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The photocycloaddition of 4-ethoxycarbonyl-5-phenyl-2H-pyrrole-2,3-dione 1 to (Z)- and (E)-d-styrenes proceeded in a stereoselective manner to give the compounds in which the styrene component added to 1 antarafacially as the major products. Including these results, the observed exo- or endo-stereoselectivity in the photocycloaddition of 1 to various acyclic olefins is well explained by assuming plural transition states, stepwise C-C bond formation, and a stereo-selection rule which may be stated as follows: 1) the first C-C bond formation always occurs suprafacially; 2) the second C-C bond formation in a polar enone–olefin pair (an enone and an olefin with a weak electron donating substituent) occurs antara-selectively from the favored π-complex, while it occurs suprafacially from the less favored transition state; and 3) in a very polar enone–olefin pair (an enone and an olefin with a strong electron donating group), the second C-C bond formation occurs suprafacially from the favored π-complex and antara-selectively from the less-favored transition state. Many other stereochemical results hitherto reported can be rationalized in terms of this stereo-selection rule.

Keywords — [2+2] photocycloaddition; 1H-pyrrole-2,3-dione; dioxopyrrolino; (Z)-d-styrene; (E)-d-styrene; enone–olefin pair; stereochemistry; stereo-selection rule

The [2+2] photocycloaddition reaction of enones to olefins has been widely utilized for the construction of complex polycyclic compounds and many examples were reviewed.2) The broad outline of the reaction pathway appears to be generally accepted as shown in Chart 1.2a,3) The reaction involves a triplet excited state of the enone, which forms an excited π-complex with an olefin. This reactive species (an exciplex) then gives a 1,4-biradical by the formation of a covalent bond between either Cγ or Cβ of the enone and one of the olefin carbons. The high regioselectivity in the formation of the head to tail (HT) adduct from an enone and an olefin (with an electron-donating substituent) pair is well explained by assuming that an “oriented π-complex or oriented exciplex” is formed from the encounter complex between the triplet excited enone and ground state olefin.4)

On the other hand, the stereochemical features of the reaction have remained obscure, although stereoselective addition of acyclic olefins to cyclic enones has often been observed.
In the photocycloaddition of 2-cyclohexenone to acyclic olefins, trans-fused bicyclo[4.2.0]octanes were usually obtained as the major product. As the reason for the formation of this strained product, the idea of rotational equilibration of the intermediate 1,4-biradicals is hardly acceptable for such a cyclic compound. Instead of this idea, a mechanism involving initial complexation of a twisted enone triplet and the olefin leading to a twisted 1,4-biradical was suggested. However, the occurrence of this sort of highly strained intermediate is still uncertain.

Epiotis and Shaik theoretically concluded that the triplet \([2 + 2]\) photoaddition of an enone–olefin pair preferentially occurs in a concerted \([2s + 2a]\) manner and suggested that the enone plays the role of the antarafacial component. From theoretical analyses of spin-inversion mechanisms leading to a final product, Shaik further elaborated the above conclusion, indicating that the stereochemistry of olefin–olefin \([2 + 2]\) photoaddition varies depending on the polarity (donor-acceptor relationship) of the olefin pair. When the olefin pair is nonpolar (i.e., both olefins are electron donors or electron acceptors) the \([2s + 2s]\) adduct is the main product. When the olefin pair is polar, the \([2s + 2a]\) adduct becomes the major product. When the olefin pair is very polar, the \([2s + 2s]\) adduct again becomes the main product. The formations of trans-fused and cis-fused cyclobutanes (shown in Chart 2) have been presented as examples of photocycloaddition of the polar and very polar olefin–olefin pairs.

