9f α-methyl, 62167-52-6; **9f** DNP α-methyl, 62167-53-7; **9g** α-methyl, 62167-54-8; **9g** DNP α-methyl, 62197-67-5; diethyl pyrrolidinomethylphosphonate 51868-96-3; 2,3-dibromopropene, 513-31-5; **9e** β-methyl, 62167-55-9; **9e** DNP β-methyl, 62167-56-0; **9f** β-methyl, 62167-57-1; **9f** DNP β-methyl, 62167-58-2; **9g** β-methyl, 62167-59-3; **9g** DNP β-methyl, 62197-69-7.

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(11) We thank Professor Ernest Wenkert, Rice University, for providing us with a sample of the authentic material for comparison.

Photocycloaddition of Bicyclic Cyclopentenones with Cyclohexene

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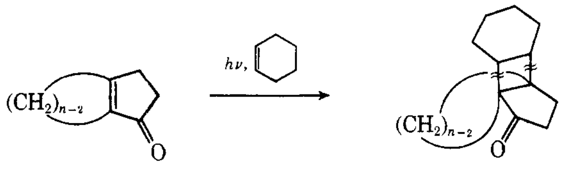
While one of the most important problems in the field of photocycloaddition of cyclic enones to an alicyclic olefin is the stereochemistry of photoannelation adducts, very few studies have been made.[1] We wish to report here the remarkable effect of the fused ring size on the photocycloaddition of a series of bicyclic cyclopentenones **1–4** with cyclohexene.

On irradiation of the enones **1**, **3**, and **4** with 10 molar excess of cyclohexene, the respective cycloadducts **5**,[2] **7**, and **8** were obtained as major products in good yields, but these cycloadducts consisted of three or four stereoisomers.[3] On the other hand, the photoreaction of the enone **2** under a similar condition gave the sole cycloadduct **6** in an 84% yield, along with small amounts of three kinds of other products (Chart I). Concerning the structure of **6**, the absolute configuration about the cyclobutane ring was established to be cis-anti-trans by means of x-ray analysis[4] (Figure 1).

Chart I



1, $n = 5$	**5a**, 21%; **b**, 35%; **c**, 12%; **d**, 5%
2, $n = 6$	**6**, 84%
3, $n = 7$	**7a**, 7%; **b**, 82%; **c**, 5%
4, $n = 8$	**8a**, 3%; **b**, 79%, **c**, 5%

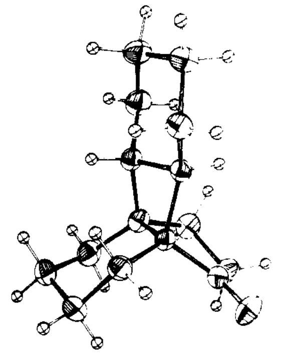


Figure 1. Molecular structure of **6**.

Table I. Phosphorescence Spectra and Lifetimes of the Enones 1–4[a]

Enone	Phosphorescence, cm^{-1} Origin	Max	10%	τ, ms
1[b]	26 000	21 200	24 800	760
2[b]	25 800	20 900	25 100	28
3	26 100	22 200	25 500	64
4	26 200	22 300	25 500	150

[a] Measured at 77 K in EPA matrix. [b] Measured by Cargill et al.[1b,6]

The quantum yield for the formation of **6** was determined to be 0.69. The stereoselective cycloaddition of **2** as well as the high quantum efficiency, compared with 0.25 for **5a–d**[1b] and 0.48 for tricyclo[6.3.0.0^{2,7}]undecan-9-ones,[5] suggests that **6** may be formed in a concerted manner via a singlet excited state of **2**. But the formation of **6** was quenched by added piperylene, and, therefore, the participation of triplet species was concluded.

It is obvious, however, from the spectroscopic data listed in Table I that there is no significant difference in the nature of each triplet excited state of **1–4**.

Consequently, it is reasonable that the observed distinction in reactivity among these enones is considered in terms of the steric effect of fused alicyclic rings on the cycloaddition via triplet 1,4-diradical intermediates derived from the enones and cyclohexene. Namely, it may be assumed that nonbonded interaction of hydrogens between ring methylenes plays a key role in the determination of the stereoisomer distribution. In the case of either **1**, having planar cyclopentene ring, or **3** and **4**, having flexible cycloheptene and cyclooctene ones, four or three isomers are formed. It is probably due to little difference in the nonbonded interaction among the four possible stereoisomers. On the other hand, in the case of **2**, having a less flexible cyclohexene ring, the nonbonded interaction may be much severer than in other cases and, as a result, only the cis-anti-trans isomer, having the least interaction, may be produced selectively.

