continue to be directed toward the understanding and synthetic exploitation of the 1,3 reactivity of 2,3-diazabutadienes.

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Registry No.—**17** (charged), 63570-24-1; **17** (unchanged), 63570-25-2; **20**, 67478-68-6; **22**, 67478-69-7; **23**, 67478-70-0; **27a**, 67478-71-1; **27b**, 67478-72-2; **27c**, 67478-73-3; **31**, 67478-74-4; **32**, 67478-75-5; **33**, 67478-76-6; **33** picrate, 67478-77-7; **34**, 67478-78-8; **35**, 63570-22-9; **38**, 67478-79-9; **40a**, 67478-80-2; **40b**, 67478-81-3; **40c**, 67478-82-4; **47**, 63570-20-7; diphenylketene, 525-06-4; phenylketene, 3496-32-0; ketene, 463-51-4; vinylketene, 50888-73-8; ethylphenylketene, 20452-67-9; diphenylacetyl chloride, 1871-76-7; phenylacetyl chloride, 103-80-0; crotonyl chloride, 10487-71-5; α-phenylbutyryl chloride, 36854-57-6.

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Stereoselectivity in Photocycloaddition of Bicyclic Enones to Olefins

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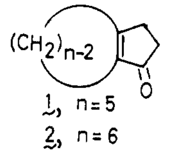
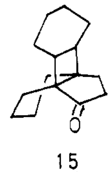
Stereoselectivity in photocycloaddition of bicyclic enones **1**, **2**, **5**, and **6** to 2-butene and cyclohexene is discussed. In the cases of **1** and **5**, having a five-membered ring fused to the double bond of monocyclic enones, from two to four kinds of cycloadducts were always obtained regardless of the ring size of the enone moieties, and, therefore, stereoselectivity is relatively low. On the other hand, in the cases of **2** and **6**, having a six-membered ring fused to the double bond of monocyclic enones, the formation of cis-anti-trans cycloadducts proceeded stereoselectively. This remarkable effect of fused ring size on stereoselectivity in photocycloaddition is ascribed to the degree of nonbonded hydrogen interaction in 1,4-diradical intermediates and can be associated with differing flexibility and rigidity of cyclohexane and cyclopentane rings.

While the stereochemistry of photocycloaddition and the factors controlling it are the most important and intriguing problems in the field of photocycloaddition of cyclic enones to olefins, relatively few studies have been made. Recently reports on the stereochemical assignment of photocycloadducts of cyclohexenone to cycloheptene,[1a] monocyclic cyclohexenone derivatives to cyclopentene,[1b] and bicyclic cyclohexenone **5** to 2-butene [1c]have appeared. In these reactions, photocycloaddition proceeded nonstereoselectively, and, therefore, two or three stereoisomers of cycloadducts were always formed. Subsequently, we reported that photocycloaddition of bicyclic cyclopentenone **2** to cyclohexene took place stereoselectively to afford cis-anti-trans adduct **15** as a sole cycloadduct, though enones **1**, **3**, and **4** gave mixtures of three or four stereoisomeric cycloadducts.[2] This marked distinction in stereoselectivity in photocycloaddition between these enones was interpreted in terms of differences in steric effects in the alicyclic rings fused to the double bond of cyclopentenone. To further clarify this concept, we have investigated the stereoselectivity in photocycloaddition of bicyclic enones **1**, **2**, **5**, and **6**, composed of five- and six-membered rings, to 2-butene and cyclohexene.



1, n=5
2, n=6
3, n=7
4, n=8



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First, we examined the photoreaction with about a 20-fold excess of *cis*- or *trans*-2-butene in methylene chloride at −70 °C. In the case of bicyclic cyclopentenone **1**, four stereoisomeric cycloadducts (**7a–d**)[3] were obtained. With bicyclic cyclohexenone **5**, as also reported by Cargill et al.,[1c] three isomeric cycloadducts (**10a–c**)[3] and keto olefin **11** were given. On the other hand, with enones **2** or **6** one of two kinds of cycloadducts (**8a** or **12a**)[3] was obtained in quantity, respectively, along with small amounts of another cycloadduct (**8b** or **12b**)[3]

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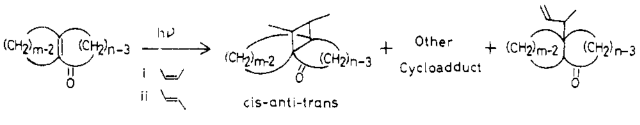
Table I. S Values of Methyl Protons in the LIS NMR Spectra of Cycloadducts 7a,b, 8a, 10a,b, and 12a

cycloadduct	registry no.	S^a
7a	67504-85-2	0.22 0.61
7b	67504-84-1	0.28 0.44
8a	67504-83-0	0.29 0.51
10a	38312-64-0	0.19 0.46
10b	38343-72-5	0.25 0.43
12a	67504-82-9	0.25 0.44

[a] $[Eu(DPM)_3]/[ketone] = 0.2–0.8$.

