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Photorearrangement of Vinylidenecyclopropanes to 1,2,3-Butatriene Derivatives

Kazuhiko Mizuno,* Hajime Maeda, Hikaru Sugita, Shogo Nishioka, Takayoshi Hirai, and Akira Sugimoto

Department of Applied Chemistry, Graduate School of Engineering,
Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

mizuno@chem.osakafu-u.ac.jp

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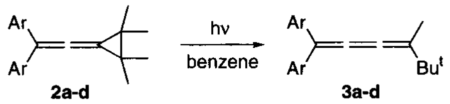
ABSTRACT

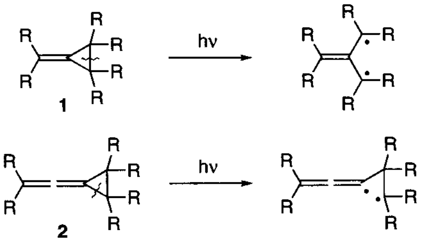


a: Ar = Ph, **b**: Ar = p-ClC$_6$H$_4$, **c**: Ar = p-MeOC$_6$H$_4$, **d**: Ar = p-MeC$_6$H$_4$

Photoirradiation of benzene solutions containing 1-diarylvinylidene-2,2,3,3-tetramethylcyclopropanes (2a–d) afforded rearranged products 1,2,3-butatrienes (3a–d) in good to high yields. Photorearrangement from 2,2,3-trimethyl and 2,2- and 2,3-dimethyl derivatives 2e–g also proceeded, but the rates of the rearrangement were lower than those of 2a–d. A singlet mechanism is proposed for this photorearrangement, where alkyl migration occurs from 1,3-biradical intermediates generated via the homolysis of the C1–C2 bond. Generation of diarylvinylidene carbenes from 1,3-biradicals might be competitive with the formation of 3.

Photochemical reactivities of methylenecyclopropanes (**1**) have attracted much attention from mechanistic, theoretical, spectroscopic, and synthetic viewpoints since the middle of the 20th century.[1] Carbon−carbon bond cleavage of methylenecyclopropane derivatives usually occurs at C2−C3 bonds; hence they isomerize via trimethylenemethane biradical intermediates or via trimethylenemethane radical cations formed by photoinduced electron transfer (Scheme 1). On the other hand, the photochemical behavior of vinylidenecyclopropanes (**2**) has been less reported, although we have recently reported a few examples of thermal[2] and photochemical[3] ring cleavage of vinylidenecyclopropanes (**2**), where the ring cleavage at C1−C2 bond of **2** might occur. Here we report an unprecedented photorearrangement from **2** to 1,2,3-butatriene derivatives (**3**) via C1−C2 bond cleavage, accompanied by the generation of vinylidene carbenes.

Scheme 1



Irradiation of a benzene solution of 1-(2′,2′-diphenylvinylidene)-2,2,3,3-tetramethylcyclopropane (**2a**, 0.03 mol dm^{-3})[4] through a Pyrex filter (>280 nm light) under argon

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(1) (a) Miyashi, T.; Ikeda, H.; Takahashi, Y.; Akiyama, K. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; Jai Press Inc.: Stamford, 1999; Vol. 6, pp 1−39. (b) Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799−807. (c) Kende, A. S.; Goldschmidt, Z.; Smith, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 7606−7607. (d) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511−6513.

(2) Mizuno, K.; Sugita, H.; Kamada, T.; Otsuji, Y. *Chem. Lett.* **1994**, 449−452.

(3) (a) Mizuno, K.; Sugita, H.; Isagawa, K.; Goto, M.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 5737−5738. (b) Mizuno, K.; Nire, K.; Sugita, H.; Otsuji, Y. *Tetrahedron Lett.* **1993**, *34*, 6563−6566. (c) Mizuno, K.; Sugita, H.; Hirai, T.; Maeda, H. *Chem. Lett.* **2000**, 1144−1145.

(4) We have developed a convenient method for the synthesis of vinylidenecyclopropanes: Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2283−2285.

