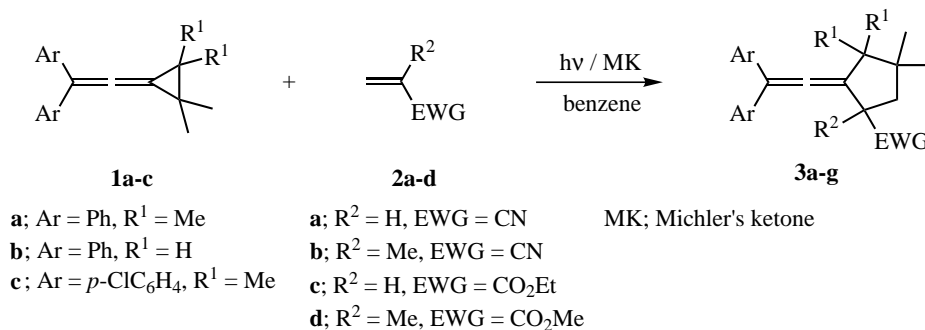


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Abstract—Irradiation of a benzene solution containing 1-diphenylvinylidene-2,2,3,3-tetramethylcyclopropane and an excess of acrylonitrile in the presence of Michler's ketone afforded 2-cyano-1-diphenylvinylidene-4,4,5,5-tetramethylcyclopentane in high yield. © 2001 Elsevier Science Ltd. All rights reserved.

In the last three decades, much attention has been focused on the photochemical reactivity of small ring compounds such as cyclopropanes, methylenecyclopropanes and so on.¹⁻⁴ From the mechanistic viewpoint, it is important to clarify the reactive species such as excited singlet and triplet states, exciplex, radical ion pairs and solvent separated radical ions. In addition, it is quite interesting to know the position of bond cleavage of small ring compounds depending on substituents, solvents and reactive species. The photoreactions of cyclopropanes and methylenecyclopropanes have excellent synthetic utility for construc-

tion of five-membered ring compounds or for introduction of a C3 unit to unsaturated compounds.²⁻⁴ However, little is known about the photoreactions of vinylidenecyclopropanes. Recently, we have reported the photorearrangements of vinylidenecyclopropanes to cyclic compounds⁵ and 1,2,3-butatriene derivatives,⁶ the (3+2) photocycloaddition of vinylidenecyclopropanes with nitriles⁷ and the *cis-trans* photoisomerization of 1-diarylvinyldiene-2,3-dimethylcyclopropanes.^{8,9} We now report a novel (3+2) photocycloaddition of diarylvinyldienecyclopropanes **1** with electron-deficient alkenes **2** to give diarylvinyldienecyclopentanes **3**.



Scheme 1.

Keywords: (3+2) photocycloaddition; vinylidenecyclopropane; electron-deficient alkene; vinylidenecyclopentane; 1,3-biradical.

* Corresponding author. Tel./fax: +81-722-54-9289; e-mail: mizuno@chem.osakafu-u.ac.jp

Table 1. (3+2) Photocycloaddition of vinylidenecyclopropanes with alkenes^a

Entry		Cyclopropane		Alkene			Product	Yield (%) ^b	Recovery of 1 (%) ^b
		Ar	R ¹	R ²		EWG			
1	1a	Ph	Me	2a	H	CN	3a	85	< 5
2	1a	Ph	Me	2b	Me	CN	3b	44	56
3	1a	Ph	Me	2c	H	CO ₂ Et	3c	32	48
4	1a	Ph	Me	2d	Me	CO ₂ Me	3d	32	49
5	1b	Ph	H	2a	H	CN	3e	71	< 5
6	1b	Ph	H	2b	Me	CN	3f	88	< 5
7	1c	<i>p</i> -ClC ₆ H ₄	Me	2b	Me	CN	3g	32	62

^a Photoirradiation was conducted by a 300 W high-pressure mercury lamp through a Uranil filter. Conditions: **1** (0.73 mmol), **2** (2 mL), MK (40 mg) in benzene (2 mL).

