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Intermediacy of cyclobutylidene in photochemical methylenecyclopropane rearrangement

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Abstract—Methylenecyclopropane **1** undergoes photochemical rearrangement to **2**. Intervention of cyclobutylidene **3** explains not only the rearrangement but also newly obtained products such as cyclobutene **4** and cyclobutylidenecyclobutane **6**. Experiments designed to generate cyclobutylidene **3** independently have provided some support for the intermediacy of **3**.

In contrast to abundant pyrolytic chemistry[1] of methylenecyclopropanes, their photochemistry[2–5] is rather sparse and awaits further investigations, particularly for direct excitation.[2,3] We have revisited the photochemistry of methylenecyclopropanes **1** and **2** in order to assess their utility as photochemical precursor to vinylidenes,[3] and found that their photochemistry is more intricate than it appeared. Expansion of our initial interest has prompted us to develop new facts in the photochemistry of **1**, which suggest the intermediacy of cyclobutylidene **3** in the photoprocess.

Photoirradiation (λ >250 nm) of a 3 ml acetonitrile solution of **1** (0.20 mmol) in a quartz tube under nitrogen led to formation of rearranged product **2** (29%) and 1,1-diphenylethylene (<1%) with recovery of **1** (45%). This result is virtually consistent with the previous report[2] and it appears to be an example of photochemical 1,3-C shift. On the other hand, careful ^{1}H NMR analysis of the reaction mixture suggested formation of additional new products albeit in much lower yields. Two compounds were isolated by repeated preparative TLC of combined reaction mixtures obtained from multiplicative irradiations. They were identified as cyclobutene **4** and cyclobutanone **5** by comparison of their spectroscopic data with those of the authentic samples synthesized independently.[6] Cyclobutene **4** was confirmed to be stable under the photolytic conditions.

With ether or cyclohexane as a solvent for photolysis of **1**, lower yields of **2** (8% or 2%, respectively) were obtained with significant amount of recovered **1** (79% or 94%, respectively). Similar photoirradiation of **1** in oxygen-saturated acetonitrile resulted in significant increase in the yield of cyclobutanone **5** (10%) with formation of **2** (39%) and a smaller amount of recovered **1** (10%). It is by no means obvious that cyclobutene **4** and cyclobutanone **5** are structurally connected to **1** by 1,3-C shift or trimethylenemethane type intermediate.

Mechanistically more suggestive results were provided by solid-state photolysis of **1**. Thus, when finely powdered **1** was photoirradiated, a dimeric product ($M^+ = 412$) was obtained in 3% yield together with **2** (4%), 1,1-diphenylethylene, and unreacted **1** (91%). Prolonged photolysis caused further consumption of the starting material but resulted in no increase in the yield of the dimeric product. The spectroscopic data[7] suggest the new product to be a cyclobutylidenecyclobutane **6**. The unique structure was established based on the spectral comparison with the independently synthesized material and the geometry was unequivocally determined to be *trans* by X-ray crystallographic analysis (Fig. 1).

These results led us to consider the intermediacy of 2,2-diphenylcyclobutylidene **3** in addition to a 1,3-shift pathway in the photoreaction scheme of **1** (Scheme 1). A simple and feasible mechanism for the generation of 2,2-diphenylcyclobutylidene **3** from **1** is the photochemical 1,2-C-shift with respect to the C1–C2 bond of **1**. Since parent cyclobutylidene is known to undergo

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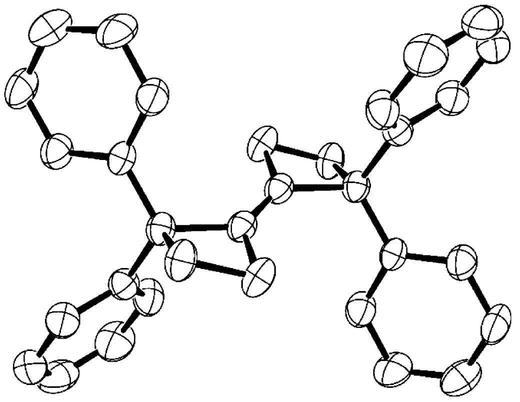


Figure 1. ORTEP drawing of **6**. Triclinic, P-1 (#2), $Z = 1$, $R = 0.088$, $a = 7.430(2)$ Å, $b = 7.538(1)$ Å, $c = 10.781(2)$ Å, $\alpha = 84.475(7)°$, $\beta = 85.988(6)°$, $\gamma = 83.07(1)°$, $V = 595.6(2)$ Å^3. Hydrogen atoms are omitted for clarity.