Experimental Section[7]

Materials. The enones **1–3** were prepared according to the procedures reported by Kulkarni and Dev,[8] by Dev,[9] and by Plattner and Büchi,[10] respectively, and **4** was prepared by a method similar to that of **3**.

General Irradiation Procedure. The enones **1–4** were irradiated with 10 molar excess of cyclohexene using a 500-W high-pressure mercury lamp through a Pyrex filter under nitrogen at room temperature, and the irradiation was continued until the enones were almost consumed (>95%). After removal of cyclohexene, the residue was distilled under reduced pressure. The products were analyzed by GLC (6 ft × 0.125 in. columns: A, 10% PEG-20M; B, 5% SE-30; C, 10% FFAP; D, 10% DEGS), and isolated by preparative GLC. Yields were estimated based on the enones reacted. [Yields and retention times on column D (temperature) are given for each adduct below.]

All the cycloadducts showed only aliphatic protons in the NMR spectra, and gave weak parent peaks with base peaks of molecular ions corresponding to the respective enone plus hydrogen in the mass spectra. The carbonyl absorptions in the IR spectra of **5a–d**, **6**, and **7a–c** were at 1715 cm^{-1} and of **8a–c** at 1710 cm^{-1}. 6-(3-Cyclohexenyl)bicyclo[4.3.0]nonan-7-one (**9**) was identified with the authentic sample prepared from **2** and 3-bromocyclohexene using the method of Stork et al.[11] The other products were identified with the authentic materials.

Irradiation of 1. Four isomeric cycloadducts **5a–d** were obtained: **5a** [21%, 10.6 min (140 °C)]; **5b** [35%, 13.7 min (140 °C)], mp 59–61 °C; **5c** [12%, 15.6 min (140 °C)]; **5d** [5%, 18.4 min (140 °C)].

Irradiation of 2. Cis-anti-trans cycloadduct **6**, adduct **9**, bicyclo[4.3.0]nonan-7-one (1%), and 3,3′-bicyclohexenyl were obtained. **6** [84%, 12.3 min (150 °C)], mp 70–71 °C. 2,4-Dinitrophenylhydrazone mp 184–185 °C. Anal. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.58; N, 14.06. Found: C, 63.25; H, 6.47; N, 14.02. **9** [3%, 17.7 min (150 °C)]: IR 1725, 720 cm^{-1}; NMR δ 0.90–2.60 (m, 20 H), 5.25–5.80 (m, 2 H); mass spectrum *m/e* 218 (M$^+$), 138, semicarbazone mp 238–240 °C. Anal. Calcd for $C_{16}H_{25}ON_3$: C, 69.78; H, 9.15; N, 15.26. Found: C, 69.62; H, 9.29; N, 15.05.

Irradiation of 3. Three isomeric cycloadducts **7a–c**, bicyclo[5.3.0]decan-8-one (3%), and 3,3′-bicyclohexenyl were obtained. **7a** [7%, 11.0 min (160 °C)]. **7b** [82%, 14.7 min (160 °C)], mp 47–48 °C. Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.48; H, 10.60. **7c** [5%, 20.1 min (160 °C)].

Irradiation of 4. Three isomeric cycloadducts **8a–c**, bicyclo[6.3.0]undecan-9-one (1%), and 3,3′-bicyclohexenyl were obtained. **8a** [3%, 12.4 min (170 °C)]. **8b** [79%, 17.0 min (170 °C)], mp 91–92 °C. Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.63; H, 10.79. **8c** [5%, 23.0 min (170 °C)].

Quantum Yield Measurement. A 0.13 M solution of **2** in cyclohexene was irradiated to about 3% conversion. After irradiation the calibrating compound was added and the amount of **6** determined by GLC (column C). Actinometry was by the ferrioxalate method.

Quenching of Photocycloaddition of 2 with Cyclohexene. A 0.05 M solution of **2** in cyclohexene was used with added piperylene (0.01–0.5 M).

Registry No.—**1**, 10515-92-1; **2**, 22118-00-9; **3**, 769-32-4; **4**, 38262-50-9; **5a**, 62264-61-3; **5b**, 62319-07-7; **5c**, 62319-08-8; **5d**, 62319-09-9; **6**, 58595-14-5; **6** 2,4-DNPH, 62264-62-4; **9** semicarbazone, 62264-63-5; **7a**, 62264-64-6; **7b**, 62319-10-2; **7c**, 62356-50-7; **8a**, 62264-65-7; **8b**, 62319-11-3; **8c**, 62319-12-4; cyclohexene, 110-83-8.