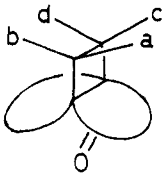
Chart I



		Number of Cycloadduct	% Yield of Product (Based on Reacted Enone)		
1 m=n=5	i	4	7b 34%,	7a 23%, 7c 3%, 7d 5%	—
	ii	4	32%,	23%, 5%, 2%	—
2 m=6, n=5	i	2	8a 80%,	8b 3%,	9 6%
	ii	2	84%,	4%,	7%
5 m=5, n=6	i	3	10b 65%,	10a 28%, 10c 4%,	11 3%
	ii	3	86%,	6%, 7%,	2%
6 m=n=6	i	2	12a 42%,	12b 5%,	13 1%
	ii	2	42%,	4%,	1%

and keto olefin (**9** or **13**). In all cases products obtained from *cis*-2-butene were essentially the same as those from *trans*-2-butene (Chart I).

The configuration of methyl groups in the cycloadducts **7a**, **7b**, **8a**, and **12a** was confirmed by LIS NMR in the same manner as Cargill's assignment of structure to **10a** and **10b**.[1c] Evidently, for the four possible positions of a methyl group, the degree of deshielding should decrease going from a to d on addition of $Eu(DPM)_3$, as shown in structure A. This is



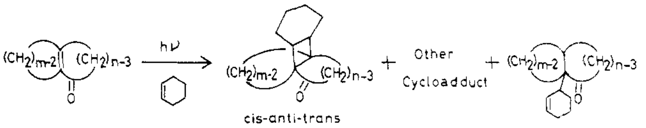
A

expressed in terms of an S value[4] and is summarized in Table I.

Among the S values of methyl protons of **10a** and **10b**, one of those of **10a** is the largest (0.46) and the other is the smallest (0.19), and those of **10b** are the two intermediate values (0.25 and 0.43).[5] Consequently, it is reasonable to assign the structures of **10a** and **10b** to cis-syn-trans and cis-anti-trans in a manner similar to Cargill's assignment.[1c] Similarly, one of S values of methyl protons of **7a** is the largest (0.61) and the other is the smallest (0.22), and those of **7b** are intermediate (0.28 and 0.44) among S values for **7a** and **7b**. Accordingly, the structures of **7a** and **7b** should be assigned to cis-syn-trans and cis-anti-trans, respectively.[6] Methyl protons of **8a** and **12a** show similar S values (**8a**, 0.29 and 0.51; **12a**, 0.25 and 0.44) to those of **7b** and **10b**, which suggests that **8a** and **12a** have the cis-anti-trans configuration. The structures of keto olefins **9** and **13** may be assigned in analogy with **11**[1c] since they show vinyl absorption in their IR and NMR spectra.

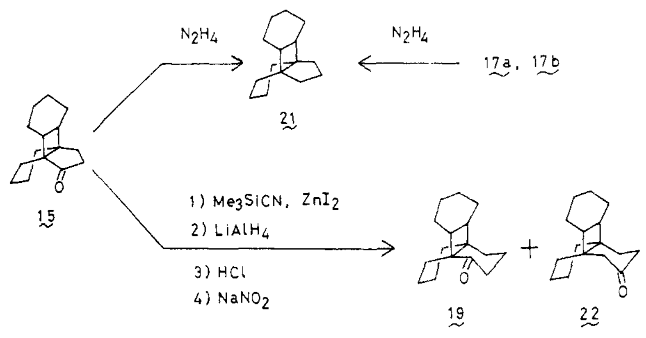
Next, the photoreaction with cyclohexene was examined. As we reported previously,[2] **1** gave four isomeric cycloadducts (**14a–d**),[3] whereas **2** gave cis-anti-trans adduct **15** as a sole