Few experimental data are available on the stereochemical pathway of the olefin component in photocycloaddition. This can only be elucidated when the stereochemistry of two termini of the olefin component in the product is established. One of the pioneering studies by de Mayo and Loutfy showed that the photoaddition of cyclopentenone to cis- and trans-dichloroethylenes afforded four stereoisomers in relative ratios shown in Chart 3. The result, as pointed out by the original authors, can not be rationalized in terms of rotational equilibration of 1,4-biradicals produced by bond formation at either the \(C_\alpha\) or \(C_\beta\) position of the enone, since such an idea gives no adequate explanation for the preferred stereochemical inversions in the olefin component. Although their tentative interpretation is that both \(\alpha\)- and \(\beta\)- bond formation pathways are operative, the data in Chart 3 rather imply that the reaction is controlled by some stereochemical selection rule. Contrary to de Mayo’s result, both cis- and trans-2-butenes, in cycloaddition with a cyclohexenone derivative, often gave a mixture of the stereoisomers with almost identical relative ratios from either compound. The failure to retain the stereochemistry of the olefin moiety in the product was explained in terms of rotational equilibration of the 1,4-biradicals.

We have shown in the preceding paper that the photocycloaddition of the dioxopyrroline to electron-rich olefins proceeds with high regio- and stereoselectivity to give the cis-fused cyclobutanes, 5-ethoxycarbonyl-1-phenyl-7-substituted-2-azabicyclo[3.2.0]heptane-3,4-diones and 3, with HT regiochemistry. The stereoselectivity in this reaction varies depending on the nature of the substituents of the olefins; olefins carrying phenyl, vinyl, thiophenyl, and
alkyl substituents gave the exo-adduct 2, while olefins having O-substituents afforded the endo-adduct 3 as the major product. The endo-adduct 3, irrespective of the nature of the C7-substituent, is thermodynamically more stable than the exo-isomer 2.1) Therefore, the stereoselective formation of the thermodynamically less stable exo-isomer 2 can not be explained as a result of product developing control, but implies that the reaction is governed by some stereochemical selection rule.

It must be emphasized that in this cycloaddition reaction the stereochemistry of the ring junction and that of the C7-substituent in the adducts 2 and 3 do not disclose how the olefinic component underwent cycloaddition to the enone molecule. This can be established only when the stereochemistry at C6 in the adduct is determined at the same time. In order to clarify this point we have carried out experiments using (Z)- and (E)-d-styrene.11)

In this paper we describe the stereochemical assignment of the photocycloadducts of dioxopyrrolone to d-styrenes and discuss the stereochemical pathways of the dioxopyrrolone–olefin photoannelation. We propose an empirical stereochemical selection rule for the enone–olefin photocycloaddition.

Photocycloaddition of Dioxopyrrolone to (Z)- and (E)-d-Styrenes

Irradiation of 1 and (Z)-d-styrene in dimethoxyethane as described in the preceding paper11 afforded the exo-adduct 4Z (22%) and the endo-adduct 5Z (3%). That the deuterium is not lost in this photoreaction was evidenced by the mass and 1H-nuclear magnetic resonance (1H-NMR) spectra of the products 4Z and 5Z. On the basis of the intensity ratio of the C6-exo-H and C6-endo-H signals (for stereochemical assignment, see below), 4Z and 5Z were identified as a 6:4 mixture of 4a and 4b and a 4:6 mixture of 5a and 5b, respectively, as shown in Fig. 1. The similar photoaddition of 1 to (E)-d-styrene afforded 4E (40%) with 4:6 ratio of 4a and 4b, and 5E (4%) with 6:4 ratio of 5a and 5b. Thus, the product distributions shown in Table I clearly indicate that the addition of (Z)- and (E)-d-styrene to 1 has proceeded in the same stereochemical manner.
Formation of two isomers relating to the C₆-deuterium stereochemistry in 4Z and 5Z could not arise from either photo-isomerization of the olefin prior to photoaddition or that of the adducts, since (Z)-d-styrene did not isomerize to (E)-d-styrene under similar irradiation, and the ratio of 4a and 4b was independent of the reaction time. The above results therefore indicate that styrene undergoes cycloaddition to 1 in an antarafacial manner (or with inversion of configuration).

