# The *exo*-Outstretching Effect Governing the Exclusive Stereoselectivity of the Intramolecular [2 + 2] Photocycloaddition of Vinylarenes

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

Intramolecular [2 + 2] photocycloaddition of a dimeric vinylpyridine **1** through a singlet-excited species efficiently formed the corresponding *syn*- and *anti*-pyridinophanes **2** and **3**. The *syn*-isomers were elucidated spectroscopically and by X-ray crystallography as *exo,syn*-configured. The high selectivity under formation of *exo,syn*-**2** was thoroughly investigated. Consequently, an *exo*-outstretching effect, which is observed around the periphery of a face-to-face-oriented system between two aromatic nuclei as a transition state, on cyclobutane ring formation was discovered for the first time.

**Introduction.** – *Rolf Huisgen* is one of the pioneers working on reaction mechanisms with the most-sophisticated methods and spectroscopic techniques available in the middle of the last century. His interest has covered reactions proceeding under non-catalytic, catalytic, thermal or photochemical conditions *etc.*¹). His careful and clear formulation of scientific arguments and statements have attracted many scientists through the generations. Moreover, in carrying out kinetics and mechanistic works, his scrutiny in the analysis of results is always understood by his co-workers, by suggesting to them not to ignore any discrepancy, tiny though it may be, which is believed to lead to some new significant discovery. In this paper, we are pleased to present some mechanistic aspects of photochemical reactions arising from a discrepancy observed at the preparative level.

Vinylarenes such as styrene have attracted much interest from photochemical and photophysical points of view [2]. Since our discovery of the facile intramolecular [2 + 2] photocycloaddition of vinylarenes towards cyclophanes in 1986, some stereoselective product formation was often observed on the cyclobutane orientation, although almost all cases show the general selectivity such as exclusive *cis*-cyclobutane ring formation and selective *syn*-arrangement of the aromatic rings. In fact, several substrates like 1-vinylnaphthalene derivatives formed an *exo*-directed cyclobutane ring exclusively, because they have vinyl groups that are entirely *exo*-directed due to the severe steric interaction between peri-H-atoms and vinyl $CH_2$ H-atoms [3]. The selectivity can be rationalized by the so-called NEER²) principle [4].

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¹) See [1]. Many examples can be found in the more than 580 papers published, a number still continuously growing.

²) Principle of 'none equilibration of excited rotamers' (NEER).

On the other hand, substrates like 2-vinylthiophene derivatives also show high stereoselectivities, affording only the *exo,syn*-isomer [5]. They have almost no preference in the vinyl group conformation at the ground state, being different from the above cases. Since the yields of 'thiophenophanes' were not high enough, no effort has been made to investigate this transformation from a mechanistic point of view.

Recently, however, we found another example of a highly stereoselective formation of cyclophane adducts from flexible vinylarene derivatives in nearly quantitative yield [6]. This result prompted us to examine the underlying stereochemical effect. In this paper, we report and discuss the stereoselectivities observed in intramolecular photoreactions of compounds having 3-vinylpyridine, styrene, and 3-methylstyrene moieties.

**Results.** – The dimeric 3-vinylpyridine derivative **1**, having a flexible ether linkage, was prepared from commercially available 2,5-dibromopyridine by a sequence of nucleophilic aromatic substitution and *Stille* coupling reactions, as summarized in *Scheme 1*. By irradiation under preparative conditions (see *Exper. Part*), it gave the *cis*-isomers [6] *exo,syn*-**2** and *anti*-**3** in 84% yield. Note that in isomer **2**, the N-atoms of the pyridine rings are *exo*-oriented relative to the cyclobutane ring. No trace of *endo,syn*-**4** was detected in the reaction mixture by analytical HPLC and NMR experiments. The result is summarized in *Scheme 2*.

Compound **5** was prepared from 4-bromophenol and 2,5-dibromopyridine (*Scheme 1*). By irradiation, it gave only isomer **6** in 78% yield (*Scheme 3*). Again, as in **2**, the N-atoms of the pyridine rings are in an *exo*-orientation relative to the formed cyclobutane ring, and the *endo*-adduct **7** was not observed.

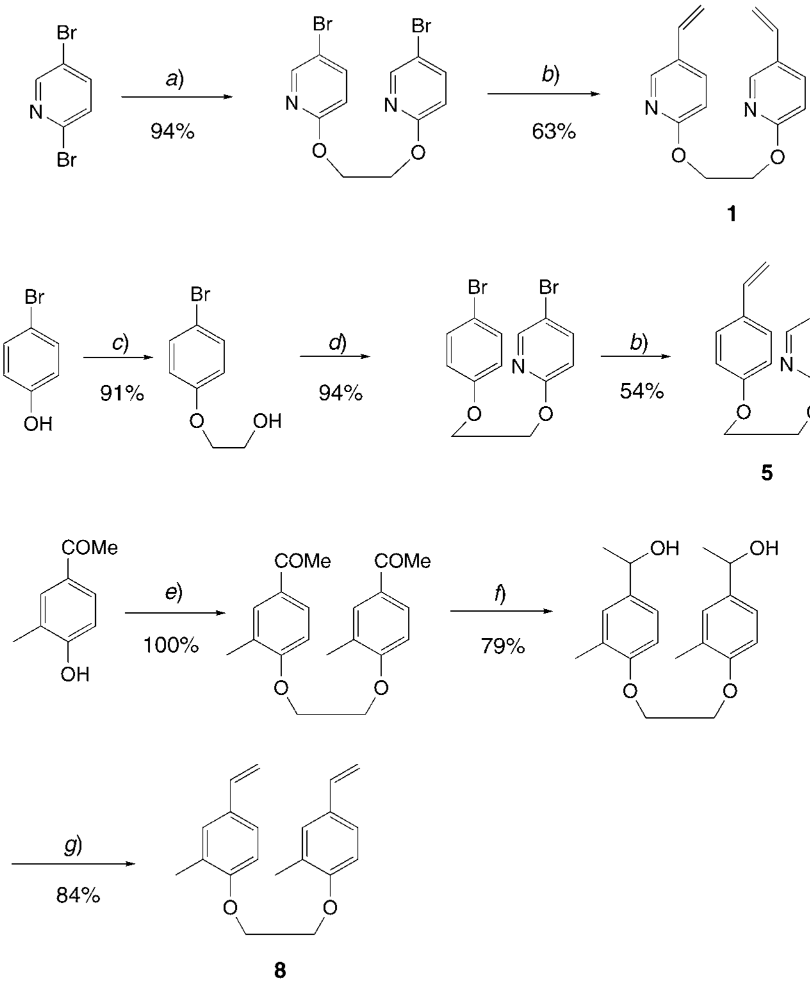
The dimeric 3-methylstyrene derivative **8** was prepared from commercially available 4-hydroxy-3-methylphenyl methyl ketone by the sequence shown in *Scheme 1* [7] in an overall yield of 66%. By irradiation, it gave also *cis*-isomers, but the major *syn*-adduct was the *endo*-isomer **9**, and not the *exo*-isomer **10** (side product together with **11**; *Scheme 4*). (Note that the relation of the substituents in **9** and the cyclobutane ring is entirely different from that of the pyridine N-atoms in **2**.)