Chart II



	Number of Cycloadduct	% Yield of Product (Based on Reacted Enone)		
1 m=n=5	4	├ 14a 21%, 14b 31%, 14c 12%, 14d 5% ┤		—
2 m=6, n=5	1	15 84%,	——	16 3%
5 m=5, n=6	2	17b 43%,	17a 24%,	18 4%
6 m=n=6	1	19 12%,	——	20 13%

Chart III



cycloadduct along with some minor products. In addition, irradiation of **5** with a 10-fold excess of cyclohexene afforded two kinds of cycloadducts (**17a** and **17b**)[3] together with small amounts of keto olefin **18**, bicyclo[4.3.0]nonan-1-one, and 3,3′-bicyclohexenyl. On the other hand, with **6** only one cycloadduct (**19**) was given, though other products such as keto olefin **20**, bicyclo[4.4.0]decan-1-one, and 3,3′-bicyclohexenyl were formed in substantial amounts in this case (Chart II).

The configuration around the cyclobutane of **17a**, **17b**, and **19** was established on the basis of the results of some reactions shown in Chart III. Since Wolff–Kishner reduction of **17a** and **17b** gave the same single hydrocarbon (**21**) in good yields, which was identical with the hydrocarbon obtained by reduction of cis-anti-trans cycloadduct **15** under similar condition,[7] **17a** and **17b** might be cis-syn-trans or cis-anti-trans adducts. Interestingly, the semicarbazone formation of **17b** proceeded quickly on treatment with semicarbazide hydrochloride and potassium acetate at room temperature, but with **17a** it took about 2 days. The above fact probably indicates that the carbonyl group of **17a** is sterically more hindered than that of **17b**.[8] Consequently, it may be reasonable to assume that **17a** has the cis-syn-trans configuration and **17b** the cis-anti-trans one.

Tiffeneau–Demjanov ring enlargement of **15** with retention of configuration around cyclobutane yielded two cyclohexanone derivatives (**22** and **19**) in a ratio of 4:1 in 26% overall yield. Since the minor ring expansion product **19** was identical with obtainable cycloadduct **19** (IR, GLC, and melting point), the structure of **19** should be assigned to cis-anti-trans.

The results in Chart I and II are summarized as follows. In the cases of both olefins with bicyclic enones **1** and **5**, where the five-membered ring fuses to the double bond of cyclopentenone and cyclohexenone, respectively, from two to four kinds of cycloadducts were always obtained in considerable amounts regardless of the ring size of the enone moieties, and therefore stereoselectivity in photocycloaddition is relatively low as well as in the case of stepwise cycloaddition of some cyclic enones to olefins reported previously.[1a,b] On the other hand, in the cases of **2** and **6**, where the six-membered ring fuses to the double bond of the monocyclic enones, the formation of cis-anti-trans cycloadducts, on the whole, proceeded stereoselectively.

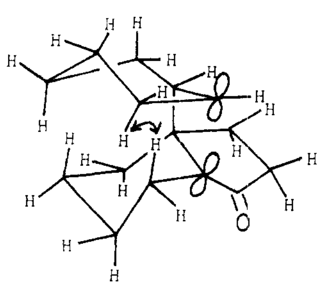
Table II. Phosphorescence Spectra and Lifetimes of Enones 5 and 6[a]

enone	phosphorescence, cm^{-1}	τ, ms
5	25 600 (origin) 21 700 (max) 24 900 (10%)	39
6	24 800 (origin) 21 900 (max) 24 300 (10%) 23 100 (sh)	490

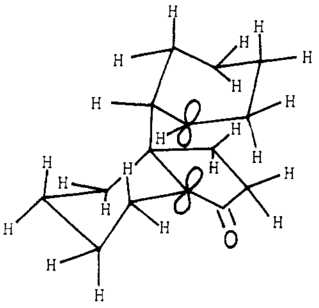
[a] Measured at 77 K in EPA matrix.

Concerning the mechanism of the present photocycloaddition, phosphorescence spectra and lifetimes of **5** and **6** were measured. It is evident from the results listed in Table II that there is no significant difference in the nature of the excited triplet states of **1**,[2] **2**,[2] **5**, and **6**.