The stereochemical assignments of 6-exo- and 6-endo-H in 4Z and 5Z (and also in 4E and 5E) were achieved by nuclear Overhauser effect (NOE) observation as follows. The deuterated exo-adduct 4Z exhibits the C₇-H (endo) signal at δ 4.19 and C₆-H signals at δ 2.68 (d) and 3.53
(d). Irradiation of the C7-endo-H at δ 4.19 enhanced the intensity of the C6-H signal at δ 2.68 by 16%, but had no effect on the intensity of the other C6-H signal at δ 3.53, indicating that the former proton is in cis relationship with C7-endo-H and the latter proton is trans to C7-H, corresponding to C6-H of 4a and 4b, respectively.

Similarly, the two C6-H signals at δ 2.48 and 3.36 in 5Z were assigned as endo and exo, respectively, which correspond to the C6-H of 5a and 5b. When the signal at δ 4.83 due to the C7-exo-H was irradiated, an NOE enhancement (36%) was observed only in the signal at δ 3.36, indicating that it is in a cis-relationship with the C7-exo-H.

The above assignment was supported by the following chemical synthesis of 4b. The photoaddition of 1 to deuterated phenylacetylene afforded the deuterated cyclobutene 6. Catalytic hydrogenation of 6 over Pd–C afforded 4b as a sole product, which showed the C6-H signal only at δ 2.69, confirming that in 4b the stereochemistry of the C6-deuterium and C7-phenyl is cis.

Stereoselection of Enone–Olefin Photocycloaddition

The regiochemistry of dioxopyrroline–olefin photocycloaddition is well explained by the concept of the oriented π-complex known for a usual enone–olefin photocycloaddition. Here we propose the following three assumptions to explain the stereochemical results of our reactions, which, we believe, are applicable not only to dioxopyrroline–olefin pairs but also to other enone–olefin pairs hitherto reported, as shown below.

1) The reaction proceeds through two or more transition states, equally or differently favored, which originate from (positionally or stereochemically) different modes of approach of the two components.

2) The two C–C bond formations in the oriented π-complex occur stepwise (though maybe only formally), at either the Cα or Cγ-position of the enone in such a way that the first bond formation results in the formation of the most stable 1,4-biradical.

3) Selection rule of stereochemistry.
   i) The first C–C bond formation always occurs suprafacially (or with retention of configuration in the π-complex). ii) In a polar pair (i.e. an enone and an olefin having weak an electron-donating group such as an alkene), the second C–C bond formation at the other terminus occurs anta-selectively (or with inversion of configuration) from the favored complex, and supra-selectively from the less favored transition. iii) In a very polar enone–olefin pair (i.e. an enone and an olefin having an O-substituent such as alkoxyethylene), the second bond formation occurs in a supra-selective manner from the favored complex and in an anta-selective manner from the less favored transition.

The first two assumptions may be a priori acceptable. The presence of plural transition states in photocycloaddition has often been considered or recognized. Concomitant formations of regio-isomeric HH and HT adduct in some photocycloadditions are typical examples. The formations of syn- and anti-adduct in cycloaddition of a cyclic enone to a cycloalkene are examples where two assumed transitions are only stereochemically different. Those are considered to be endo- and exo-complexes, respectively.

The energy levels of the transition state are dependent on electronic factors such as orbital overlapping and dipole–dipole interaction and on steric hindrance to the approach. Generally the endo isomer would be favored because it would gain maximum orbital overlapping, unless steric interaction is excessive. The preferred formation of the cis-syn-cis adduct from the reaction of uracil and vinylene carbonate pair, and the exclusive formation of the cis-syn-cis adduct from 4-hydroxycoumarin and cyclopentene pair show that the endo-complex is favored by the molecular orbital interaction. On the other hand, the adduct from cyclopentenone–cyclopentene pair usually has the cis-anti-cis stereochemistry, suggesting that the endo-complex is less favored than the exo-complex. The addition of 2-
acetoxycyclopentenone to 4,4-dimethyloclopentene\textsuperscript{16d)} leads to the nearly exclusive formation of the adduct with cis-anti-cis configuration, while dihydrofuran gives nearly equal amounts of the syn- and anti-isomers.\textsuperscript{2c)} The presence of an oxygen atom in the ring system may reduce the steric hindrance and increase the molecular orbital interaction.