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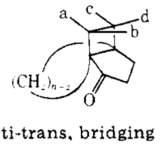
(2) Cargill et al. reported that four isomeric cycloadducts were obtained on irradiation of **1** with cyclohexene in methylene chloride,[1b] which is in agreement with our result.

(3) Generally, photocycloaddition of the cyclic enone to an alicyclic olefin gives a number of stereoisomers.[1] In the present case, the formation of four stereoisomers is possible, and the nomenclature is as follows:



cis-anti-trans, bridging a to d
cis-syn-trans, bridging b to c
cis-anti-cis, bridging a to c
cis-syn-cis, bridging b to d

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(7) Melting points are uncorrected. Infrared spectra were recorded using a JASCO IR-G spectrometer. NMR spectra were obtained in a JEOL JNM-PS-100 spectrometer using CCl_4 as a solvent and Me_4Si as an internal standard. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC separation was conducted on a Varian Aerograph 90-P gas chromatograph. Phosphorescence spectra were recorded on a Hitachi MPF-3 spectrometer.

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Oxidation of L-Cystine by Dimethyl Sulfoxide. Cysteic Acid–Sulfoxide Compounds

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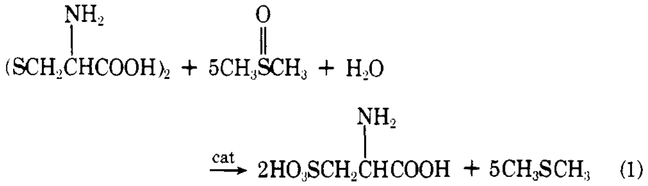
The oxidation of disulfides to sulfonic acids by dimethyl sulfoxide (Me_2SO) has been described;[1] however, L-cystine is insoluble in Me_2SO and satisfactory oxidation is not accomplished without modification of the procedure. The needed changes are an increase in the amount of halogen or hydrogen halide catalyst to about twice the number of moles of L-cystine and a significantly lower reaction temperature. With an appropriately high concentration of mixed I_2–HCl catalyst, oxidation occurs smoothly at room temperature, the water necessary for stoichiometry (eq 1) and reaction moderation being supplied through the use of concentrated hydrochloric acid.



$$(SCH_2\overset{NH_2}{\overset{|}{C}}HCOOH)_2 + 5CH_3\overset{O}{\overset{\|}{S}}CH_3 + H_2O \xrightarrow{cat} 2HO_3SCH_2\overset{NH_2}{\overset{|}{C}}HCOOH + 5CH_3SCH_3 \qquad (1)$$

Addition of acetone to the reaction mixture gave abundant precipitate, but this was not the expected L-cysteic acid (CysA). Accumulated evidence—high weight of product, acidic and oxidizing properties, elemental analysis, conversion to CysA by solvent extraction or vacuum drying, and ready formation by direct combination of CysA and Me_2SO—established that this was a 1:1 compound of CysA and Me_2SO.

My obtaining this molecular complex led to investigation of related compounds. It was found that CysA also dissolves in tetramethylene sulfoxide (TMSO) and, on addition of acetone, the corresponding TMSO compound precipitates. CysA has quite limited solubility in methyl phenyl sulfoxide, so, in this instance, no complex is obtained. The combinations DL-cysteic acid–Me_2SO and DL-homocysteic acid with both Me_2SO and TMSO were also checked. The corresponding molecular complexes were obtained; though, with DL-homocysteic acid, these were syrups from which it appeared that the compounds slowly crystallized.

The explanation for formation of these compounds would appear to lie in the ability of the oxygen of sulfoxides such as Me_2SO and TMSO to serve as a proton acceptor.[2] Such salts of strong acids have been reported[3] though the mole ratio is not always 1:1. CysA and, most likely, the other cysteic acids exist as the ammonium sulfonate zwitterion,[4] the carboxyl group being un-ionized. This leads to the interpretation of the subject compounds as carboxylic acid salts or associates of sulfoxides. These have also been investigated and isolated.[5] Those that I have obtained differ in being significantly more stable and amenable to characterization.

Experimental Section

General. The Me_2SO, iodine, hydrochloric and hydrobromic acids, and solvents were reagent grade. Other materials were a quality,