Recently, it has been pointed out that in stepwise photocycloaddition reactions, steric effects in diradical intermediates are important in determining product stereochemistry.[9] In the present case, differences in stereoselectivity in photocycloaddition may be interpreted in terms of steric effects in 1,4-diradical intermediates such as **23** and **24**, assuming that the initial bond formation occurs at the β position of the enones.[10] Namely, in the cases of **2** and **6**, having a cyclohexane ring fused to the double bond, significant nonbonded interaction between the axial hydrogens of the cyclohexane rings α to the radical centers may be produced in the intermediate **23**. Therefore, reversion to starting material rather than cyclization might occur predominantly from this intermediate.[12] In intermediate **24**, however, unfavorable nonbonded interaction between hydrogens may be reduced, and consequently cis-anti-trans cycloadducts are formed through **24** exclusively.[13] In the cases of **1** and **5**, having a cyclopentane ring fused to the double bond, there may be little difference in nonbonded hydrogen interaction between the two kinds of 1,4-diradical intermediates corresponding to **23** and **24** owing to the planarity of both cyclopentane rings, and therefore at least two isomeric cycloadducts may be formed indiscriminately.



23



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Moreover, the higher stereoselectivity observed with cyclohexene than with *cis*- and *trans*-2-butene is attributable to the rigidity of the cyclohexene ring, which may make the unfavorable nonbonded interaction of allyl hydrogens larger in 1,4-diradical intermediates like **23**.

In conclusion, this work shows that five- and six-membered rings fused to the double bond of alicyclic enones have dramatically different effects on stereoselectivity in photocycloaddition to olefins. This difference is ascribed to the degree of nonbonded hydrogen interaction in 1,4-diradical intermediates and can be associated with the differing flexibility and rigidity of cyclohexane and cyclopentane rings.

Experimental Section[14]

General Irradiation Procedure. Enones **1** and **2** were prepared according to the procedures reported by Kulkarni and Dev[15] and Dev,[16] respectively, and enones **5** and **6** were prepared by the method of Hill and Conley.[17] Irradiation with cyclohexene was carried out as described previously,[2] and with *cis*- and *trans*-2-butene it was carried out with about a 20-fold excess of olefin in methylene chloride at −70 °C. The progress of the reaction was monitored by GLC, and irradiation was continued until the enones were almost consumed (>95%). After removal of olefin and solvent, the residue was distilled under reduced pressure. Products were analyzed by GLC (1 m × 3 mm 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 reacted enones. [Yields and retention times on column C (temperature) are given for each adduct below.] The carbonyl absorptions in the IR spectra of cycloadducts **7a–d** and **8a,b** were at 1710 cm^{-1}, of **12a,b** and **17a** at 1680 cm^{-1}, and of **17b** and **19** at 1670 cm^{-1}. In the mass spectra, cycloadducts to 2-butene showed weak parent peaks with base peaks of molecular ions corresponding to the respective enone, and those to cyclohexene showed base peaks corresponding to the respective enone plus hydrogen. Cycloadducts **17a,b** and **19** showed only aliphatic protons in their NMR spectra. Keto olefins **18** and **20**, bicyclo[4.3.0]nonan-1-one. bicyclo[4.4.0]decan-1-one, and 3,3′-bicyclohexenyl were identified with authentic materials (IR and GLC). Authentic samples of **18** and **20** were prepared from **5** or **6** and 3-bromocyclohexene using the method of Stork et al.[18]

Irradiation of 1 with 2-Butene. Cis-syn-trans adduct **7a**, cis-anti-trans adduct **7b**, and two other cycloadducts (**7c** and **7d**) were obtained. Yields with *trans*-2-butene are given in parentheses. **7a** [23% (23%), 6.2 min (110 °C)]: NMR δ 0.98 (d, 3 H), 1.02 (d, 3 H), 1.20–2.80 (m, 12 H). Semicarbazone, mp 196–197 °C. Anal. Calcd for $C_{13}H_{21}ON_3$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.09; H, 9.02; N, 17.56. **7b** [34% (32%), 7.6 min (110 °C)]: NMR δ 0.92 (d, 3 H), 0.99 (d, 3 H), 1.20–2.80 (m, 12 H). Semicarbazone, mp 199–200 °C. Anal. Calcd for $C_{13}H_{21}ON_3$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.07; H, 8.99; N, 17.77. **7c** [3% (5%), 9.8 min (110 °C)]. **7d** [5% (2%), 13.9 min (110 °C)].