We should point out that in the reaction of a cyclic enone with monosubstituted olefins two stereoisomeric exo- and endo-exciplexes both leading to HT regiochemistry are possibly present. This has been overlooked in most cases, probably because the stereochemistry of the olefin moiety has seldom been established rigidly.

The second assumption is well known for the 1,4-biradical mechanism, although we do not envisage a clear biradical species but only assume the order of bond formation. The 1,4-biradical (A) formed from a complex of an enone and an olefin monosubstituted by an electron donating group due to coupling at C$_y$, where the pair always gives the HT adduct, is obviously a more stable species than that formed by C$_y$-coupling (B). In this case the first bond formation occurs at C$_y$. The 1,4-biradical (C) formed by C$_y$-coupling from a complex of an enone and an olefin 1,2-disubstituted by groups of the same or nearly the same electronic properties should be more stable than the biradical formed by C$_y$-coupling (D), where the first bond formation would be at C$_y$, although the energy differences between these two species might be small. [In the reaction of an enone and olefins monosubstituted by an electron withdrawing group, the first bond formation would occur at C$_y$, since the 1,4-biradical (E) derived from the oriented $\pi$-complex leading to the HH adduct must be more stable than that in the case of C$_y$-coupling (F). In some instances a re-orientation mechanism was proposed.\textsuperscript{17}] Our assumption does not conflict with the concerted mechanism. Even if the reaction is concerted, as suggested by Epiotis and Shaik,\textsuperscript{7a)} the interpretation remains valid when a very short-lived biradical is considered in the course of a stepwise mechanism.

In contrast to assumptions 1) and 2), the third assumption (selection rule of stereochemistry) is purely empirical. The next section deals with this subject. Here we only point out the fact that trans stereochemistry in a cyclobutane adduct appears not only at the enone

\begin{itemize}
  \item [i)]\begin{align*}
    \text{O} & \quad \text{D} \\
    \text{(A)} & \quad \overset{>}{\text{B}}
  \end{align*}
  \\
  \item [ii)]\begin{align*}
    \text{O} & \quad \text{R} \quad \text{R} \\
    \text{(C)} \quad \overset{>}{\text{D}}
  \end{align*}
  \\
  \item [iii)]\begin{align*}
    \text{O} & \quad \text{W} \\
    \text{(E)} \quad \overset{>}{\text{F}}
  \end{align*}
\end{itemize}

\begin{center}
\textbf{Chart 6. The Order of C–C Bond Formation}
\end{center}

\begin{itemize}
  \item [i)] Olefin monosubstituted by an electron-donating group.
  \item [ii)] Olefin 1,2-disubstituted by groups of the same or nearly the same electronic properties.
  \item [iii)] Olefin monosubstituted by an electron-withdrawing group.
\end{itemize}
component, but also, in some instances, at the olefin component. In cyclohexenone–olefin reactions, the antarafacial component, if present, is always the cyclohexenone. The triplet species in the encounter complex is undoubtedly the enone. However, in the oriented π-complex after intersystem crossing, either the enone or the olefin can be an antarafacial component. In fact, the reaction of cyclopentenones with cyclohexenes and that of bicyclic enones with cyclohexenes, where the enones are geometrically such that it is difficult or impossible to adopt trans configuration, afford the cyclobutanes having trans-stereochemistry at the olefin component.

Interpretations of Stereochemical Results in Enone–Olefin Pairs

By adopting the above three assumptions, the stereochemical results of the enone–olefin photoannelations can be well interpreted. For the dioxopyrroline-(Z)- and (E)-d-styrene pairs, the product distribution can be explained as shown in Chart 7. The endo-complex 7 should be more favored than the exo-complex 8 as the oriented transition state formed from an encounter complex, because it has the least steric hindrance at the endo face and because of an orbital overlapping effect between the electron deficient dioxopyrroline ring and phenyl group, although the exo-complex 8 is not much less favored, because of phenyl–phenyl π–π overlapping. These products are assumed to be formed in a ratio of 6:4. From the favored endo-complex 7, the first C–C bond formation occurs suprafacially at Cα, then the following bond formation at Cβ with antaraf-selectivity to give the exo-adduct 4a with 8-fold preference over 5b, while from the less favored exo-complex 8, supra-selective addition at Cβ gives the exo-adduct 4b with 8-fold preference over 5a. The exo-selectivity observed in 1-butene, butadienes, and phenylthioethylenene can be similarly rationalized in terms of the supra-