The total yield of cyclophanes **9**–**11** was 53%, high enough for mechanistic considerations under exclusion of artifacts. In contrast, compound **8** gave cyclophanes in relatively low yields. This can be rationalized by its tendency to polymerize: styrenes are easily polymerized under irradiation, but vinylpyridines are not.

The structures of compounds **2**, **3**, **6**, and **9**–**11** were determined thoroughly by NMR experiments. Products **2**, **9**, and **10** have $C_s$ symmetry, and, thus, gave rise to simple spectra. Resolution and CD spectroscopy were applied to determine the chiral nature of **3** (see *Exper. Part*). X-Ray crystallography gave definite structural evidence for the most-important and major products **2**, **6**, and **9**, as shown in *Fig. 1* [6]. Between **2** and **3**, and among **9**, **10**, and **11**, no isomerization was observed over several months, as well as for **6** and **7** (not obtained). Therefore, their ratios are not those attained after any ground-state equilibrium or isomerization. Moreover, prolonged irradiation of the photo-adducts obtained caused their decomposition, but the isomer ratios remained constant.

The steric energy dependence on the dihedral angle $C_{Ar}-C_{Ar}-O-CH_2$ of 2-methoxy-5-vinylpyridine (**12**) and 1-methoxy-2-methyl-4-vinylbenzene (**13**) as models

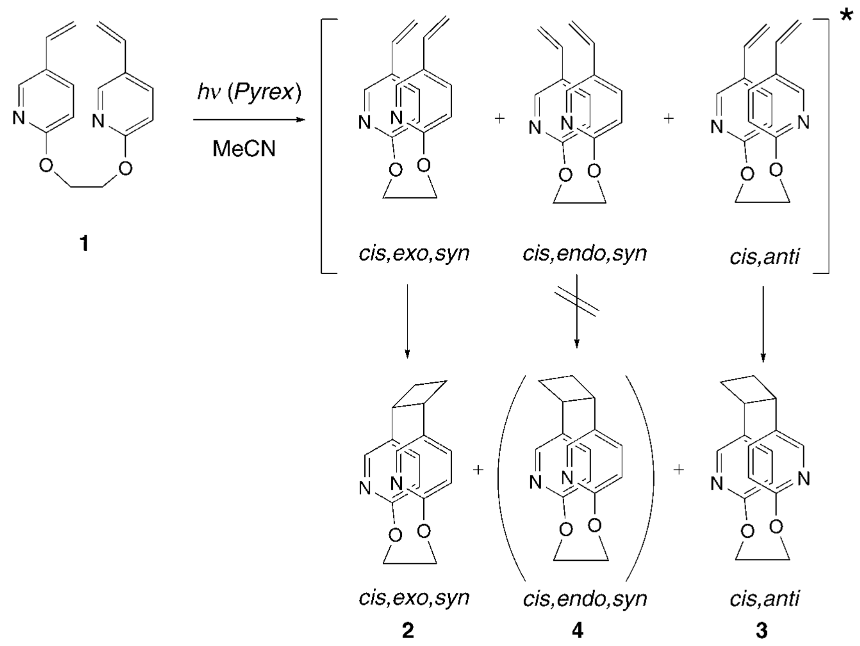
*Scheme 1*



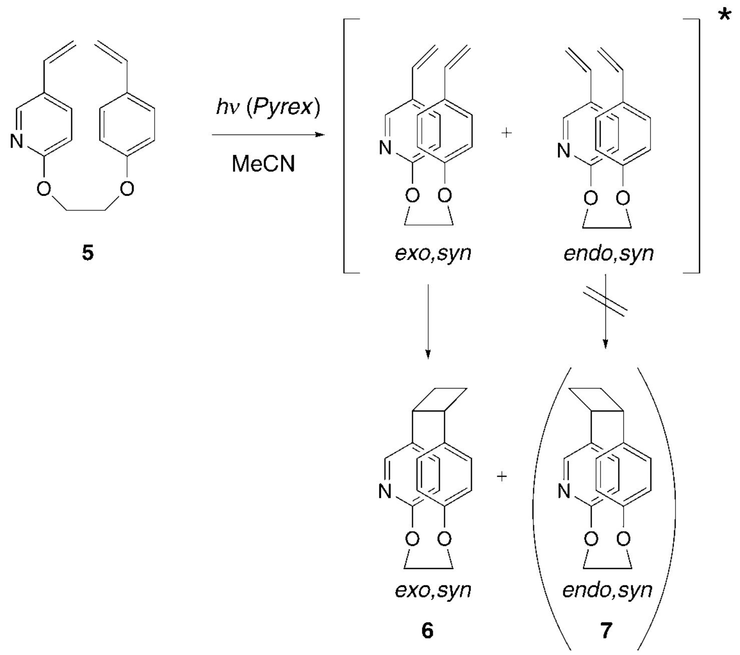
*a*) $HO(CH_2)_2OH$, NaH, THF/DMF. *b*) $(H_2C{=}CH)SnBu_3$, $[Pd(PPh_3)_4]$, 2,6-di(*tert*-butyl)-4-methylphenol, toluene. *c*) 1. NaOH, $THF/H_2O$; 2. $ClCH_2CH_2OH$, $THF/H_2O$. *d*) 1. NaH, THF; 2. 2,5-dibromopyridine, THF/DMF. *e*) $TsOCH_2CH_2OTs$, $K_2CO_3$, DMF. *f*) $NaBH_4$, EtOH. *g*) $TsO^-HPy^+$, benzene.

of **1** and **8**, respectively, was calculated by the MM2 method. The data are shown in *Fig. 2*. According to these data, lone-pairs of the O- and N-atoms in **12**, and the Me and $CH_2$ groups in **13**, interact strongly repulsively in a certain dihedral-angle range $\omega$, while they hardly perturb each other around less than 90° (minima). Hence, the aromatic N-atom and the Me group do determine considerably the conformations in the ground state, which are naturally reflected in the arrangements of the two aromatic nuclei that make up the excimer (face-to-face transition state) of the intramolecular reaction. In *Fig. 3*, the most-stable conformers are depicted, showing two major factors, $\omega$ and steric