Irradiation of 2 with 2-Butene. Cis-anti-trans adduct **8a**, cycloadduct **8b**, and keto olefin **9** were obtained. **8a** [80% (84%), 7.8 min (130 °C)]: NMR δ 0.92 (d, 6 H), 1.00–2.50 (m, 14 H). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.91; H, 10.46. **8b** [3% (4%), 9.5 min (130 °C)]. **9** [6% (7%), 12.1 min (130 °C)]: IR 3060, 1720, 900 cm^{-1}; MS *m/e* 192 (M^+), 137; NMR δ 0.90 (d, 3 H), 1.00–2.80 (m, 14 H), 4.90–6.00 (m, 3 H).

Irradiation of 6 with 2-Butene. Cis-anti-trans adduct **12a**, cycloadduct **12b**, and keto olefin **13** were obtained. **12a** [42% (42%), 9.5 min (140 °C)]: NMR δ 0.82 (d, 3 H), 0.90 (d, 3 H), 1.10–2.60 (m, 16 H). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.26; H, 10.91. **12b** [5% (4%), 12.6 min (140 °C)]: NMR δ 0.90 (d, 3 H), 1.00 (d, 3 H), 1.10–2.50 (m, 16 H). **13** [4% (5%), 15.6 min (140 °C)]: IR 3070, 1690, 900 cm^{-1}; MS *m/e* 206 (M^+), 151; NMR δ 0.92 (d, 3 H), 1.10–2.80 (m, 16 H), 4.80–6.00 (m, 3 H).

Irradiation of 5 with Cyclohexene. Cis-syn-trans adduct **17a**, cis-anti-trans adduct **17b**, keto olefin **18**, bicyclo[4.3.0]nonan-1-one (3%), and 3,3′-bicyclohexenyl were obtained. **17a** [24%, 10.5 min (160 °C)]. Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.33; H, 10.18. Upon treatment with semicarbazide hydrochloride and potassium acetate in absolute ethanol at room temperature, **17a** afforded semicarbazone after about 2 days, mp 220–222 °C. Anal. Calcd for $C_{16}H_{25}ON_3$: C, 69.78; H, 9.15; N, 15.26. Found: C, 69.54; H, 9.24; N, 15.33.

17b [43%, 13.2 min (160 °C)], mp 97–98 °C. Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.25; H, 10.14. **17b** quickly gave its semicarbazone under similar conditions as above, mp 209–210 °C. Anal. Calcd for $C_{16}H_{25}ON_3$: C, 69.78; H, 9.15; N, 15.26. Found: C, 69.79; H, 9.19; N, 15.36.

18 [4%, 15.2 min (160 °C)]: IR 3030, 1685, 710 cm^{-1}; MS *m/e* 218 (M^+), 138; NMR δ 0.95–2.70 (m, 20 H), 5.10–5.90 (m, 2 H). Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.25; H, 10.35.

Irradiation of 6 with Cyclohexene. Cis-anti-trans adduct **19**, keto olefin **20**, bicyclo[4.4.0]decan-1-one (18%), and 3,3′-bicyclohexenyl were obtained. **19** [12%, 10.0 min (180 °C)] mp 105–106 °C. Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.77; H, 10.54. **20** [13%, 13.8 min (180 °C)]: IR 3030, 1690, 710 cm^{-1}; MS *m/e* 232 (M^+), 152; NMR δ 1.00–2.70 (m, 22 H), 4.90–5.80 (m, 2 H). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.45; H, 10.27.

Wolff–Kishner Reduction of 17a and 17b. **17a** (0.268 g, 1.23 mmol) and 1.4 g of potassium hydroxide in 20 mL of 85% hydrazine hydrate and 10 mL of diethylene glycol were heated at 150 °C for 3 h. Excess hydrazine hydrate was distilled off, and the mixture was heated at 220 °C for 4 h. After cooling, the mixture was neutralized with dilute hydrochloric acid and extracted with ether. Evaporation of the ether and distillation under reduced pressure gave 0.145 g (58%) of **21**. Reduction of **17b** under similar conditions gave the same hydrocarbon **21** in 70% yield, which was identical with the sample prepared by reduction of **15**[7] (IR and GLC).