Chart 7. Interpretation of the Stereochemical Results of the Photocycloaddition Reaction of 1 to (Z)-d-Styrene in Terms of the Stereo-Selection Rule
selective addition at C₃ and antara-selective addition at C₇ from the favored endo-complex. For those pairs, inversion always occurs at the olefin component, since the enone component can not invert its configuration due to the great strain of the five membered ring system.

Another explanation may be possible for this styrene addition; that is, either the 1,4-biradical 9 or 10 formed from the endo or exo-complex comes into rotational equilibrium to give the phenyl exo-oriented product 4Z (4E) with 8-fold preference over 5Z (5E) due to a phenyl-phenyl attractive interaction which produces a parallel array of the two phenyl groups. This mechanism can explain the exo-selectivity observed with butadiene, in which phenyl-vinyl attractive interaction is expected to operate in the biradical, leading to the exo-adduct 2. However, this idea provides no basis for explaining the exo-selectivity observed with 1-butene and phenylthioethylene.

![Chart 8](image.png)

Chart 8. Attempted Interpretation of the Stereochemical Results of the Photocycloaddition Reaction of 1 to (Z)-d-Styrene in Terms of Rotational Equilibration of the Intermediate 1,4-Biradical

![Chart 9](image.png)

Chart 9. Photocycloaddition Reaction of 1 to Cyclopentadiene (after Tsuda et al.)²³
endo-Selectivity of the olefins carrying an O-substituent\(^1\) can be explained by considering that the pair is very polar, because the electron rich O-substituent and the dioxopyrroline ring are expected to have strong attractive interactions. Thus, the endo-adduct 3 is formed supra-selectively from the favored endo-complex. An alternative explanation is that the intermediate formed from these pairs is a long lived biradical, so that the product is the thermodynamically more stable endo-isomer 3. If we take this approach, the more stereo-selective addition of isopropenyl acetate (endo-O : exo-O = 6 : 1) in contrast to the thermodynamic equilibration (endo-O : exo-O = 2 : 3)\(^1\) in the above product is still to be explained. The intermediate from phenylthioethylene should be a similarly long-lived biradical. However, the result is different. Consequently, we can predict that as the polarity of the enone–olefin pair increases, the formation of the endo-adduct becomes preferred. In fact, ethoxyethylene affords the endo-

Chart 10. Interpretation of Loutfy and de Mayo’s Results in Terms of the Stereo-Selection Rule
adduct 3 in 10-fold excess, while phenylthioethylene affords the *exo*-adduct 2 in 1.5-fold excess. The polarity of the latter pair is not as large as that of the former pair. In accordance with this interpretation a 1,1-disubstituted olefin carrying the *O*-tetramethylsilane (*O*-TMS) group exclusively afforded the *endo*-**O** adduct.\textsuperscript{19}

We have previously reported\textsuperscript{20} that the photoaddition of 1 to cyclopentadiene gave the dihydropyridone 11 as a major product, together with a cyclobutane 12\textsuperscript{21} and a hydroindole 13 (Chart 9). This implies the intermediary formation of the unstable *trans*-fused cyclobutane 14\textsuperscript{22} as a result of antarafacial addition of the cyclopentadiene component. This highly strained species would undergo 1,3-shift (either photochemically or thermally) of the C<sub>1</sub>–C<sub>7</sub> bond, followed by cheletropic loss of CO to afford 11. Cyclopentene and indene also gave this type of photoadduct as a major product.\textsuperscript{23}

