum (a) is normalized to spectrum (b) at 420 nm.

fairly intense absorption at λ_{max} 380 nm and broad and weaker absorption around 420 nm (Fig. 1(b)). The former absorption can be ascribed to pyridine ylide of carbene **8** because it was not observed in the absence of pyridine. The latter was easily assigned as being due to triplet excited state of **10** because of its similar spectral shape and kinetic behavior to that observed by 308 nm excitation.

It is desirable to directly measure the growth rate (k_{obs}) for pyridine ylide absorption so that the rate constant for pyridine ylide formation (k_{pyr}) and the lifetime of carbene **5** ($\tau = 1/k_0$) can be determined from the slope and the intercept of a plot of k_{obs} versus concentration of pyridine according to the equation: $k_{obs} = k_0 + k_{pyr}$ [pyridine] [24,25]. Unfortunately, k_{obs} in this case turned out to be too fast to measure with our instruments, presumably because the lifetime of cyclobutylidene **5** is very short. Moreover, the initial intensity of ylide absorption was found to fluctuate and show poor reproducibility. Accordingly, Stern–Volmer type analysis did not afford meaningful results either.

Similar LFP (Nd: YAG, 266 nm) of a solution of methylenecyclopropane **1a** in cyclohexane or acetonitrile containing pyridine resulted in no transient absorptions ascribable to pyridine ylide. It is unlikely that the lifetime of cyclobutylidene **8** is too short to be trapped by added pyridine because the above experiments showed it is a trappable species. If we assume a rate constant for pyridine ylide formation to be 1×10^8–10^9 M^{-1} s^{-1}, 1.0 M pyridine could easily trap the carbene with its lifetime of ca. 1–10 ns, which is slightly shorter than that of parent cyclobutylidene: 4–20 ns in cyclohexane [23]. Thus, it is more likely that the efficiency for generation of carbene **8** from **1a** is practically too low for LFP detection. The quantum yield for generation of carbene **8** from **1a** can be roughly estimated to be 0.004–0.01 if the reported quantum yield of 0.07 for formation of diphenylethylene **3** [3a] and the branching ratio of **8** being in the range of 0.0–1.7 are taken into account in conjunction with the chemical yields of diphenylethylene **3**

Table 3
Thermal reaction of **9a** and **10**
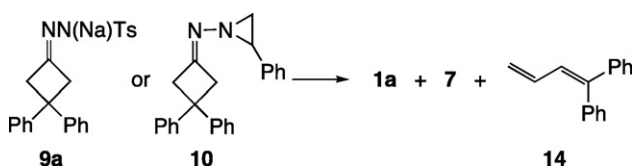
Entry	Precursor	Conditions	Conv. (%)	Products (yield/%)	**1a**/(**7** + **14**)
1	**9a**	150 °C, 5 min, no solvent	ca. 85	**1a** (2), **7** (0), **14** (6)	0.33
2	**9a**	150 °C, 4 h, diglyme	100	**1a** (7), **7** (0), **14** (83)	0.08
3	**10**	83 °C, 8 h, DME	6	**1a** (0), **7** (2), **14** (0)	0
4	**10**	111 °C, 8 h, toluene	16	**1a** (5), **7** (0), **14** (3)	1.7
5	**10**	130 °C, 2 h, diglyme	47	**1a** (0), **7** (0), **14** (13)	0

Precursor (0.10 mmol) in a 5 ml solvent was heated under nitrogen and the resulting reaction mixture was analyzed by ^{1}H NMR (300 MHz). DME: dimethoxyethane.

(9–8%) and **7** (0.5%) at the early stage of photolysis (Table 1, entry 1 and 3).

3.4. Thermolysis of precursors 9a and 10

It is important to compare the results obtained by different methods. Thus, we sought to generate carbene **8** independently by thermolysis of precursors **9a** and **10**. When sodium salt **9a** was heated to 150 °C for 5 min without solvent, **1a** (2%) and butadiene **14** (6%) were produced (Table 3, entry 1). With diglyme as a solvent remarkable increase in the yield of **14** (83%) was observed (entry 2). Control experiment suggests that cyclobutene **7** is labile at the thermolysis temperature and undergo facile ring opening to give butadiene **14**. Therefore, the preference in the product distribution should be discussed in terms of the ratio **1a**/(**7** + **14**).

When iminocyclobutane **10** in dimethoxyethane was heated to reflux (83 °C) for 8 h, formation of cyclobutene **7** was observed (entry 3). It is noteworthy that no formation of **1a** was detected under the condition. In toluene at reflux temperature, **1a** and butadiene **14** were produced in comparable yields (entry 4) but with diglyme as a solvent, **14** was found to be the exclusive product (entry 5). It is evident that preference in the product distribution is strongly dependent on the conditions, particularly

solvents used. Indeed, the ratios **1a**/(**7** + **14**) turned out to be 0 or 1.7 depending on the solvent.