Ring Enlargement of 15. To a mixture of 1.0 g (5.0 mmol) of **15** and catalytic amounts of zinc iodide was added dropwise 0.59 g (6.0 mmol) of trimethylsilyl cyanide,[19] and the mixture was stirred at room temperature for 2 h and filtered. The filter was rinsed with dry ether, and the combined filtrate was evaporated to give 1.37 g (86%) of cyanotrimethylsilyloxy compound: IR 2210, 1240, 1100, 830 cm^{-1}.

A 1.37-g (4.31 mmol) amount of the above cyanide in 10 mL of ether was added dropwise to a suspension of 0.25 g (6.6 mmol) of lithium aluminum hydride in 10 mL of ether, and the mixture was refluxed for 2 h. Excess hydride was decomposed by water, and dilute sodium hydroxide solution was added and then filtered. The filtrate was extracted with ether, and the organic layer was washed with saturated sodium chloride solution and dried (Na_2SO_4). After filtration, gaseous hydrogen chloride was bubbled into the ethereal solution for 2 h. The white solid that formed was filtered, washed with ether, and dried to afford 0.775 g (62%) of the hydrochloride salt of the aminomethylhydroxy compound: IR 3350 cm^{-1}.

To a solution of 0.775 g (2.69 mmol) of the above amine hydrochloride salt and 0.232 g (2.89 mmol) of sodium acetate in 25 mL of acetic acid and 10 mL of water was added dropwise 0.186 g (2.69 mmol) of sodium nitrite in 5 mL of water, and the mixture was stirred at room temperature for 2 h. The mixture was poured into water and extracted with ether. The organic layer was washed with dilute sodium bicarbonate solution and saturated sodium chloride solution and then dried (Na_2SO_4). The ether was evaporated and the residue distilled under reduced pressure to afford 0.274 g (44%; 26% from **15**) of a mixture of the two ketones **19** and **22** in a ratio of 1:4. **19** thus prepared was identical with the sample obtained by photocycloaddition of **6** to cyclohexene (IR, GLC, and melting point). **22**: mp 74–75 °C; IR 1690 cm^{-1}; MS *m/e* 232 (M^+), 150; NMR δ 1.00–2.50 (m). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.57; H, 10.46.

Registry No.—1, 10515-92-1; **2**, 22118-00-9; **5**, 22118-01-0; **6**, 18631-96-4; *cis-syn-cis*-**7**, 67452-38-4; *cis-anti-cis*-**7**, 67504-81-8; **7a** semicarbazone, 67452-96-4; **7b** semicarbazone, 67504-80-7; **8b**, 67452-39-5; **9**, 67452-40-8; **12b**, 67452-41-9; **13**, 67452-87-3; **15**, 67504-49-8; **5** cyanotrimethylsilyloxy derivative, 67452-94-2; **15** aminomethylhydroxy HCl derivative, 67452-95-3; **17a**, 67452-88-4; **17a** semicarbazone, 67452-89-5; **17b**, 67504-47-6; **17b** semicarbazone, 67504-48-7; **18**, 67452-90-8; **19**, 67452-91-9; **20**, 67452-92-0; **21**, 63305-46-4; **22**, 67452-93-1; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; cyclohexene, 110-83-8.

References and Notes

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(3) Compound numbers a–d were assigned in order of GLC retention times on column C (see Experimental Section) and do not refer to the stereochemistry.

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(5) This result is almost consistent with that reported by Cargill et al.[1c]

(6) δ values of methyl protons of **7a, 7b,** and **8b** are slightly larger than those of **10a, 10b,** and **12a,** presumably because of the difference in coordination distance between Eu^{3+} and the carbonyl groups of cyclopentanone and cyclohexanone.

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(8) Similarly, cis-anti-trans adduct **7b** readily gave its semicarbazone, but cis-syn-trans adduct **7a** gave it after 3 days.

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(10) The mechanistic pathway involving the initial bond formation at the β position of the enones is favored in the photocycloaddition of 2-cyclopentenone to 1,2-dichloroethylene[11] and enone **5** to 2-butene.[1c]

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(13) As for the selective cyclization, in the case of cycloaddition to cyclohexene, to form cis-anti-trans adducts which seem to be less favorable than the corresponding cis-syn-cis adducts in the thermodynamic sense, it may be reasonable to assume that the ring closure to give the observed adducts is rapid, though the relative thermodynamic stability of stereoisomers of these tetracyclic compounds is uncertain at present.

(14) Melting points are uncorrected. Infrared spectra were recorded using a JASCO IR-G spectrometer. NMR spectra were obtained on 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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