The above assumptions also give a reasonable explanation for the results of Loutfy and de Mayo (Chart 10).\textsuperscript{9} The cyclopentenone-*cis* and *trans*- dichloroethylene pairs are considered to be polar. The favored oriented π-complexes formed from these pairs are those of 15 and 17, where one chlorine atom is close to the carbonyl group, since the dipole–dipole interaction between C=O of the excited enone and C–Cl of the ground state olefin should be attractive. The product distributions indicate that the ratio of favored to less favored complexes (15/16 and 17/18) is 7/3 in both reactions. The first C–C bond formation occurs supra-selectively at C<sub>β</sub> in all complexes, since both termini of the olefin are substituted by the same group. In *cis*-dichloroethylene the favored complex 15 yields cyclobutanes 19 and 20 with antara-selective coupling (2.6 times) at the α-position, while the less favored complex 16 gives 21 and 22 with supra-selective coupling (1.7 times) at the α-position. In the case of *trans*-dichloroethylene, 17 and 18 similarly form cyclobutanes with antara- (21/22 = 2.3) and supra-selectivity (19/20 = 3.1) at C<sub>α</sub>, respectively.

The stereo-selection rule that we proposed here seems to work reliably for predicting the stereochemistry of [2 + 2] photocycloaddition of enone–olefin pairs. Although there are some exceptions,\textsuperscript{10,24} many examples hitherto reported in the literature, *i.e.* the *exo-* or *endo*- selectivity in photo-cycloaddition of cyclic enones to monosubstituted olefins,\textsuperscript{13,23} the *trans* addition of cyclohexenes to cyclopentenones\textsuperscript{18b,c} and the *trans* addition of cyclohexenones to cyclopentenes,\textsuperscript{51} can be rationalized in terms of this rule. However, we have to emphasize that at the present stage this rule is an empirical one, for which a theoretical background is awaited.

**Experimental**

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto micro hot-stage apparatus, and are uncorrected. Infrared (IR) spectra were taken in Nujol mulls with a Hitachi 260-10 spectrometer and are given in cm<sup>−1</sup>. Ultraviolet (UV) spectra were recorded in dioxane with a Hitachi 200-10 spectrophotometer. 1H-NMR (100 MHz) spectra were taken in CDCl<sub>3</sub> solution with TMS as an internal standard on a JEOL FX-100 spectrometer. High-resolution mass spectra (MS) were recorded on a JEOL JMS-D300 mass spectrometer. For column chromatography, silica gel (Wako-gel C-200) was used. Thin layer chromatography (TLC) was performed on precoated Silica gel 60 F<sub>254</sub> plates (Merck). The photolysis solution was irradiated internally using a 300 W high-pressure mercury lamp (Eikosha Halos PIH 300) with a Pyrex filter.

**The Photocycloaddition of 1 to (Z)- and (E)-d-Styrene**

1. (Z)-d-Styrene——A solution of 1 (1 g, 4 mmol) and (Z)-d-styrene (1.3 g, 12 mmol) in dimethoxyethane (DME) (300 ml) was irradiated for 45 min under ice cooling. The residue obtained by evaporation of the solvent was crystallized from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O to give 4Z. Chromatography of the mother liquor over SiO<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> and crystallization of the eluate from CH<sub>2</sub>Cl<sub>2</sub>–Et<sub>2</sub>O gave another crop of 4Z and 5Z.

   4Z: Yield 310 mg, 22% colorless prisms, mp 215–223°C. IR: 1765, 1740 sh, 1720. 1H-NMR δ: 0.63 (3H, t, J = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 2.68 (0.4H, d, J = 10 Hz, C<sub>α</sub>-H), 3.53 (0.6H, d, J = 10 Hz, C<sub>α</sub>-H), 3.73 (2H, q, J = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 4.19 (1H, d, J = 10 Hz, C<sub>α</sub>-H), 7.1 (10H, m, Ar-H). MS m/z: M<sup>+</sup> Calcd for C<sub>21</sub>H<sub>18</sub>DNO<sub>4</sub> 350.1377. Found: 350.1372.

   5Z: Yield 43 mg, 3% colorless prisms, mp 173–185°C. IR: 3310, 1765, 1735, 1710. 1H-NMR δ: 0.72 (3H, t, J =
7 Hz, COOCH₂CH₃), 2.48 (0.4H, d, J = 9 Hz, C₆-H), 3.36 (0.6H, d, J = 9 Hz, C₆-H), 3.78 (2H, q, J = 7 Hz, COOCH₂CH₃), 4.83 (1H, d, J = 9 Hz, C₇-H), 7.0−7.5 (10H, m, Ar-H). MS m/z: M⁺ Calcd for C₂₁H₁₈DNO₄ 350.1378. Found: 350.1415.