These results are reminiscent of a polar transition state for the 1,2-H shift in 1-phenylethylidene suggested by Sugiyama et al. [26], in which corresponding rate can be accelerated by more than a factor of 30 in polar acetonitrile. On the other hand, remarkable rate enhancement was also observed for not only 1,2-H shift but also 1,2-C shift of parent cyclobutylidene in a polar solvent [23]. 1,2-C shift is rather special for parent cyclobutylidene, because it rearranges through a dipolar, non-classical transition state according to theoretical calculations [27]. It is conceivable that two phenyl groups in cyclobutylidene **8** bring about a sizable effect on its transition state structure to reduce the dipolar nature. Eventually, the 1,2-C shift process in **8** can be less sensitive to solvent polarity whereas the 1,2-H shift remains to be accelerated by a polar solvent such as acetonitrile. Consequently, the ratios **1a**/(**7** + **14**) are significantly lower than the value of 4.0 for parent cyclobutylidene.

If the observed range of values, 0–1.7, is taken into account, formation of cyclobutene **7** in 0.5% would require generation of cyclobutylidene **8** in 0.5–1.35%, which corresponds to 10–45% of the yield of **2a** (3–5%) at the early stage of photoreaction of **1a** (Table 1, entry 1 and 3). In other words, the efficiency of 1,2-shift pathway to generate **8** (Scheme 3,

Table 4
Thermal reaction of 2,2-diphenlymethylenecyclopropane **1a**
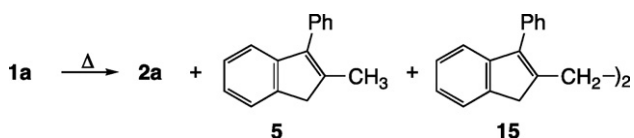
Entry	Conditions	Time (h)	Conv. (%)	Products (yield/%)
1	140 °C, neat	6	10	**2a** (trace), **5** (2), **15** (trace)
2	150 °C, diglyme (5 ml)	0.5	ca. 5	**2a** (0), **5**(trace)
3	150 °C, neat	6	42	**2a** (trace), **5** (5), **15** (5)
4	160 °C, diglyme (5 ml)	2	92	**2a** (2), **5** (48), **15** (4)
5	160 °C, diglyme (5 ml)	5	99	**2a** (6), **5** (36), **15** (5)
6	160 °C, diglyme (10 ml)	6	99	**2a** (11), **5**(56), **15**(17)

Compound **1a** (0.10 mmol) was heated for a specified period of time. After workup, the resulting reaction mixture was analyzed by ^{1}H NMR (300 MHz).
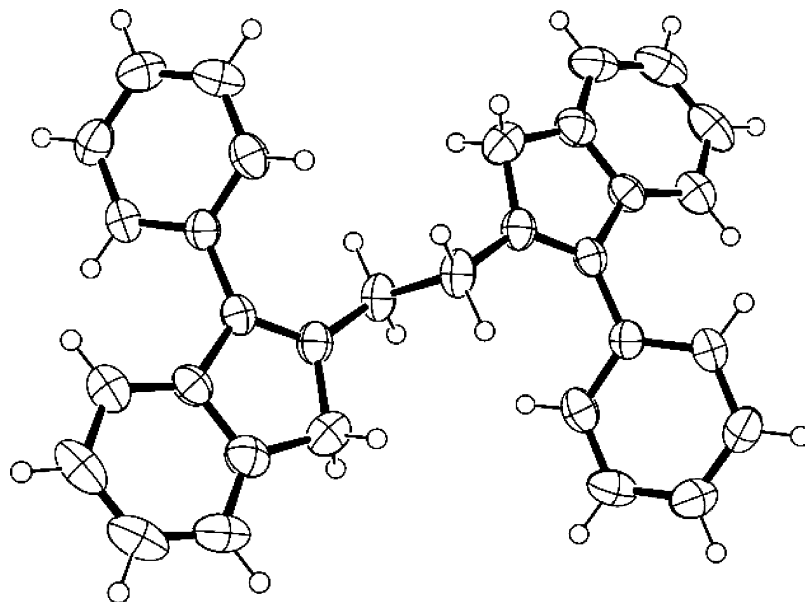
Fig. 2. ORTEP drawing of **15**. Monoclinic, $P2_1/a$ (#14), $Z = 2$, $R = 0.064$, $a = 7.0349(1)$ Å, $b = 15.9261(7)$ Å, $c = 10.6489(2)$ Å, $\beta = 106.317(2)°$, $V = 1145.03(6)$ Å^3.

b) is as high as 17–47% relative to 1,3-C shift to give **2a** (Scheme 3, a).