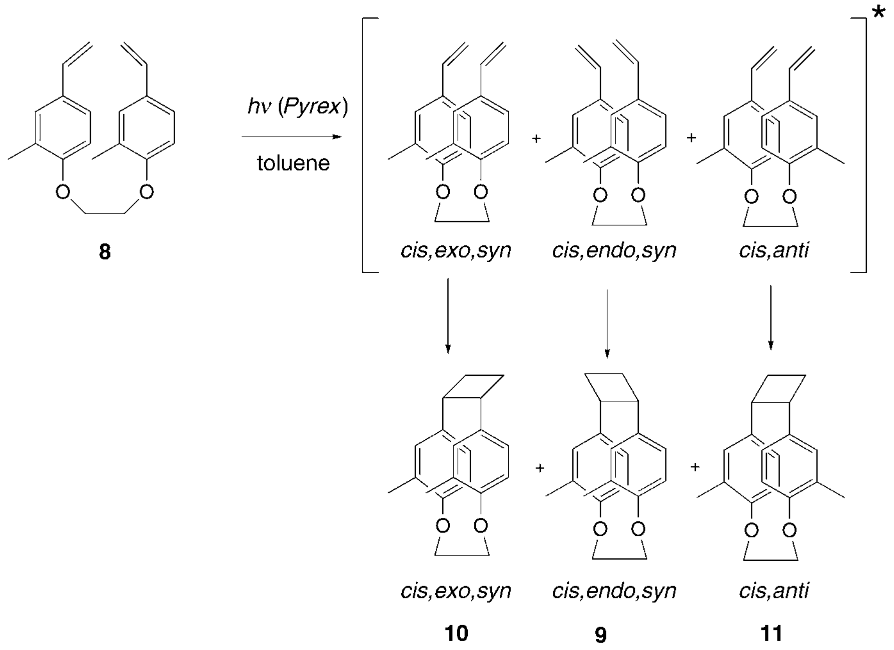
*Scheme 2*



*Scheme 3*



*Scheme 4*



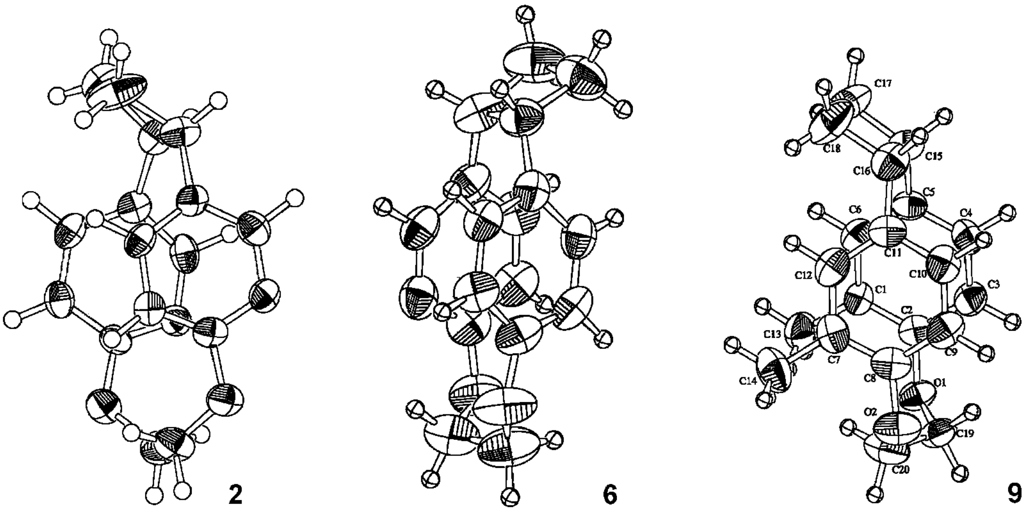


Fig. 1. *X-Ray crystal structures* (ORTEP) *of compounds* **2**, **6**, *and* **9**

interaction between the edges of molecules, which determine the structures of the face-to-face transition state.

As shown in *Table 1*, $O_2$ and the triplet quencher 1,3-pentadiene (mixture of *cis* and *trans*) [8] hardly affected the photoreaction of **1**, especially the isomer ratio. The latter

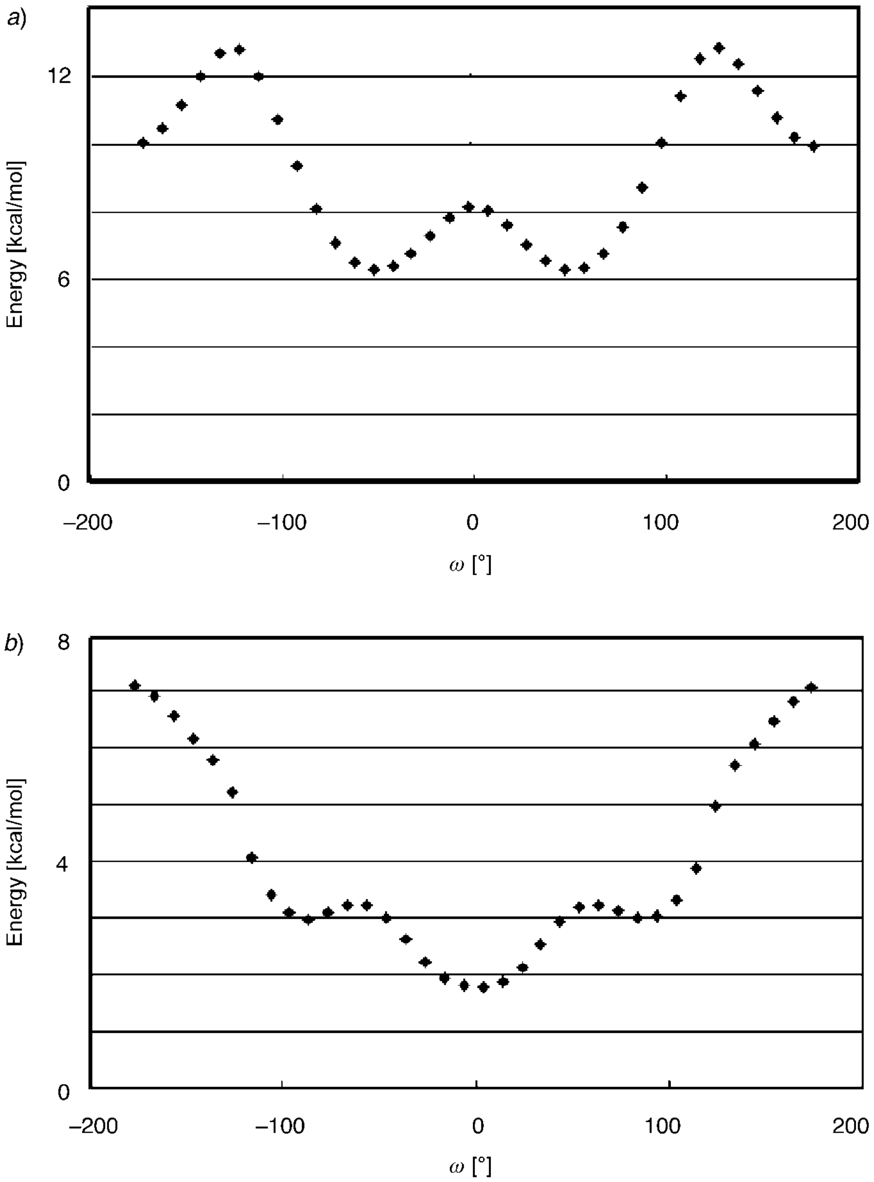


Fig. 2. *Dependence of the steric energy on the dihedral angle* ω ($C_{Ar}-C_{Ar}-O-C$) *for* a) *2-methoxy-5-vinylpyridine* (**12**) *and* b) *1-methoxy-2-methyl-4-vinylbenzene* (**13**) *as models for compounds* **1** *and* **8**, *resp.*

would be influenced largely if long-lived triplet-excited species played an important role in the photoprocess.

