The Stereochemistry of the Photochemical Rearrangement of 1-Substituted 1a,7b-Dihydro-1*H*-cyclopropa[*a*]naphthalenes under Sensitized Conditions[1)]

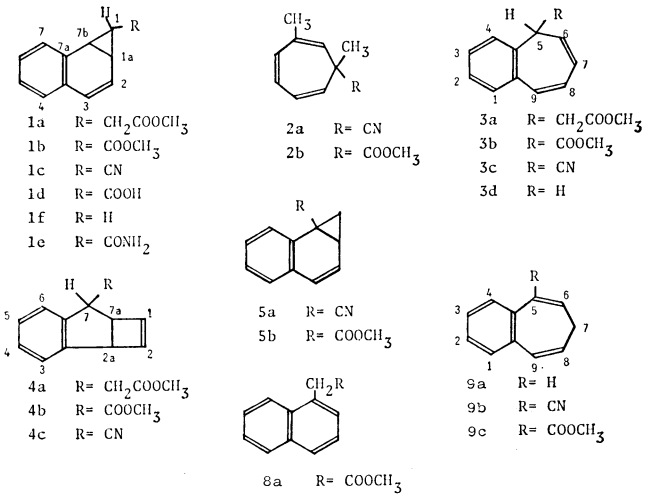
Masahiko KATO,* Hisako KOBAYASHI, Hiroyuki YAMAMOTO,
Koji SETO, Satoru ITO, and Toshio MIWA
Faculty of Science, Osaka City University, Sugimoto-3, Sumiyoshi-ku, Osaka 558

(Received December 21, 1981)

The photolysis of 1-substituted 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes in the presence of Michler's ketone leads principally to 5-substituted 5*H*-benzocycloheptenes as primary products *via* a stepwise mechanism. The reaction proceeds smoothly with inversion of the migrating carbon if there is no steric hindrance, but it proceeds predominantly with retention if the inversion course is severely suppressed by steric hindrance. The marked difference in the *exo-endo* ratio of the secondary photocyclization products depending on the irradiation conditions was also recognized for 1-methoxycarbonylmethyl derivative.

The stereochemical course of the photochemical Berson-Willcott rearrangements had been reported by us for 1-methoxycarbonylmethyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**1a**) under direct irradiation[2)] and by Klärner for 7-cyano- and 7-methoxycarbonyl-2,7-dimethyl-1,3,5-cycloheptatriene (**2**) under sensitized irradiation.[3)] In both cases, the rearrangements proceeded principally by way of inversion at the migrating carbon center. In the former case, in parallel with a result for the 4-*t*-butyl derivative of **1a**,[4)] we suggested a concerted mechanism controlled by the Woodward-Hoffmann rule, while in the latter, Klärner proposed a biradical pathway.

In the course of a photochemical study of 1-*exo*-methoxycarbonyl derivative (**1b**) in the presence of several sensitizers, 5-methoxycarbonyl-5*H*-benzocycloheptene (**3b**)[5)] was obtained as a primary product but 7-methoxycarbonyl-7*H*-benzocycloheptene or the secondary photo-products derived from it were not detected. This and the results by Klärner[3)] suggest that the reaction course and the stereochemistry under such photolytic conditions might be different from the results of direct irradiation. Interest has also been focused on the effect of a substituent on C-1, *i.e.*, electron-attracting or releasing, which would affect the bond strength of the three-membered rings not only in their ground state[6)] but also in the excited states.[6)] In order to clarify these points, we studied the stereochemical course of sensitized reactions of a series of 1-substituted 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes (**1**) using their racemic and optically active forms. The substituents chosen were methoxycarbonylmethyl as an electron-releasing group, and methoxycarbonyl and cyano as electron-attracting groups with large and small steric requirement, respectively.



Scheme 1.

*Photochemistry of 1-*exo*-Methoxycarbonyl Derivative (**1b**). Irradiation in the Presence of Michler's Ketone*: Irradiation of **1b** in benzene with 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) for 2.5 h gave a recovery of material corresponding to 75% of the initial weight of **1b**, from which **1b** (30%), **3b** (30%), and **8a** (10%) were separated. Under these conditions, the cyclization products from **3b** were negligible but prolonged irradiation gave a small amount of an *exo-endo* mixture of 7-methoxycarbonyl-2a,7a-dihydro-7*H*-cyclobut[*a*]-indene (**4b**), which was not detected under direct irradiation.