3.5. Thermal reaction of 2,2-diphenlymethylenecyclopropane 1a

2,2-Diphenlymethylenecyclopropane **1a** is reported to undergo thermal rearrangement to indene **5** at 135–140 °C [8]. However, details including the yield of **5** were not mentioned in the literatures. Although no formation of indene **5** was detected in the thermolytic experiments with precursors **9a** and **10** (Table 3), it does not necessarily mean that **1a** is stable under the conditions. It is important to examine the thermal stability of **1a** independently in order to assure the ratios **1a**/(**7 + 14**) observed in Table 2 and 3. Thus, preliminary thermolytic experiments with **1a** were carried out and the results are summarized in Table 4.

The first three sets of experiments (entries 1–3) suggest that marginal temperature is 150 °C, at which precursor **9** was decomposed to give methylenecyclopropane **1a** and butadiene **14**. However, it is shown that at least 58% of **1a** could survive with formation of indene **5** (5%) in a limited amount (entry 3). At higher temperature (160 °C), it was easily shown that indene **5** is not the sole product and that **1a** does undergo structural isomerization to **2a** (entry 4–6), which is to revise the earlier results. The observed yields themselves are not high because competing rearrangement to **5** is much faster. Also unexpected but interesting is the formation of coupling product **15**, whose structure was unequivocally determined by X-ray crystallography (Fig. 2). Although product **15** appears to be structurally related to indene **5**, control experiments suggest that they do not interconvert each other under the conditions for their formation. We note that nitrogen saturation sometimes leads to suppressed formation of **15**. However, it is not always reproducible and oxygenation does not necessarily increase the yield of **15**.
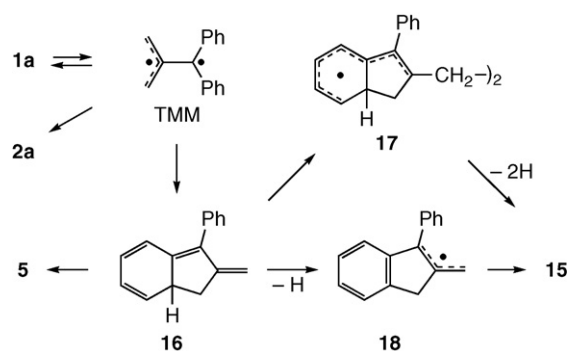
Scheme 4.

Since we have shown the thermal rearrangement from **1a** to **2a**, it is mechanistically economical to postulate a trimethylenemethane type of species (TMM) as a common intermediate for degeneracy, interconversion between **1a** and **2a**, and formation of tetraene **16** (Scheme 4). As already proposed [8b], tetraene **16** should be an important precursor to indene **5**. It is also conceivable that oxygen play a subtle and important role for the oxidative coupling of tetraene **16** leading to the formation of **15**. Dimeric coupling of tetraene **16** and dehydrogenation of the resulting dimer **17** would afford final product **15**. Another possibility for production of **15** is that formation of radical **18** by dehydrogenous oxidation of **16** is followed by the dimerization.

4. Conclusions

Present studies on the photochemistry and thermal reaction of methylenecyclopropane **1a** revealed the formation of new key products and made important additions and revisions in their mechanisms. In the photochemistry of methylenecyclopropane **1a**, a 1,2-C shift pathway (Scheme 3, arrow b) followed by 1,2-H shift of the resulting cyclobutylidene intermediate **8** is postulated to be operative as a new additional

process. In the thermal reaction of **1a**, on the other hand, a trimethylenemethane type of species (TMM) is proposed to be a common intermediate for degeneracy, rearrangement from **1a** to **2a**, and formation of tetraene **16** (Scheme 4). Tetraene **16** would produce indene **5** and coupling product **15**. LFP experiments with precursor **10** showed that cyclobutylidene **8** is a detectable species with an estimated lifetime of ca. 1 ns, which is slightly shorter than that of parent cyclobutylidene (4–20 ns in cyclohexane). A series of experiments designed to independently generate cyclobutylidene **8** provided the methylenecyclopropane/cyclobutene branching ratio (**1a/7**) to be in the range between 0 and 1.7, which is much lower than the value of 4.0 for parent cyclobutylidene. If the observed range of values, 0–1.7, is taken into account, formation of cyclobutene **7** in 0.5% would require generation of cyclobutylidene **8** in 0.5–1.35%, which corresponds to 10–45% of the yield of **2a** at the early stage of photoreaction of **1a**. In other words, the relative efficiency of 1,2-shift pathway to generate **8** is as high as 17–47% relative to 1,3-C shift to give **2a**.

Acknowledgment

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