It was found that the absorption, fluorescence, and excitation spectra of **1** (*Fig. 4*) resemble much those of its half model **12**. Yet, the fluorescence lifetime of the former

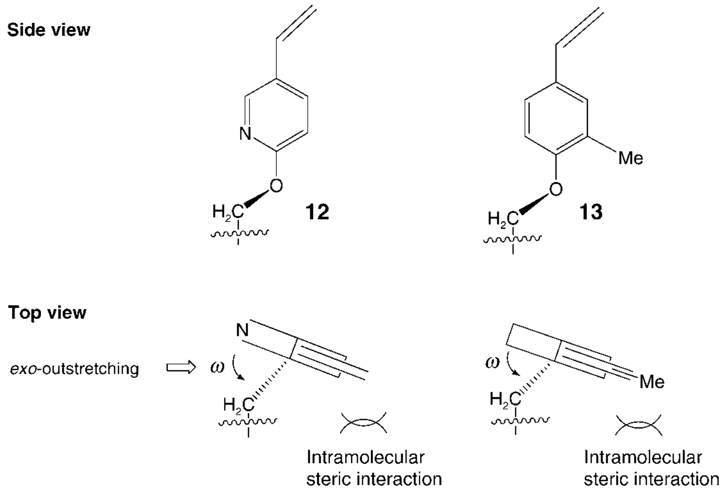


Fig. 3. *Representations of the more-stable conformers of* **12** *and* **13** *as models for the face-to-face transition state* (drawn as half components in *syn*-arrangement). The *exo*-outstretching towards the vinyl group is indicated.

Table 1. *Yields and Isomers Ratios in the Photoreaction of* **1**. Conditions: Substrate, 2 mM; solvent, MeCN; bubbling $N_2$ or $O_2$ for 30 min before reaction; irradiation by a 400-W Hg lamp (*Pyrex* filter) for 5 min from a distance of 5 cm.

| Condition | TQ[a]) | Yield [%][b]) | | | | Ratio **2**/**3** |
|---|---|---|---|---|---|---|
| | | **1** | **2** | **3** | Total | |
| $O_2$-free | – | 59.2 | 24.1 | 14.2 | 97.5 | 1 : 0.59 |
| $O_2$-sat. | – | 59.1 | 24.9 | 16.0 | 100.0 | 1 : 0.64 |
| $O_2$-free | 1 equiv. | 55.4 | 26.3 | 16.5 | 98.2 | 1 : 0.63 |
| $O_2$-free | 3 equiv. | 55.8 | 29.1 | 13.6 | 98.5 | 1 : 0.47 |
| $O_2$-free | 30 equiv. | 58.8 | 25.0 | 16.2 | 100.0 | 1 : 0.65 |

[a]) Triplet quencher (mixture of *cis*- and *trans*-1,3-pentadiene). [b]) Exper. error < ± 0.6%.

(2.47 ns at 350 nm) was distinctly shorter than for the latter (3.41 ns at 350 nm) in cyclohexane, when excited at 300 nm. This 28% reduction in lifetime is probably due to the formation of an intermediate biradical with a singlet-excited vinylpyridine moiety encountering a ground-state one intramolecularly [9].

**Discussion.** – An asynchronous, nonconcerted mechanism is generally accepted for many vinylarene [2 + 2] photocycloaddition reactions when carried out in nonpolar media without sensitizers or additives [2f]. Such processes follow a stepwise mechanism after the formation of a *singlet* biradical (*Scheme 5*), instead of a concerted mechanism along the conservation of orbital symmetry (*Woodward–Hoffmann* rule [10]).

The reactions of **1**, **5**, and **8** are expected to proceed through a short-lived singlet biradical (*Table 1*), formed by the reactions of singlet-excited moieties. Therefore, the

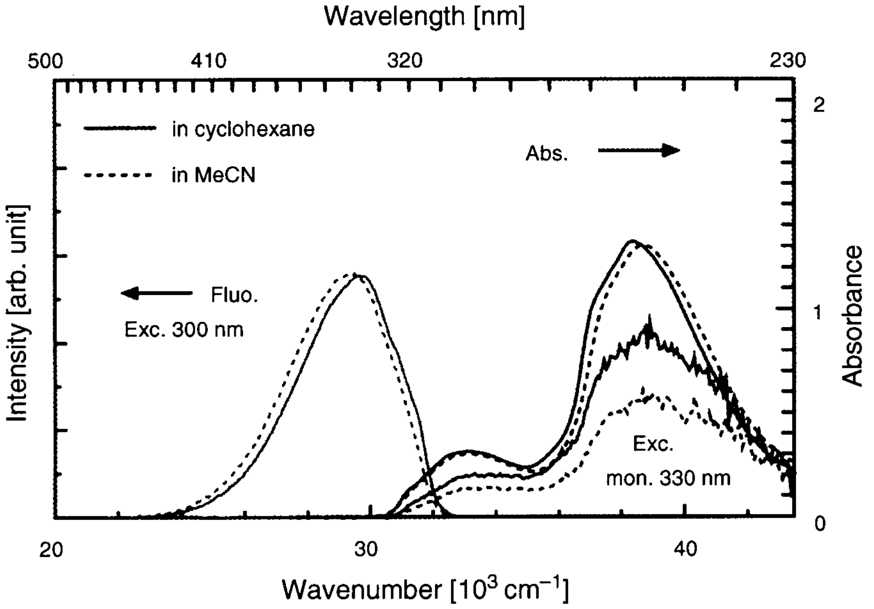
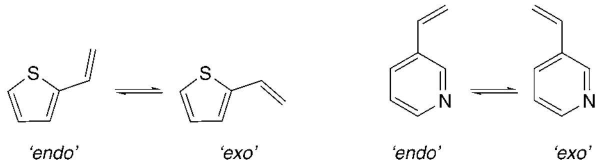


Fig. 4. *Absorption* (Abs.), *fluorescence* (Fluo.), *and fluorescence excitation* (Exc.) *spectra of* **1** *in MeCN* vs. *cyclohexane at 295 K.* 2-Methoxy-5-vinylpyridine showed the same spectra (data not shown).