^b Isolated yields.

Irradiation of a benzene solution containing 1-diphenylvinylidene-2,2,3,3-tetramethylcyclopropane (**1a**)¹⁰ and a large excess of acrylonitrile (**2a**) in the presence of a small amount of Michler's ketone (MK) as a triplet sensitizer¹¹ through a Uranil filter (>320 nm light) under an argon atmosphere gave 2-cyano-1-diphenylvinylidene-4,4,5,5-tetramethylcyclopentane (**3a**) in 85% isolated yield.¹² Similar photoreactions of **1a** with methacrylonitrile (**2b**), ethyl acrylate (**2c**) and methyl methacrylate (**2d**) afforded the corresponding (3+2) photocycloadducts **3b–d** in moderate yields, respectively. The photoreactions of 1-diphenylvinylidene-2,2-dimethylcyclopropane (**1b**) and 1-bis(4-chlorophenyl)vinylidene-2,2,3,3-tetramethylcyclopropane (**1c**) with **2a–b** also afforded the corresponding (3+2) photocycloadducts **3e–g** in good to moderate yields.¹³ The results are summarized in Scheme 1 and Table 1. However, β -substituted alkenes such as crotononitrile, *trans*-1,2-dicyanoethene and *cyclo*-2-hexenone did not react with **1a**, and the starting materials were mostly recovered. Moreover, these vinylidenecyclopropanes did not react with electron-rich alkenes such as alkyl vinyl ethers, styrene derivatives, cyclohexene and 2,3-dimethyl-2-butene.

These (3+2) photocycloadducts were isolated by column chromatography on silica gel. Their structures were determined by their spectral properties (¹H NMR, ¹³C NMR, IR and mass) and elemental analyses.¹² The characteristic IR absorption spectrum of **3a** showed 2242 and 1953 cm⁻¹, which were assigned to the cyano and allenyl groups, respectively. The ¹³C NMR signal at 200.2 ppm was assigned to the central carbon of the allenyl group. Finally, the structure of **3a** was confirmed by the X-ray crystallographic analysis shown in Fig. 1.

The photoreaction did not proceed in the absence of triplet sensitizers such as MK, benzophenone and acetophenone. Pyrene having lower triplet energy did not sensitize this photocycloaddition. These results suggest that the energy gap between the excited singlet and triplet energies of **1** is large, and the intersystem crossing from the excited singlet state of **1** to its triplet state is a slow process.⁸

From these results, we propose a triplet 1,3-biradical mechanism for the (3+2) photocycloaddition of electron-deficient alkenes **2** to 1-diarylvinylidenecyclopropanes **1**, as shown in Scheme 2. The excited triplet state of **1**, which is produced by efficient energy transfer from a triplet sensitizer such as MK to **1**, generates triplet 1,3-biradical **4** through bond cleavage at the 1,2-position. This result is quite interesting because methylenecyclopropane derivatives are usually cleaved at their 2,3-positions to give trimethylenemethane intermediates as a reactive species.^{1d,4c,4d,14} The regioselective (3+2) photocycloaddition can be reasonably explained by the simple radical reactions of electron-deficient alkenes with nucleophilic radicals.¹⁶ The nucleophilic tertiary alkyl radical in the 1,3-biradical **4** attacks the β -position of the electron-deficient alkenes **2** to produce 1,5-biradical **5**, then cyclizes to diarylvinylidenecyclopentanes **3**.