10.1021/ol000379u CCC: $20.00

Scheme 2

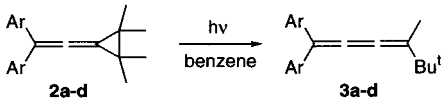


Table 1. Photorearrangement of **2a**−**d** to **3a**−**d**[a]

entry	substrate	Ar	product	isolated yield (%)	Φ[b]
1	**2a**	C_6H_5	**3a**	55	0.008
2	**2b**	*p*-ClC_6H_4	**3b**	85	0.016
3	**2c**	*p*-$MeOC_6H_4$	**3c**	45	0.008
4	**2d**	*p*-MeC_6H_4	**3d**	62	0.017

[a] [**2**] = 3.0×10^{-2} mol dm^{-3} in benzene. [b] Quantum yield for the formation of **3** at 313 nm irradiation ([**2**] = 9.5×10^{-5} mol dm^{-3} in benzene).

atmosphere gave 1,1-diphenyl-4,5,5-trimethyl-1,2,3-hexatriene (**3a**)[5] in a 55% isolated yield (Scheme 2, Table 1). Similar irradiation of *p*-chloro, *p*-methoxy, and *p*-methyl derivatives **2b**−**d** afforded the corresponding 1,2,3-butatrienes **3b**−**d** in good to high yields.[6] Quantum yields for the formation of **3a**−**d** were 0.008−0.017 at 313 nm. Structures of products were determined by their spectral data and confirmed by X-ray analysis of *p*-chloro derivative **3b** (Figure 1).

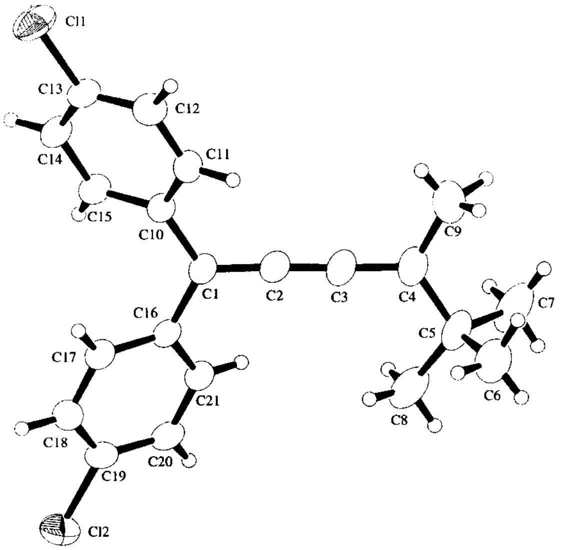


Figure 1. ORTEP drawing of **3b**. Monoclinic, $P2_1/c$ (No. 14), $Z = 4$, $R = 0.043$, $a = 7.6341(9)$ Å, $b = 21.718(2)$ Å, $c = 11.394(2)$ Å, $\beta = 97.61(1)°$, $V = 1872.6(4)$ Å^3. Selected bond lengths: C1−C2, 1.341(4) Å; C2−C3, 1.241(4) Å; C3−C4, 1.334(4) Å. Selected bond angles: C1−C2−C3, 177.5(3)°, C2−C3−C4, 177.9(4)°.

The linear structure of **3b** is shown in the ORTEP drawing indicating a 1,2,3-butatriene structure. The bond length between two central carbons (C2 and C3) is 1.241 Å, which is shorter than those of ethylene (1.339 Å) and allene (1.308 Å) but longer than that of acetylene (1.202 Å). UV−vis spectrum of **3** showed a characteristic absorption maximum at 340 nm assigned to a 1,1-diaryl-1,2,3-butatriene structure.[5]

The time-dependent UV spectrum for the irradiation of **2a** showed spectral change from **2a** to **3a** with three isosbestic points at 240, 265, and 310 nm, which indicated that **3a** was the sole product in the photoreaction of **2a** (Figure 2a).[7] Similar photorearrangement from 2,2,3-trimethyl and 2,2- and 2,3-dimethyl derivatives **2e**−**g** also proceeded as indicated by the UV spectral changes (Figure 2b−d), but the rates for the formation of the corresponding 1,2,3-butatrienes were quite low ($\Phi < 10^{-3}$) and products were not isolated.[8]