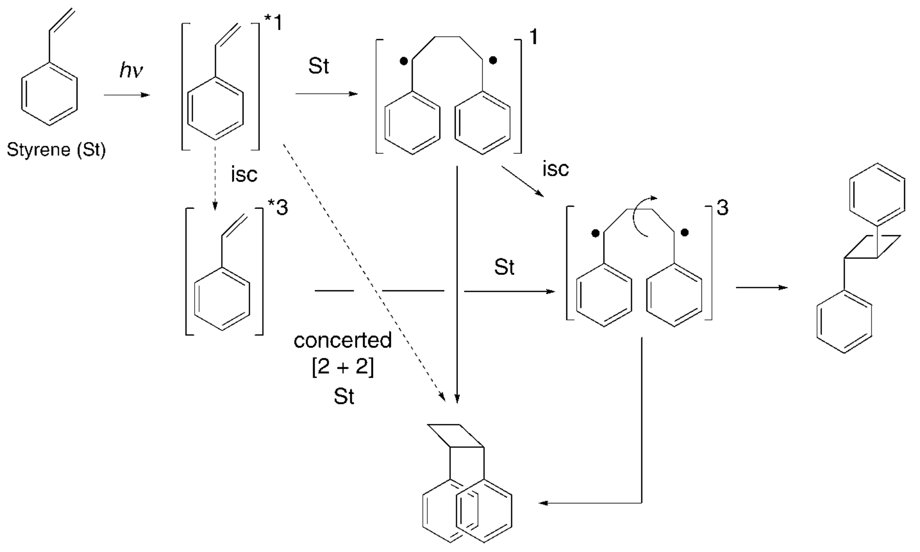
high stereoselectivity must arise from the preferable conformer at the ground state, as schematically shown in *Fig. 5*. As mentioned in the *Introduction*, some nonsymmetric vinylarenes have preferable conformers with respect to their vinyl groups. Therefore, it was examined whether 3-vinylpyridine, which is the key structure of **1**, has any conformational preference, together with 2-vinylthiophene. As shown in *Table 2*, their conformers have almost the same heat of formation, indicating that these molecules are not in a preferable conformation at the ground state. In other words, the rotation about the $\sigma$-bond between the vinyl and pyridyl groups is not responsible for the stereoselectivity observed in this work.

Table 2. *PM3-Calculated Heats of Formation* ($\Delta H_f^0$) *for Conformers of 2-Vinylthiophene and 3-Vinylpyridine*



| Conformer | $\Delta H_f^0$ [kcal/mol] | $\Delta\Delta H_f^0$ [kcal/mol] |
|---|---|---|
| *endo*-2-Vinylthiophene | 48.45 | 0.74 |
| *exo*-2-Vinylthiophene | 47.71 | |
| *endo*-3-Vinylpyridine | 46.53 | 0.08 |
| *exo*-3-Vinylpyridine | 46.45 | |

Scheme 5. *Currently Accepted [2+2] Photocycloaddition Mechanism for Styrenes*



To the best of our knowledge, excimers of vinylarenes have been observed neither by fluorescence nor absorption spectroscopy. It is considered that excimer-type combination of two vinylarene molecules is fast, giving rise to a singlet 1,4-biradical, even though it has never been detected spectroscopically. Therefore, it is reasonably assumed that the face-to-face combination of two vinylarene molecules produces a singlet 1,4-biradical, as long as the stereoelectronic conditions are satisfied. Otherwise, it cleaves the weak bond and returns to the starting locally excited state or ground state. Also, once a singlet 1,4-biradical is formed, it ends up close to the cyclobutane ring very rapidly. In other words, the rate-determining step is the bond-formation between the $\beta$-C-atoms of two vinyl groups, which must be sufficiently close together at the very moment, *i.e.*, between 1.6 Å (slightly longer than the C−C single-bond length [11]) and 3.7 Å (the longest distance for the successful [2+2] photocycloaddition of cinnamic acid derivatives in crystalline states [12]). Eventually, the moieties involved in the intramolecular bond-formation of the short-lived species, like singlet-excited styrenes, must be well arranged or organized in terms of angle, distance, orientation, *etc.*

According to the conformational dependence of **1** (see *Fig. 2*), the aromatic 3-CH group (opposite to the N-atom) and the $CH_2$ group of the tether restrict the conformation about the $C_{Ar}-O$ bond. The preferable rotamer has a certain range of $\omega$ angles, as depicted for **12** and **13** in *Fig. 6*. In other words, the major initial cofacial *syn*-combination has the *exo*-outstretched structure **12** (or **13**), through which **1**, **5**, and **8** gave *exo*-**2**, *exo*-**6**, and *endo*-**9** as major products, respectively. Since the isomer **10** was also obtained as a minor product, the *exo*-outstretching effect due to the Me···Me steric repulsion, as well as the most-favorable conformer with $\omega = 0$, is also considered to occur to a relatively small extent in this system (*Scheme 6*).

The experimental results obtained can be also rationalized through the concerted mechanism of the *Woodward–Hoffmann* rules, if a small time-lag or a tilted interaction

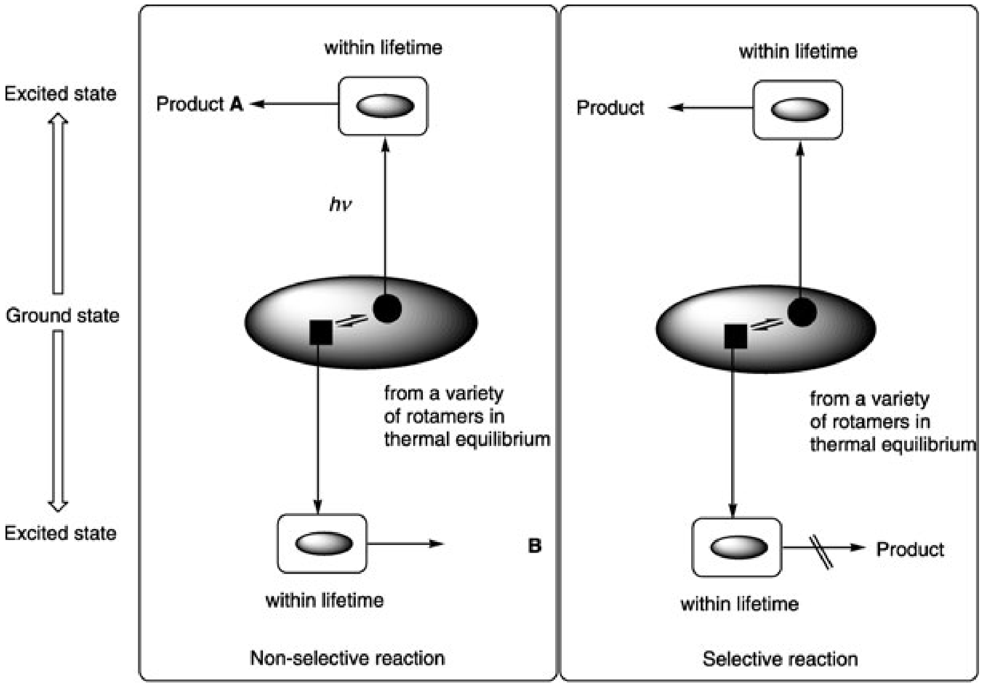
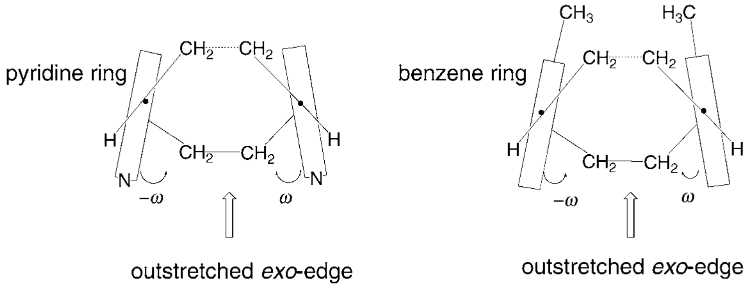