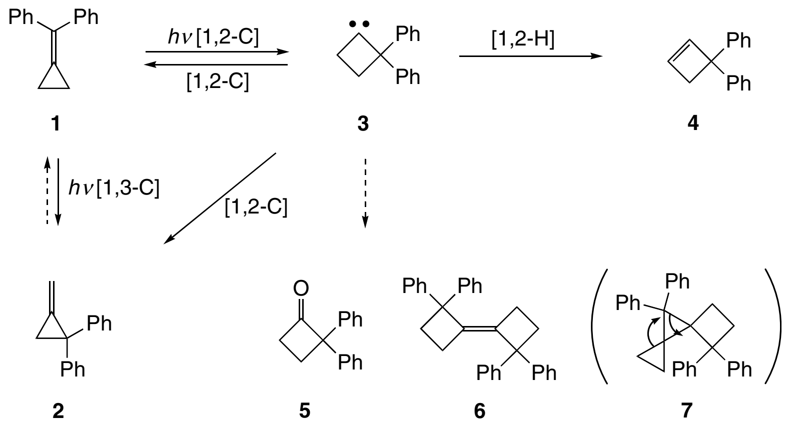
preferential 1,2-C shift to form methylenecyclopropane over 1,2-H shift to form cyclobutene,[12–15] intervention of 2,2-diphenylcyclobutylidene **3** would rationally explain the observed rearrangement of **1** to **2** with formation of cyclobutene **4** as a minor product.

There have been several comparable precedents for photochemical 1,2-C and 1,2-H migrations of alkenes. For example, Kropp and co-workers have reported evidence for carbene intermediates in the photochemistry of tetraalkyl alkenes and proposed the involvement of π,R(3s) Rydberg excited state for the occurrence of 1,2-C shift.[8] Similar rearrangement of cycloheptene to give methylenecyclohexane and bicyclo[4.1.0]heptane through a photogenerated cyclohexylcarbene intermediate is reported by Inoue and co-workers.[9] Later, Hixson reported photochemical 1,2-H-shift to generate carbenes from phenylalkenes.[10] Recent laser flash photolysis studies on phenylallenes have indicated that vinylcarbenes, generated by photochemical 1,2-H shift of phenylallenes, are protonated by alcohols to give allyl cations.[11]

Since it is important to know the reactivity of **3** itself in terms of branching ratio for two types of 1,2-C shifts and 1,2-H shift, we sought to generate carbene **3** independently by thermolysis and photolysis of typical precursors such as tosylhydrazone sodium salt[16] and oxadiazoline.[15,17] Thus, potential precursors, **8** and **9** were synthesized to examine. When sodium salt **8** was heated to 150 °C for 15 min, **1** (84%) and **2** (2.6%) were produced (Table 1). Comparable result was obtained with diglyme as a solvent. Again, no formation of cyclobutene **4** was detected by ^{1}H NMR. It turned out, however, that no appropriate judgment could be made as to the ratio of 1,2-C/1,2-H because control experiments showed that cyclobutene **4** decomposes easily under the thermolysis conditions. On the other hand, photolysis of a solution of sodium salt **8** in dimethoxyethane afforded a mixture of **1** (54%), **2** (9.6%),[18] and cyclobutene **4** (3.3%). Similar photolysis of oxadiazoline **9** resulted in **1** (97%) and relatively lower yield of **2** (1.6%) and cyclobutene **4** (<1%). In either case, no formation of dimer **6** was detected.

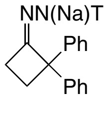
The observed preference for 1,2-C (**1**+**2**) over 1,2-H migration (**4**) in the photolysis of **8** and **9** is similar or maybe more pronounced than that observed for a parent system.[12,13] Indeed, it explains formation of cyclobutene **4** in much lower yield relative to **2** in the photoreaction of **1**. According to the recent calculation by Sulzbach et al.,[14] singlet cyclobutylidene possesses a non-classical bicyclic structure and the transition state for 1,2-C migration is only 10.5 kcal mol^{-1} above the ground state. Because of the structural similarity between the ground-state geometry of singlet cyclobutylidene and the transition state for 1,2-C migration, the 1,2-C rearrangement becomes quite facile with respect to 1,2-H migration.