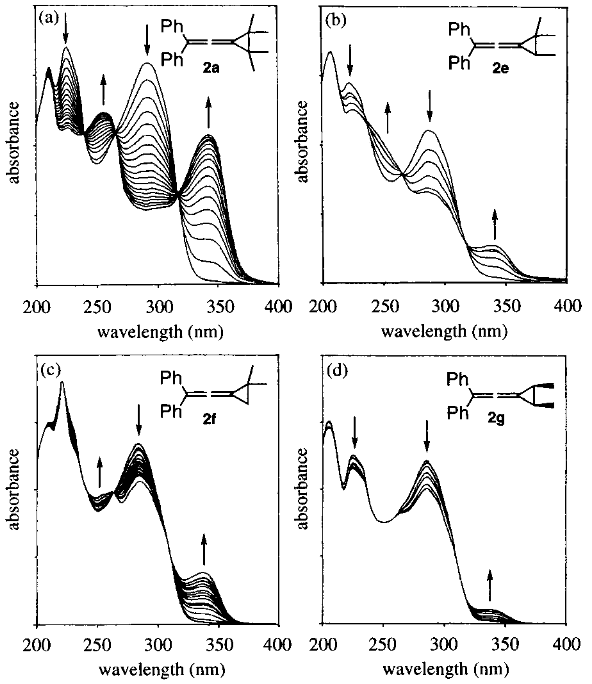
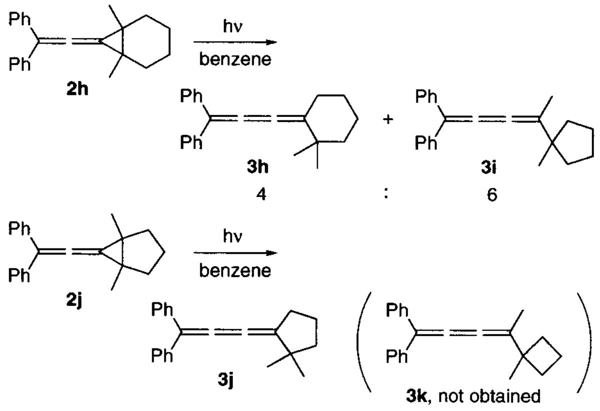


Figure 2. UV spectral changes in the photorearrangement of vinylidenecyclopropanes **2a**, **2e**−**g** to 1,2,3-butatriene derivatives **3a**, **3e**−**g**. Direct irradiation of cyclohexane solutions (1.0×10^{-4} mol dm^{-3}) of (a) **2a** at 3 min intervals, (b) **2e** at 10 min intervals, (c) **2f** at 30 min intervals, and (d) **2g** at 30 min intervals.

The bicyclic vinylidenecyclopropanes **2h** and **2j** also rearranged to the 1,2,3-butatriene derivatives (Scheme 3). The former gave **3h** and **3i** in a 4:6 ratio, and the latter gave **3j** exclusively. This is reasonably explained in terms of the higher strain energy of the cyclobutane ring of **3k**.

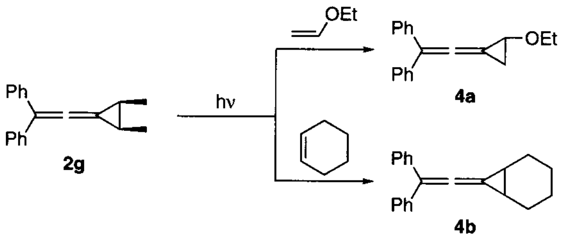
The photorearrangement of **2** was not sensitized by triplet sensitizers such as benzophenone and Michler's ketone and was not quenched by 2-methyl-1,3-butadiene or molecular dioxygen. Photoirradiation of **2a**−**d** in methanol did not disturb this rearrangement, and no methanol-incorporated product was obtained. Irradiation of 2,3-dimethyl derivative **2g** in the presence of a large excess of ethyl vinyl ether gave