Fig. 5. *Rationalization of the selectivity of photoreactions by means of the NEER*[2]) *principle*



singlet biradical **12**

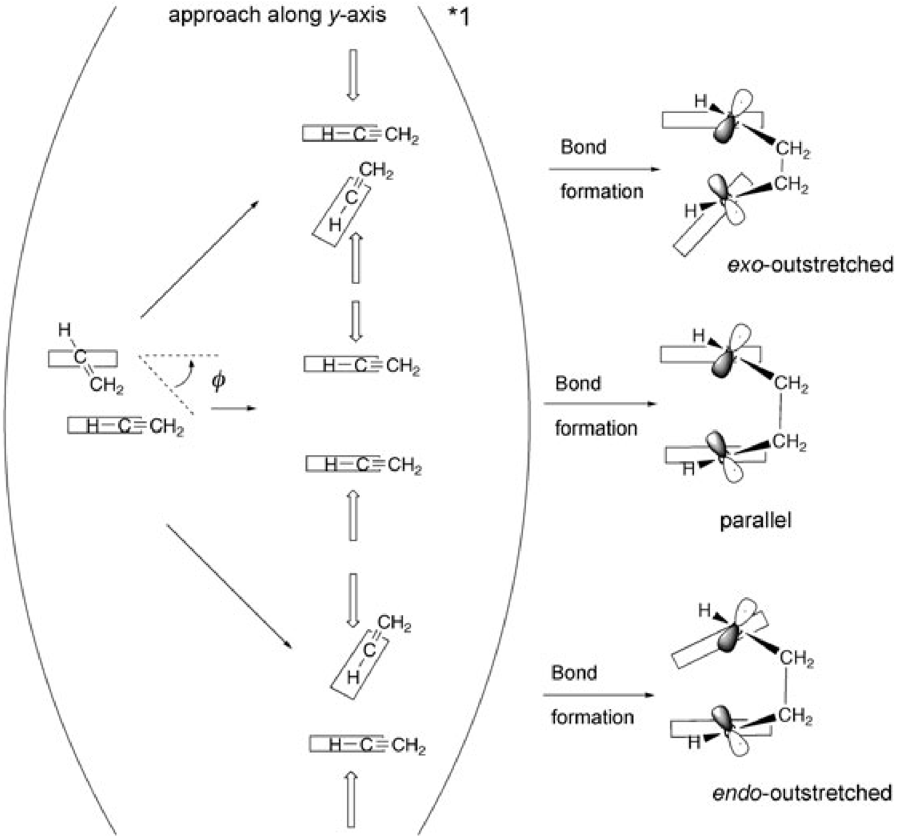
singlet biradical **13**

Fig. 6. Conformational analysis of moieties **12** and **13** upon photocyclization

of two vinyl groups is allowed for their $\alpha$- and $\beta$-positions to contact each other, respectively, before making the C–C bonds. Since the electron density is usually higher in $\beta$-position than in $\alpha$-position of vinylarenes, the *exo*-outstretched transition state is also favorable to initiate the reaction in this alternative mechanism.

**Conclusions.** – The [2+2] photocycloaddition of the dimeric 3-vinylpyridine derivative **1** gave rise to *syn*- and *anti*-pyridinophanes **2** and **3**. The major *syn*-adducts

Scheme 6. *Possible Intramolecular Arrangements for two Vinylarene Moieties*



were elucidated as *exo*-isomers by spectroscopic methods and X-ray crystallography [6]. The unusually high selectivity was thoroughly secured. An *exo*-outstretching effect governs the stereoselectivity of the intramolecular photocycloaddition of vinylarenes. The effect was confirmed by several other examples, including products from the analogues **5** and **8**.

## Experimental Part

1. *General.* Toluene and THF were purified by distillation over Na after prolonged reflux under $N_2$ atmosphere. Reagent-grade DMF was dried over 4-Å molecular sieves. Reagent-grade MeCN was purified by distillation after drying over 4-Å molecular sieves. AcOEt, cyclohexane, and penta-1,3-diene (*cis*/*trans* mixture) were purified by distillation. HPLC Analysis was carried out on an *ODS* column (MeOH). CD Spectra were recorded in MeCN at r.t. Transient spectra were taken in MeCN and cyclohexane. For laser-flash-photolysis experiments, the 308-nm pulse of a XeCl excimer laser was used as an excitation source. Fluorescence lifetimes were determined with a time-correlated single-photon counting fluorometer. NMR Spectra were recorded on a 500-MHz FT-NMR spectrometer; chemical shifts $\delta$ in ppm rel. to $Me_4Si$ as internal standard, coupling constants $J$ in Hz. Mass spectroscopy: in $m/z$. Elemental analyses were carried out at the Technical Research Center for Instrumental Analysis, Gunma University. MM2 and PM3 Calculations were performed with MOPAC.

2. *Preparation of Starting Materials.* 2.1. *2,2′-[1,2-Ethanediylbis(oxy)]bis[5-ethenylpyridine]* (**1**) [6]. *General Procedure* (*GP 1*). A soln. of 2,5-Dibromopyridine and ethane-1,2-diol in THF/DMF was allowed to react with NaH to afford 2,2′-[1,2-ethanediylbis(oxy)]bis[5-bromopyridine] in 94% yield (*Scheme 1*). The dibromide was subjected to $Pd^0$-catalyzed coupling with tributyl(ethenyl)tin to afford the desired dimer **1** in 63% yield [6]. Colorless solid. M.p. 64.8–65.6°. $^1H$-NMR ($CDCl_3$): 8.10 (*d*, *J* = 2.5, 2 H); 7.70 (*dd*, *J* = 8.5, 2.5, 2 H); 6.78 (*d*, *J* = 8.5, 2 H); 6.66 (*dd*, *J* = 17.7, 11.0, 2 H); 5.65 (*d*, *J* = 17.7, 2 H); 5.22 (*d*, *J* = 11.0, 2 H); 4.67 (*s*, 4 H).