In view of considerably high **1**/**2** ratio in the 1,2-C migrations (Table 1), significant fraction of cyclobutylidene **3** generated by direct excitation of **1** would rearrange back to **1**. It is evident that the phenyl groups would lend a strong directing effect to carbene **3** by stabilizing the transition state for formation of **1** from **3**, leading to preferential formation of **1**. In contrast, the other type of 1,2-C migration process, leading to **2**, would be affected rather limitedly by the phenyl groups, so that the rate can be slightly higher than that of the parent. Thus, the observed **1**/**2** ratio ranging from 5.6

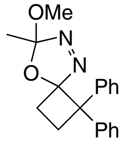


Scheme 1.

Table 1. Photolysis and thermolysis of **8** and **9**



8



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Entry	Precursor	Conditions	Conv. (%)	Products (yield (%))
1	**8**	150 °C, 5 min, no solvent	95	**1** (84), **2** (2.6), **5** (<1)
2	**8**	150 °C, 5 min, diglyme	99	**1** (89), **2** (1.8), **5** (<1)
3	**8**	*hν*, 7 h, dimethoxyethane	97	**1** (54), **2** (9.6), **4** (3.3), **5** (<1)
4	**9**	*hν*, 5 h, dimethoxyethane	100	**1** (97), **2** (1.6), **4** (<1), **5** (<1)

Precursor (0.20 mmol) was heated or irradiated ($\lambda > 300$) under nitrogen and the resulting reaction mixture was analyzed by ^{1}H NMR (300 MHz).

to 61 may lead to a rough estimate that the rate of 1,2-C migration of **3** to **1** would be at least 5.6–61 times faster than that of the parent. In other words, 2,2-diphenylcyclobutylidene **3** would have 5.6–61 times shorter lifetime relative to that of the parent; reportedly 4–20 ns in cyclohexane-d_{12} and 0.3–1 ns in acetonitrile, respectively.[15]

In this regard, the lifetime of **3** may be practically too short to react with **1** in solution to form an adduct such as **7**, whose spiropentane–methylenecyclobutane-type skeletal rearrangement can explain the formation of dimer **6**. However, formation of adduct **7** may be marginally possible in the solid-state photolysis of **1**, particularly when crystal structure of **1** adopts special molecular orientation and packing.

Another possibility is the involvement of triplet state of **3**. Recent theoretical calculations for parent cyclobutylidene suggest that its triplet state is thermally accessible because the singlet–triplet energy separation ($\Delta E_{\text{S-T}} = -5.9$ kcal mol^{-1}) is smaller than the barriers to 1,2-C and 1,2-H migrations to methylenecyclopropane and cyclobutene, respectively.[19] It may be an interesting interpretation that formation of cyclobutanone **5** is also an indication of intervening triplet state of **3**. At this stage, however, this point is yet to be fully investigated.

Acknowledgements

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6. Cyclobutene **4** was synthesized by the reaction of *n*-BuLi with tosylhydrazone of cyclobutanone **5**. Cyclobutanone **5** was synthesized by the oxidation of **1** with MCPBA.
7. Data of **6**: mp 176.2–176.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 7.34–7.31 (m, 8H), 7.26–7.22 (m, 12H), 2.63 (t, $J = 8.1$ Hz, 4H), 2.21 (t, $J = 8.1$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) 146.34 (4C, Ph), 139.61 (2C, C=C), 128.06 (8C, Ph), 128.02 (8C, Ph), 125.94 (4C, Ph), 60.21 (2C, $>CPh_2$), 35.15 (2C, CH_2), 25.62 (2C, CH_2); MS (EI) $m/z = 412$ (M^+), 204 (100%). HRMS $m/z = 412.2197$, calcd. for $C_{32}H_{28} = 412.2191$.
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18. The (**1**+**2**)/**4** ratio and **1**/**2** ratio observed in entry 3 is not so high compared to other cases. This may be due to involvement of excited-state diazo compound. Detail will be subjected to further investigations. For excited-state diazo compounds, see Refs. 15 and 16c, and the references cited therein.

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