Scheme 3



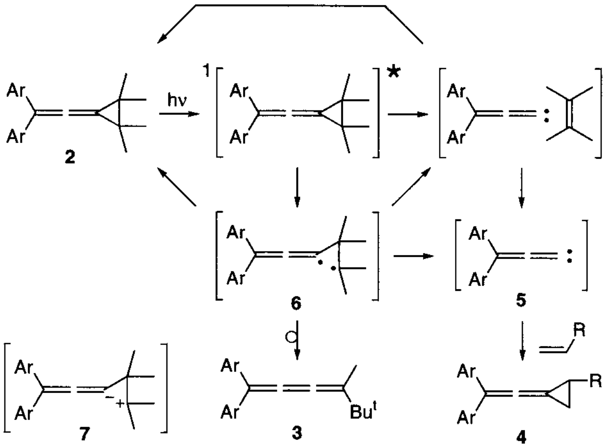
2-ethoxy-1-(diphenylvinylidene)cyclopropane **4a** in a 25% isolated yield (Scheme 4). Similar irradiation of **2g** in the presence of cyclohexene gave the corresponding vinylidenecyclopropane **4b**, although the yield was low. These results clearly demonstrate the formation of diphenylvinylidene carbene **5**, which is trapped by alkenes.[9] This carbene was not generated by the triplet sensitization.

Scheme 4



On the basis of these results, we propose a singlet mechanism for the formation of 1,2,3-butatriene derivatives and the generation of vinylidene carbenes as shown in Scheme 5. Homolysis of the C1−C2 bond of **2** occurs via the excited singlet state of **2** generated by the direct irradiation to give singlet 1,3-biradical intermediate **6**.[3c] This biradical intermediate **6** smoothly rearranges to 1,2,3-butatriene **3** by the migration of an alkyl group. An alternative pathway via heterolytic cleavage of the C1−C2 bond of **2** to give dipolar intermediate **7** seems unlikely. The formation of vinylidene carbene **5** might be a competitive pathway for this rearrangement, although it is not clear at this stage whether **5** is produced via **6** or a concerted two

Scheme 5



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(5) For synthesis of 1,2,3-butatrienes: (a) Kajigaeshi, S.; Kuroda, N.; Matsumoto, G.; Wada, E.; Nagashima, A. *Tetrahedron Lett.* **1971**, 4887−4888. (b) Yoshida, T.; Williams, R. M.; Negishi, E. *J. Am. Chem. Soc.* **1974**, *96*, 3688−3690. (c) Bee, L. K.; Beeby, J.; Everett, J. W.; Garratt, P. J. *J. Org. Chem.* **1975**, *40*, 2212−2214. (d) Bestmann, H. J.; Schmid, G. *Tetrahedron Lett.* **1975**, 4025−4026. (e) Visser, R. G.; Brandsma, L.; Bos, H. J. T. *Tetrahedron Lett.* **1981**, *22*, 2827−2828. (f) Kleijn, H.; Tigchelaar, M.; Bullee, R. J.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *J. Organomet. Chem.* **1982**, *240*, 329−333. (g) Iyoda, M.; Tanake, S.; Nishioka, K.; Oda, M. *Tetrahedron Lett.* **1983**, *24*, 2861−2864. (h) Iyoda, M.; Nishioka, K.; Nose, M.; Tanaka, S.; Oda, M. *Chem. Lett.* **1984**, 131−134. (i) Angus, R. O., Jr.; Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 2880−2883. (j) Iyoda, M.; Sakaitani, M.; Miyazaki, T.; Oda, M. *Chem. Lett.* **1984**, 2005−2006. (k) Nader, F. W.; Wacker, C.-D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 851−852. (l) Fritch, J. R.; Vollhardt, K. P. C. *Isr. J. Chem.* **1985**, *26*, 131−135. (m) Sakurai, H.; Kudo, M.; Sakamoto, K.; Nakadaira, Y.; Kira, M.; Sekiguchi, A. *Chem. Lett.* **1988**, 1441−1444. (n) Weber, E.; Seichter, W.; Wang, R.-J.; Mak, T. C. W. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 659−667. (o) Negishi, E.; Yoshida, T.; Abramovitch, A.; Lew, G.; Williams, R. M. *Tetrahedron* **1991**, *47*, 343−356. (p) Morken, P. A.; Baenziger, N. C.; Burton, D. J.; Bachand, P. C.; Davis, C. R.; Pedersen, S. D.; Hansen, S. W. *J. Chem. Soc., Chem. Commun.* **1991**, 566−567. (q) Herges, R.; Hoock, C. *Synthesis* **1991**, 1151−1152. (r) Komatsu, K.; Kamo, H.; Tsuji, R.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 3219−3221. (s) Morken, P. A.; Bachand, P. C.; Swenson, D. C.; Burton, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 5430−5439. (t) Chow, H.-F.; Cao, X.-P.; Leung, M. *J. Chem. Soc., Chem. Commun.* **1994**, 2121−2122. (u) Ogasawara, M.; Ikeda, H.; Ohtsuki, K.; Hayashi, T. *Chem. Lett.* **2000**, 776−777.