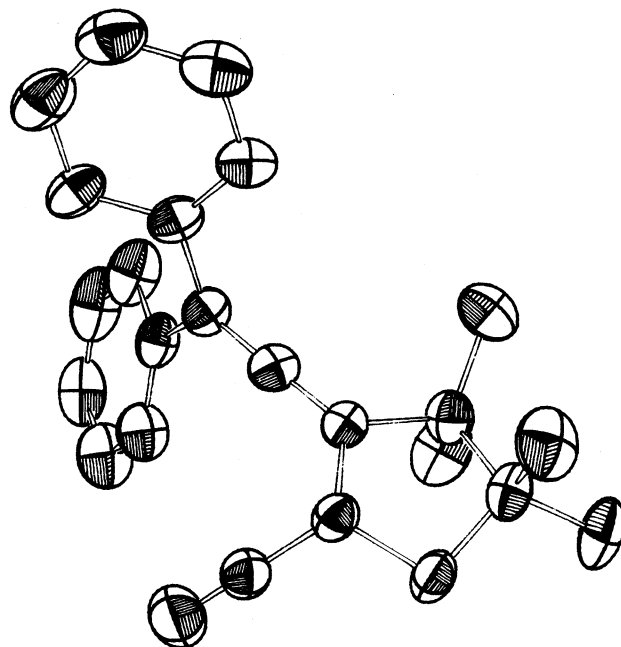
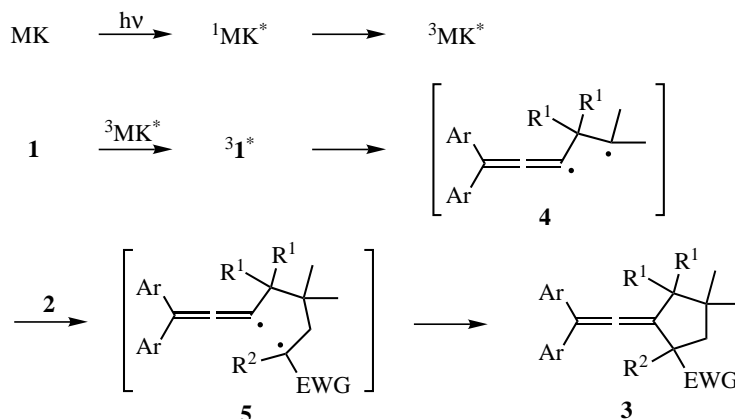


Figure 1. ORTEP drawing of **3a**. Crystal data: C₂₄H₂₅N, monoclinic,¹⁵ space group *P*2₁/*c*, *z*=4, *R*=0.103, *R*_w=0.114, *a*=9.749, *b*=21.015, *c*=9.544 Å, β =90°, *V*=1955.4 Å³, *D*_{calcd}=1.112 g/cm³. Hydrogen atoms are omitted for clarity.



Scheme 2.

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8.12; N, 3.81%. Data for **3c**: oil; ^1H NMR (270 MHz, CDCl_3) δ 0.94 (s, 3H), 1.00 (s, 3H), 1.01 (t, $J=7.3$ Hz, 3H), 1.04 (s, 3H), 1.12 (s, 3H), 1.78 (dd, $J=9.2, 12.8$ Hz, 1H), 2.23 (dd, $J=9.2, 12.8$ Hz, 1H), 3.73 (dd, $J=9.2, 9.2$ Hz, 1H), 3.99 (q, $J=7.3$ Hz, 1H), 4.03 (q, $J=7.3$ Hz, 1H), 7.19–7.36 (m, 10H); ^{13}C NMR (67 MHz, CDCl_3) δ 14.0, 22.5, 22.9, 25.1, 25.5, 41.1, 43.6, 44.8, 49.5, 60.8, 114.1, 117.0, 127.0, 127.1, 128.0, 128.2, 128.3, 128.5, 137.3, 137.7, 174.0, 200.4; IR (KBr) ν 1950, 1734 cm^{-1} ; MS (EI) m/z (%) = 91 (91), 178 (75), 215 (70), 233 (57), 285 (51), 345 (43), 374 (M^+ , 100). Anal. calcd for $\text{C}_{26}\text{H}_{30}\text{O}_2$: C, 83.38; H, 8.07; O, 8.54. Found: C, 83.13; H, 8.52%.

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