2.2. *5-Ethenyl-2-[2-(4-ethenylphenoxy)ethoxy]pyridine* (**5**). Prepared in analogy to *GP 1*. Colorless solid. M.p. 103.4–104.2°. $^1H$-NMR ($CDCl_3$): 8.11 (*d*, *J* = 2.1, 1 H); 7.71 (*dd*, *J* = 8.9, 2.1, 1 H); 7.37 (*d*, *J* = 8.9, 1 H); 7.34 (*d*, *J* = 8.6, 1 H); 6.91 (*d*, *J* = 8.9, 1 H); 6.83 (*d*, *J* = 8.9, 1 H); 6.78 (*d*, *J* = 8.6, 1 H); 6.67–6.62 (*m*, 2 H); 5.65 (*d*, *J* = 17.7, 1 H); 5.62 (*dd*, *J* = 17.7, 0.9, 1 H); 5.23 (*d*, *J* = 11.0, 1 H); 5.13 (*dd*, *J* = 11.0, 0.9, 1 H); 4.69–4.67 (*m*, 2 H); 4.34 (*m*, 2 H). HR-EI-MS: 267.1255 ($M^+$, $C_{17}H_{17}NO_2^+$; calc. 267.1259).

2.3. *1,1′-[1,2-Ethanediylbis(oxy)]bis[4-ethenyl-2-methylbenzene]* (**8**) [7]. Prepared in analogy to *GP 1*. Colorless solid. M.p. 118.0–118.9°. $^1H$-NMR ($CDCl_3$): 7.23 (*s*, 2 H); 7.20 (*d*, *J* = 8.3, 2 H); 6.84 (*d*, *J* = 8.3, 2 H); 6.64 (*dd*, *J* = 17.7, 11.0, 2 H); 5.61 (*d*, *J* = 17.7, 2 H); 5.11 (*d*, *J* = 11.0, 2 H); 4.34 (*s*, 4 H); 2.22 (*s*, 6 H).

3. *Photochemical Cyclization Reactions.* 3.1. *10,13-Dioxa-8,15-diazatetracyclo[12.2.2.2$^{6,9}$.0$^{2,5}$]eicosa-6,8,14,16,17,19-hexaene* (**2** and **3**). *General Procedure* (*GP 2*). A 1000-ml flask with a magnetic stirring bar was loaded with a soln. of **1** (400 mg, 1.5 mmol) in MeCN (750 ml), and through this soln. $N_2$ gas was bubbled for 20 min. Then, the soln. was irradiated with a 400-W high-pressure Hg lamp using a *Pyrex* filter. The reaction was monitored by HPLC and TLC. After the disappearance of **1** (*ca.* 2 h), the mixture was evaporated, and the crude product was purified by column chromatography (CC) ($SiO_2$, toluene/AcOEt) to afford the *syn-* and *anti-*isomers **2** and **3**, resp. Racemic (±)-**3** was resolved by means of chiral HPLC (*Chiralcel OD*; i-PrOH) into its antipodes.

Data of **2** (*syn*-isomer). Isolated yield: 42%. Colorless solid. M.p. 119.4–120.1°. $^1H$-NMR ($CDCl_3$): 7.28 (*d*, *J* = 2.5, 2 H); 6.94 (*dd*, *J* = 8.3, 2.5, 2 H); 6.33 (*d*, *J* = 8.3, 2 H); 5.17, 5.14 (*q*-like *AB* system, *J* = 6.3 each, 2 H); 4.42, 4,39 (*q*-like *AB* system, *J* = 6.3 each, 2 H); 4.12–4.07 (*m*, 2 H); 2.54–2.48 (*m*, 2 H); 2.42–2.36 (*m*, 2 H). Anal. calc. for $C_{16}H_{16}N_2O_2$: C 71.62, H 6.01, N 10.44; found: C 71.61, H 6.01, N 10.35. X-Ray crystallography: see *Sect. 5* and *Fig. 1*.

*Data of* **3** (*anti*-isomer)[3]. Isolated yield: 42%. Colorless solid. M.p. 110.0–111.0°. $[\alpha]_D^{25} = +197.4$ and $-199.6$ ($c = 0.1$, MeCN) for (+)- and (−)-**3**, resp. CD: Two perfectly symmetrical curves for the antipodes were observed. $^1H$-NMR ($CDCl_3$): 7.42 (*dd*, *J* = 8.5, 2.5, 1 H); 6.99 (*dd*, *J* = 8.5, 2.5, 1 H); 6.84 (*d*, *J* = 2.5, 1 H); 6.69 (*d*, *J* = 8.5, 1 H); 6.58 (*d*, *J* = 2.5, 1 H); 6.54 (*d*, *J* = 8.5, 1 H); 5.55–5.44 (*m*, 2 H); 4.16–4.08 (*m*, 3 H); 3.88–3.84 (*m*, 1 H); 2.65–2.51 (*m*, 2 H); 2.30–2.21 (*m*, 2 H). Anal. calc. for $C_{16}H_{16}N_2O_2$: C 71.62, H 6.01, N 10.44; found: C 71.92, H 6.20, N 10.34.

3.2. *10,13-Dioxa-8-azatetracyclo[12.2.2.2$^{6,9}$.0$^{2,5}$]eicosa-6,8,14,16,17,19-hexaene* (**6**). Prepared according to *GP 2*. Isolated yield: 78%. Colorless solid. M.p. 126.4–127.2°. $^1H$-NMR ($CDCl_3$): 7.26 (*dd*, *J* = 7.9, 2.1, 1 H); 6.88 (*d*, *J* = 2.1, 1 H); 6.72 (*dd*, *J* = 8.5, 2.4, 1 H); 6.63 (*dd*, *J* = 8.5, 2.4, 1 H); 6.43 (*d*, *J* = 7.9, 1 H); 6.41 (*dd*, *J* = 8.5, 2.4, 1 H); 6.28 (*dd*, *J* = 8.5, 2.4, 1 H); 5.49 (*dd*, *J* = 14.7, 5.8, 1 H); 4.63 (*dd*, *J* = 14.7, 5.8, 1 H); 4.40 (*dd*, *J* = 14.7, 5.8, 1 H); 4.17–4.11 (*m*, 2 H); 3.99–3.97 (*m*, 1 H); 2.62–2.49 (*m*, 2 H); 2.36–2.29 (*m*, 2 H). HR-EI-MS: 267.1259 ($M^+$, $C_{17}H_{17}NO_2^+$; calc. 267.1259). X-Ray crystallography: see *Sect. 5* and *Fig. 1*.