(ii) (E)-d-Styrene—A solution of 1 (1 g, 4 mmol) and (E)-d-styrene (1.3 g, 12 mmol) in DME (300 ml) was irradiated as above. Work-up as above gave 4E and 5E.

4E: Yield 570 mg, 40%, colorless prisms, mp 213−223 ºC. 1H-NMR δ: 0.63 (3H, t, J = 7 Hz, COOCH₂CH₃), 2.68 (0.6H, d, J = 10 Hz, C₆-H), 3.53 (0.4H, d, J = 10 Hz, C₆-H), 3.73 (2H, q, J = 7 Hz, COOCH₂CH₃), 4.19 (1H, d, J = 10 Hz, C₇-H), 7.1 (10H, m, Ar-H).

5E: Yield 57 mg, 4%, colorless prisms, mp 173−185 ºC. 1H-NMR δ: 0.72 (3H, t, J = 7 Hz, COOCH₂CH₃), 2.48 (0.6H, d, J = 9 Hz, C₆-H), 3.36 (0.4H, d, J = 9 Hz, C₆-H), 3.78 (2H, q, J = 7 Hz, COOCH₂CH₃), 4.83 (1H, d, J = 9 Hz, C₇-H), 7.0−7.5 (10H, m, Ar-H).

Photocycloaddition of 1 to d-Phenylacetylene—A solution of 1 (1 g, 4 mmol) and d-phenylacetylene (1.3 g, 12 mmol) in DME (300 ml) was irradiated for 45 min under ice cooling. After evaporation of the solvent, the residue in CH₂Cl₂ was chromatographed over SiO₂ to give rel-(1S,5R)-6-deutero-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]hept-6-ene-3,4-dione 6 (200 mg, 14%) as pale yellow prisms from CH₂Cl₂–Et₂O, mp 165−175 ºC. IR: 1770, 1740, 1710. 1H-NMR δ: 0.79 (3H, t, J = 7 Hz, COOCH₂CH₃), 3.73 (2H, q, J = 7 Hz, COOCH₂CH₃), 7.27 (5H, br s, aromatic-H), 7.31 (5H, br s, Ar-H). UV λmax nm (ε): 253 (15900). MS m/z: M⁺ Calcd for C₂₁H₁₆DNO₄ 348.1220. Found: 348.1267.

Catalytic Hydrogenation of 6—The deuterated cyclobutene 6 (700 mg) in EtOH (40 ml) was hydrogenated over 10% Pd-C under 4.2 atmospheres pressure for 3 h at room temperature. The product in CH₂Cl₂ was passed through a short column of SiO₂ and recrystallized from CH₂Cl₂–MeOH to give rel-(1S,5R,6R,7R)-6-deutero-5-ethoxycarbonyl-1,7-diphenyl-2-azabicyclo[3.2.0]heptane-3,4-dione 4b (450 mg, 63%) as colorless prisms, mp 200−212 ºC. IR: 1765, 1740 sh, 1720. 1H-NMR δ: 0.63 (3H, t, J = 7 Hz, COOCH₂CH₃), 2.68 (1H, d, J = 10 Hz, C₆-H), 3.73 (2H, q, J = 7 Hz, COOCH₂CH₃), 4.19 (1H, d, J = 10 Hz, C₇-H), 7.1 (10H, m, Ar-H). MS m/z: M⁺ Calcd for C₂₁H₁₈DNO₄ 350.1377. Found: 350.1384.

References and Notes
21) Although cis-syn-cis configuration was suggested\(^{20}\) for this compound, we now wish to revise the structure to anti-configuration on the basis of spectral and chemical evidence. The details will be reported elsewhere.
22) This may be the first evidence that a cyclopentene component can undergo cycloaddition to an enone in an antarafacial manner.