When we used **1b**-1-d_1 for photolysis, we obtained only **3b**-5-d_1 as new products; this result supports the regiospecific rearrangement at C-1.

In the same experiment, (+)-**1b** ($[\alpha]_D$ +124°) gave **3b** ($[\alpha]_D$ −2.82°) in addition to a recovery of **1b** ($[\alpha]_D$ +114°).

Identification of the Products: **3b** was identical with a sample obtained by alcoholysis of the corresponding nitrile (**3c**) reported previously.[5)] An *exo-endo* mixture of **4b** was separated by VPC. The mass spectra of the two components showed very similar fragmentation patterns except for their relative intensities: peaks at *m/e* 200 (M^+), 174 ($M^+-C_2H_2$), 141 (base peak, $M^+-COOCH_3$), 115 ($M^+-CHCHCOOCH_3$).

The UV spectra of *exo*-**4b** and *endo*-**4b** are very similar and are characteristic of benzocyclopentenes.[7)] The NMR spectra of both compounds could be accounted for by structure **4b** (Aromatic H: aliphatic H: olefinic H: OCH_3=4:3:2:3) and the coupling patterns between the olefinic protons and H_{7b}'s of *exo*- and *endo*-**4b** were quite similar to those of known *exo*- and *endo*-**4a**, respectively.[8,9)]

*Irradiation of Optically Active 1-Methoxycarbonylmethyl Derivative (**1a**)*: Because of its facile double epimerization above room temperature, the *exo*-ester (**1a**), carefully obtained below 3 °C from the known (+)-(1*R*)-**1d**[1)] ($[\alpha]_D$ +147°, >95% optically pure), was irradiated in dichloromethane in the presence of Michler's ketone below 0 °C for 5 min. After chromatographic

separation of the products from the sensitizer, they were identified and estimated to consist of **1a** (53%), **3a** (38%),[2] and **4a** (*endo* (6%)+*exo* (1.5%)).[8] Repeated chromatography on silica gel of the mixture gave **3a** and *endo*-**4a** in optically active forms (**3a**, $[\alpha]_D$ +65° (76% enantiomer excess (e.e.); *endo*-**4a**, $[\alpha]_D$ +81° (76% e.e.)).

In a separate experiment, (+)-(5S)-**3a** ($[\alpha]_D$ +86°, >95% optically pure) was similarly photolyzed in benzene to give a product (30%) consisting of *exo*- and *endo*-**4a** (1:5) which retained their optical activities [*endo*-**4a**, $[\alpha]_D$ −107° (>95% optically pure); *exo*-**4a**, $[\alpha]_D$ +180°]; these determined the (7*S*)-configuration for both (+)-*exo*-**4a** and (−)-*endo*-**4a**.

Therefore, the stereochemistry of the rearrangement of *exo*-**1a** to **3a** under the above conditions is deduced to be 88% retention of the C-1 configuration; this result is opposite to the one for the same rearrangement under direct irradiation.[2,5] When we use (+)-**1a** (*exo*:*endo*=2:1; $[\alpha]_D$ +24.7°) after thermal equilibration as the starting material, we obtain (+)-**3a** in 16% e.e. (58% retention) after 20% conversion. In this case, if a rearrangement starting from *exo*-**1a**, which forms 67% of the starting ester, proceeds with 88% retention as observed above, the calculated percentage of retention originating from *exo*-**1a** will be 59% in the total rearrangement, which is well coincident with the observed value (58%). Therefore, the *endo*-**1a**, composing 33% of the starting material, is supposed to rearrange solely to (−)-**3a** through inversion of the C-1 configuration. The longer irradiation time (72% conversion) using an *exo-endo* mixture of optically active **1a** (2:1) gave *endo*-**4a**, instead of **3a**, as the main product with the same enantiomer excess within the experimental error (19% e.e.; 59% retention).