3.3. *8,15-Dimethyl-10,13-dioxatetracyclo[12.2.2.2$^{6,9}$.0$^{2,5}$]eicosa-6,8,14,16,17,19-hexaene* (isomers **9**–**11**). Prepared according to *GP 2*.

*Data of* cis,endo,syn-*Isomer* **9**. Isolated yield: 27%. Colorless solid. M.p. 176.0–176.9°. $^1H$-NMR ($CDCl_3$): 6.64 (*s*, 2 H); 6.43 (*d*, *J* = 8.2, 2 H); 6.31 (*d*, *J* = 8.2, 2 H); 4.34 (*s*, 4 H); 4.10–4.08 (*m*, 2 H); 2.49 (*m*, 4 H); 2.18 (*s*, 6 H). Anal. calc. for $C_{20}H_{22}O_2$: C 81.60, H 7.53; found: C 81.48, H 7.60. X-Ray crystallography: see *Sect. 5* and *Fig. 1*.

*Data of* cis,exo,syn-*Isomer* **10**. Isolated yield: 3%. Colorless solid. $^1H$-NMR ($CDCl_3$): 6.72 (*d*, *J* = 8.2, 2 H); 6.54 (*d*, *J* = 8.2, 2 H); 6.28 (*s*, 2 H); 4.34 (*s*, 4 H); 4.06–4.03 (*m*, 2 H); 2.49 (*m*, 4 H); 2.10 (*s*, 6 H). HR-EI-MS: 294.1630 ($M^+$, $C_{20}H_{22}O_2^+$; calc. 294.1620).

*Data of* cis,anti-*Isomer* **11**. Isolated yield: 29%. Colorless solid. M.p. 101.3–102.1°. $^1H$-NMR ($CDCl_3$): 6.72 (*d*, *J* = 2.1, 1 H); 6.51 (*d*, *J* = 8.3, 1 H); 6.46 (*dd*, *J* = 8.3, 2.1, 1 H); 6.40 (*d*, *J* = 8.3, 1 H); 6.33 (*d*, *J* = 2.1, 1 H); 6.08 (*dd*, *J* = 8.3, 2.1, 1 H); 4.43–4.41 (*m*, 2 H); 4.36–4.28 (*m*, 2 H); 4.11–4.08 (*m*, 1 H); 4.06–3.95 (*m*, 1 H); 2.56–2.37 (*m*, 4 H); 2.16 (*s*, 3 H); 2.06 (*s*, 3 H). Anal. calc. for $C_{20}H_{22}O_2$: C 81.60, H 7.53; found: C 81.72, H 7.70.

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[3] For the X-ray crystal structure of a homologue of **3**, see [6].

4. *Photoreaction in the Presence of a Triplet Quencher.* Into a 50-ml *Pyrex* test tube were placed compound **1** (5 mg, 20 µmol) and a defined amount of penta-1,3-diene (*cis*/*trans* mixture) dissolved in $O_2$-free MeCN (10 ml) (*Table 1*). The test tube was set at a carousel having a water-cooling lamp socket, and irradiated for 5 min from a distance of 3 cm by a 400-W high-pressure Hg lamp. The mixture was then kept in the dark and analyzed by HPLC. The amounts of remaining starting material **1** and products were obtained from calibration curves. Related experiments were run similarly.

5. *X-Ray Crystal-Structure Analyses.* 5.1. *Crystal Growth.* A soln. of **2** (5.0 mg) was prepared in acetone (0.1 ml) at 50°, and then allowed to stand at r.t. for 1 d. This resulted in transparent, prismatic crystals. For compound **6** (10.0 mg), transparent, prismatic crystals were obtained from a MeOH soln. (0.5 ml) by slow evaporation of the solvent under $N_2$ atmosphere. In the case of **10** (10.0 mg), mica-like, transparent crystals were obtained from a binary soln. in MeOH (0.3 ml) and $CH_2Cl_2$ (0.1 ml) at r.t. by slow evaporation under $N_2$ atmosphere.

5.2. *Data Collection and Refinement*. The crystallographic data were recorded on a *Rigaku AFC7S* instrument. The structures were solved by direct methods (*Table 3*), and expanded using *Fourier* techniques (DIRDIF-94 program system). Crystallographic data (excluding structure factors) for compounds **2**, **6**, and **9** (see *Fig. 1*) have been deposited with the *Cambridge Crystallographic Data Centre* (CCDC) as supplementary publication numbers CCDC-258070, -258071, and -258135, resp. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033; e-mail: data_request@ccdc.cam.ac.uk; internet: http://www.ccdc.cam.ac.uk/data_request/cif).

Table 3. *Crystal Data of Compounds* **2**, **6**, *and* **9**

| | **2** | **6** | **9** |
|---|---|---|---|
| Formula | $C_{16}H_{16}N_2O_2$ | $C_{17}H_{17}NO_2$ | $C_{20}H_{22}O_2$ |
| $M_r$ | 268.31 | 267.33 | 294.39 |
| $T$ (°C) | 20.0 | 20.0 | 20.0 |
| $F(000)$ | 568 | 568 | 632 |
| Crystal size (mm) | 0.20 × 0.20 × 0.30 | 0.20 × 0.20 × 0.30 | 0.20 × 0.20 × 0.30 |
| $\mu$ (mm$^{-1}$) | 0.093 | 0.086 | 0.078 |
| Crystal system | monoclinic | orthorhombic | monoclinic |
| Lattice parameters: | | | |
| $a$ [Å] | 7.739(2) | 15.236(5) | 8.215(2) |
| $b$ [Å] | 15.377(3) | 7.318(5) | 11.768(1) |
| $c$ [Å] | 11.167(3) | 12.137(7) | 16.464(2) |
| $\beta$ (°) | 105.50(2) | – | 98.78(1) |
| $V$ (Å$^3$) | 1280.6(5) | 1353(2) | 1572.8(4) |
| Space group | $P2_1/c$ | $Pca2_1$ | $P2_1/a$ |
| $Z$ | 4 | 4 | 4 |
| $D_{\text{calc.}}$ [g/cm$^3$] | 1.392 | 1.312 | 1.243 |
| $2\theta_{\max}$ (°) | 55.0 | 55.0 | 55.0 |
| Refl. collected | 3279 | 1823 | 4065 |
| Independent refl. | 2945 | 1632 | 3624 |
| No. of variables | 182 | 183 | 200 |
| $R_1$ [$I > 2\sigma(I)$] | 0.071 | 0.048 | 0.070 |
| $wR_2$ (all data) | 0.173 | 0.129 | 0.184 |
| Goodness of fit on $F^2$ | 1.15 | 1.09 | 1.17 |

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