(6) Data for **3b**: mp 129−130 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.26−7.40 (m, 8 H), 2.06 (s, 3 H), 1.20 (s, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 158.9, 150.4, 137.4, 133.2, 132.7, 129.9, 129.5, 128.7, 128.6, 109.9, 109.3, 38.0, 29.5, 20.4; IR (neat) 2962, 2044, 1903, 1604, 1485 cm^{-1}; UV (cyclohexane) $\lambda_{\max} = 268$, 345 nm; MS (EI) $m/z = 343$ (M$^+$).

(7) This is also supported by time-dependent ^{1}H NMR studies in benzene-d_6. The allenyl absorption band of **2** at ca. 1970 cm^{-1} disappeared upon irradiation, and a new absorption band appeared at ca. 2050 cm^{-1} characterized to the 1,2,3-butatriene structure.

(8) In the reaction of **2g**, ^{1}H NMR and IR spectra showed that the *cis*−*trans* isomerization is a major pathway along with the formation of 1,2,3-butatriene as a minor extent. See ref 3c.

(9) For generation and trapping of vinylidene carbenes: (a) Hartzler, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 4990−4996. (b) Hartzler, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 4997−4999. (c) Hartzler, H. D. *J. Org. Chem.* **1964**, *29*, 1311−1312. (d) Crombie, L.; Griffiths, P. J.; Walker, B. J. *Chem. Commun.* **1969**, 1206−1207. (e) Craig, J. C.; Beard, C. D. *Chem. Commun.* **1971**, 691−692. (f) Craig, J. C.; Beard, C. D. *Chem. Commun.* **1971**, 692−693. (g) Patrick, T. B. *Tetrahedron Lett.* **1974**, 1407−1408. (h) Sasaki, T.; Eguchi, S.; Ogawa, T. *J. Org. Chem.* **1974**, *39*, 1927−1930. (i) Beard, C. D.; Craig, J. C.; Solomon, M. D. *J. Am. Chem. Soc.* **1974**, *96*, 7944−7949. (j) Beard, C. D.; Craig, J. C. *J. Am. Chem. Soc.* **1974**, *96*, 7950−7954. (k) Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 6478−6481. (l) Sasaki, T.; Eguchi, S.; Ohno, M.; Nakata, F. *J. Org. Chem.* **1976**, *41*, 2408−2411. (m) Patrick, T. B.; Schmidt, D. J. *J. Org. Chem.* **1977**, *42*, 3354−3356. (n) Harada, T.; Nozaki, Y.; Oku, A. *Tetrahedron Lett.* **1983**, *24*, 5665−5668. (o) Baird, M. S.; Buxton, S. R.; Hussain, H. H. *J. Chem. Res., Synop.* **1986**, 310−311. (p) Baird, M. S.; Hussain, H. H.; Nethercott, W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1845−1853. (q) Maier, G.; Reisenauer, H. P.; Schwab, W.; Cársky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 5183−5188. (r) Birtwistle, I.; Rogers, V. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1347−1351. (s) Sugita, H.; Mizuno, K.; Mori, T.; Isagawa, K.; Otsuji, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 984−986. (t) Dua, S.; Bowie, J. H.; Sheldon, J. C. *J. Chem. Soc., Perkin Trans. 2* **1994**, 543−546.

carbon−carbon bond cleavage of **2**. Most of **5** probably reacts with the eliminated alkene in cage to regenerate **2**. Some escaped carbene **5** attacks the added alkenes to give **4**.

In conclusion, we have developed a novel skeletal rearrangement from vinylidenecyclopropane derivatives to 1,2,3-butatrienes via the homolytic cleavage of the C1−C2 bond. This photorearrangement occurs from the excited singlet states of vinylidenecyclopropanes accompanied by the formation of vinylidenecarbenes.

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Supporting Information Available: Experimental details, spectral data of **3a−d**, and X-ray report of **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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