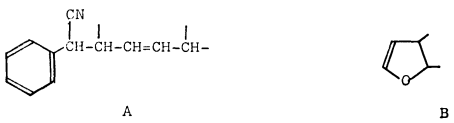
*Photochemistry of 1-Cyano Derivative (**1c**). Synthesis of (1R)-(−)-1-endo-Cyano Derivative (1-endo-**1c**)*: Because of the double epimerization of *exo*-**1a**, *endo*-**1a**, and *endo*-**1b**,[5] we could not make clear the stereochemistry of the photochemical *exo-endo* isomerization for these compounds under the above conditions. In hopes of obtaining a thermally stable and optically active **1c**, we synthesized it from an optically active acid **1d** under mild conditions. Thus, from (+)-**1d** ($[\alpha]_D$ +143°) we obtained (+)-**1c** as colorless crystals ($[\alpha]_D$ +103°, mp 76 °C) by dehydration with trifluoroacetic anhydride[10] *via* the amide,[11] **1e** ($[\alpha]_D$ +201°, mp 261—262 °C). The obtained nitrile **1c** showed a characteristic 1-*endo* proton triplet (J=4.3 Hz) at δ 0.69 ppm. Upon heating this nitrile **1c** at 130 °C for 20 min, an *exo-endo* (2:3) mixture of **1c** was obtained, from which *endo*-**1c** was isolated as colorless crystals, mp 153 °C, $[\alpha]_D$ −579°. In the NMR spectrum, the latter showed a triplet of C-1 proton at δ 2.19 ppm with a *cis* vicinal proton coupling (J=8.3 Hz) characteristic to the cyclopropane ring.[5,12] The UV spectrum was very similar in shape to that of *exo*-**1c**, but the maximum (270 nm (log ε 3.89)) appeared at a shorter wavelength than that of *exo*-**1c** (273 nm (log ε 3.89)). From the absolute configuration of the starting (+)-**1d**, the absolute configuration of (+)-*exo*-**1c** must be (1*R*). Therefore, the configuration of (−)-*endo*-**1c** corresponds to (1*R*), because the latter should be formed *via* a symmetry-allowed double Cope rearrangement from the former.[13,14] The minus sign in *endo*-**1c** is coincident with the existence of an enantiomeric benzonorcaradiene moiety against (1*R*)-(+)-*exo*-**1c**.[15]

*Irradiation of **1c***: Solutions of racemic *exo*- and of *endo*-**1c** in benzene were irradiated for 15 min in the presence of Michler's ketone to give 68% and 88% recovery of the initial amount of the starting material, respectively. The products were *exo*-**1c**, *endo*-**1c**, and 7b-cyano-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**5a**)[16] in 34.9%, 6.2%, and 25.4%, respectively from *exo*-**1c** and 44.8%, 15.7%, and 25.0%, respectively from *endo*-**1c**.

In an independent experiment, we observed that 5-cyano-5*H*-benzocycloheptene (**3c**) rearranged readily to **5a** under the same conditions. Therefore, both isomers of **1c** interconvert with each other and probably rearrange to **5a** *via* **3c**.

In order to test the possibility of trapping **3c**, if it were formed from **1c**, an authentic sample of **3c** was irradiated with Michler's ketone in furan as a solvent instead of benzene; we obtained, in addition to **5a** (25%), a 1:1 adduct (*adduct*-1; 23%) composed of furan and **3c** as expected. In the direct irradiation of **3c** in furan, we obtained two kinds of 1:1 adducts (40%): one was identical with the above *adduct*-1 and the other was an isomer (*adduct*-2).

The Structures of Adduct-1 and -2: The NMR spectra of these two adducts showed quite similar coupling patterns over all the region; therefore, it is reasonable to suppose that they have the same molecular framework. The confirmation of the existence of vicinal couplings by the stepwise decoupling experiment on the NMR signals of the *adduct*-1 revealed a carbon skeleton (**A**) and a 2,3-dihydrofuran moiety (**B**)[17] in *adduct*-1. As the two fragments contain all of the carbons and hydrogens in the molecule, we can obtain the structures **6** and **7** from their spectral analysis. Of **6** and **7**, the latter, in which the proton H_{10} is located in proximity to the oxygen of the furan ring, was chosen for the adduct by considering its NMR spectrum. The *syn* structures, **7a** and **7c**, rather than the *anti*, **7b** and **7d**, were selected because their NMR spectra, taken with a shift reagent, showed an extraordinary lower field shift of H_{10} and the least shifts of H_{12} and H_5 signals. The larger lower field shifts of H_{11} as well as H_{10} signals in *adduct*-1 compared

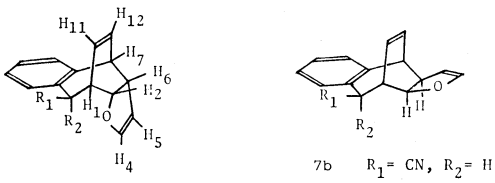


A B

Scheme 2.

7 6

Scheme 3.



7a R_1= CN, R_2= H
7c R_1= H, R_2= CN
10a R_1= CH_2COOCH_3, R_2= H
10b R_1= R_2= H

7b R_1= CN, R_2= H
7d R_1= H, R_2= CN

Scheme 4.

Table 1. The induced shifts in NMR signals of the furan adduct-1 and -2 observed by the addition of $Eu(fod)_3$

Added $Eu(fod)_3$	Observed proton chemical shifts (δ)					
	H_2	H_4	H_5	H_{10}	H_{11}	H_{12}
Adduct-1 (2.2 mg/0.4 mL $CDCl_3$)						
0.0 mg	4.98	6.20	4.43	4.55	6.07	6.71
3.5 mg	5.17	6.31	4.50	4.81	6.20	6.77
$\Delta\delta H_1/\Delta\delta H_{12}$	3.17	1.83	1.16	4.33	2.17	1.00
Adduct-2 (1.2 mg/0.4 mL $CDCl_3$)						
0.0 mg	5.04	6.15	4.45	4.22	6.08	6.57
3.0 mg	5.26	6.43	4.58	4.58	6.21	6.71
$\Delta\delta H_1/\Delta\delta H_{12}$	1.57	2.00	0.98	2.57	0.93	1.00

with those of the same proton signals in *adduct*-2 suggested the structure **7a** for *adduct*-1 and **7c** for *adduct*-2.

*Irradiation of (1*R)-exo-*(+)-**1c** in Furan*: Irradiation of *exo*-(+)-**1c**, $[\alpha]_D$ +103°, in furan in the presence of Michler's ketone was performed as mentioned above. The isolated products were, in addition to *exo*-(+)-**1c** ($[\alpha]_D$ +110°; 56%), *endo*-(+)-**1c** ($[\alpha]_D$ +572°; 19%), **5a** (13%), and *adduct*-1 ($[\alpha]_D$ −0.8°; 12%).

*Photochemistry of **1f**-1,1-d_2.* *Synthesis of **1f**-1,1-d_2*: In all the above-mentioned examples of the sensitized irradiation of 1-substituted **1**, the products detected were only the ones derived from the rearrangement of C-1 toward C-7a. This fact was quite different from the results obtained under direct irradiation. In order to test whether such regioselectivity of rearrangement under sensitized conditions is available in the simplest case, we studied the rearrangement of **1f**-1,1-d_2. Though **1f**-1,1-d_2 was previously prepared from naphthalene with dideuteriocarbene,[18] the yield and deuterium content were unsatisfactory. So we prepared it starting from 1,2-dihydronaphthalene as follows: addition of dibromocarbene, reduction with tributyltin deuteride,[19,20] and NBS bromination followed by dehydrobromination with calcium hydrogen phosphate in DMF.[21] The deuterium content of C-1 of **1f**-1,1-d_2 was estimated to be 97% by H NMR spectrum.

*Irradiation of **1f**-1,1-d_2*: **1f**-1,1-d_2 dissolved in benzene was irradiated with Michler's ketone for 15 min to give a mixture of **1f**-d_2[18] (**C**), 5*H*-benzocycloheptene-d_2 (mainly **3d**-5,5-d_2)[18] (**D**), and 1-(methyl-d_2)naphthalene (**11b**-d_2) in a ratio of 11.2:9.0:1.0; this was estimated by a combination of VPC and NMR measurements. A longer irradiation time did not increase the amount of **3d**, because the latter was found to be transformed back to **1f** under the same conditions in an independent experiment.

The deuterium distribution in compound **C** was studied carefully with use of the FT-NMR spectrum. Thus the integrated area of the signal of the proton bound to C-1a did not change compared with that of the olefinic proton signals (2H). On the other hand, the area due to the proton bound to C-7b decreases, in compensation for the increase of those due to the *exo*- and *endo*-protons on C-1. The results allowed us to estimate that compound **C** contained **1f**-1,1-d_2 and **1f**-1,7b-d_2 in a ratio of 3.2:1.

Similar irradiation of 7*H*-benzocycloheptene (**12a**) gave a mixture of **9a**, **1f**, **3d**, and **8b** in a ratio of 73.5:20:6.5:trace, respectively. From this experiment, it is clear that **9a**-7,7-d_2, if it were formed from **1f**-1,1-d_2 in the above experiment, should partly survive and partly give **1f**-1,1a-d_2 by [1,7]D-shift from C-7 to C-6 and simultaneous bond formation between C-5 and C-7.

The fact that no deuterium incorporation was found in C-1a of compound **C** shows that the rearrangement proceeds through one direction, similar to other cases mentioned above. It is noteworthy that, while 1-methylnaphthalene was identified, neither naphthalene nor 2-methylnaphthalene was detected in the sensitized reaction.

*Formation of the Furan Adducts of **1a** and **1f**.* Irradiation of **1a** and **1f** in furan in the presence of Michler's ketone gave *adduct*-3 and -4, respectively. Their similarities in the proton NMR spectral pattern to those of *adduct*-1, except for the signals due to substituent and/or H_1, determined the structures: **10a** and **10b**, respectively. *Adduct*-3 was obtained in 44% yield from the irradiation of **3a** in furan in the presence of the sensitizer.

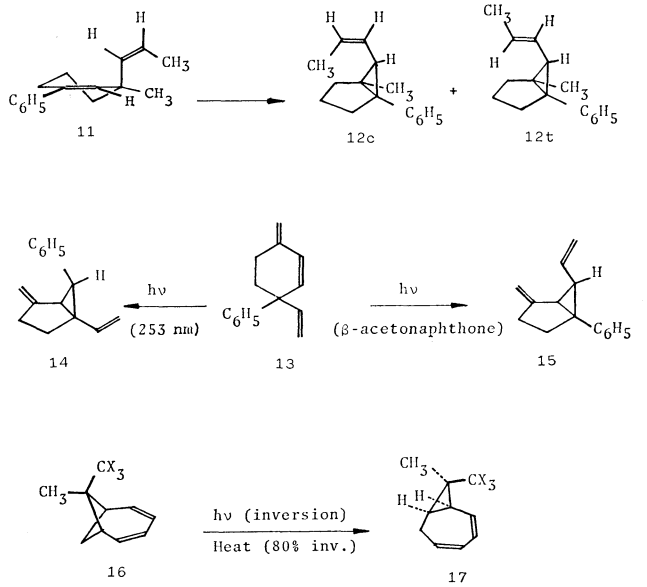
Discussion

The photochemical Berson-Willcott rearrangement of benzonorcaradiene was initially reported by Ciganek on 1,1-dicyano-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene in 1968.[22] The stereochemical course of the photochemical rearrangement of tropilidenes was studied by Klärner[3] under benzophenone sensitized conditions on 1,3-dimethyl-2,4,6-cycloheptatriene-1-carboxylic ester and nitrile (**2a** and **2b**), which proceed mainly with inversion at the migrating carbon center of their norcaradiene tautomers. They proposed a stepwise mechanism through the biradical intermediates keeping the substituents *exo* in order to relieve the repulsion between π-electrons to predict inversion and partial racemization.

In the above experiment, we found that the stereochemical course of the rearrangement of **1a** under Michler's ketone-sensitized irradiation was quite different in nature from that under direct irradiation. Fukui deduced as follows: "In a triplet-state reaction each bond, which is to be newly formed through the overlapping of AO's of the two parts where the orbital interaction is considered, should be formed so as to result in a structure having two unpaired electrons not in conjugation with each other by virtue of that

bond. Excited singlet-state reactions are not necessarily subject to such a limitation."[23]

There are many examples in which different products are produced under sensitized irradiation from those under the direct type,[24] but little is known concerning the case which gives the same products with different stereochemistry depending on the irradiation conditions. Mariano reported that the di-π-methane rearrangement of **11** gives stereospecifically *cis* product (**12c**) from its excited singlet but mainly *trans* (**12t**) on sensitized irradiation.[25] Swenton described the different behavior of **13** under direct irradiation and under 2-acetonaphthone sensitization.[26] These examples are not similar to our case precisely in the sense of whether the migrating carbon changes the stereochemistry or not. Our results obtained on *exo*-**1a** are unique because of its completely opposite stereochemistry toward **3a** depending on the irradiation conditions. It is noteworthy that the optical purities of the products from direct irradiation are the same within the experimental error and hence stereochemistry is not altered whether we use *exo*-**1a**, obtained below 3 °C from pure (1*R*)-(+)-**1d**, or an thermally equilibrated *exo*-*endo* mixture (2:1) of **1a** obtained from the same acid.[27] This means that, under the direct irradiation, the *exo*-**1a** and *endo*-**1a** follow the same stereochemistry, 80% inversion and 20% retention of the configuration at the migrating center. These facts suggest the presence of different mechanisms for the two modes of irradiation; under direct irradiation, both *exo*- and *endo*-**1a** follow mainly the same symmetry-allowed suprafacial [1,5]sigmatropic shift with inversion at the migrating center, but under sensitized conditions, they follow a stepwise process with either the stereochemistry governed by the principle of the least motion or that of releasing the steric hindrance in the process. Thus, under the sensitized irradiation, the rearrangement of *endo*-**1a** proceeds with inversion at the migrating center in accordance with the principle of least motion[28] with little change in spatial environment, while that of the *exo*-**1a** proceeds mainly with retention at the center, avoiding the steric hindrance caused by the substituent on C-1 and a hydrogen on C-7 in the least motion movement. Borden reported such a least motion pathway for the thermal [1,5]sigmatropic shift of **16**, contrary to the prediction of the Woodward-Hoffmann rule. Direct irradiation of **16** also affords **17** with high stereoselectivity.[29]



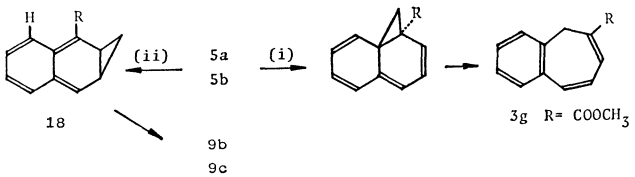
Scheme 5.

The suppression of the reaction by steric repulsion was recognized in the case of a kinetic study on the rearrangement of 3-isopropyl derivative of *exo*-**1a** compared with that of *endo*-**1a** under direct irradiation.[30] Swenton found, in addition to the path ii products, the presence of path i products in the case of direct irradiation of **5b**. He attributed this to the steric hindrance between a peri-hydrogen and the methoxycarbonyl group present in the intermediate (**18**). Such obstruction to path ii is not seen in the case of photolysis of **5a**.[16]

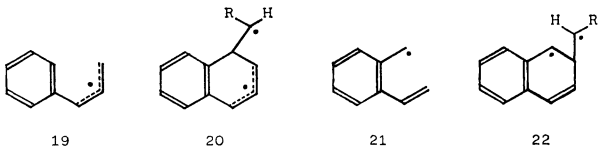
In the study of **1a**, it was difficult to recover *exo*-**1a** without contamination of *endo*-**1a** owing to its thermal instability; even so, the stepwise mechanism under sensitized conditions was supported by the findings that (1*R*)-*exo*-**1c** was recovered from the reaction mixture without racemization and at the same time (1*S*)-*endo*-**1c** was obtained with high optical rotation[31] when (1*R*)-*exo*-**1c** was irradiated in furan. Simple Hückel calculations predict the resonance energy of 1-phenylallyl radical (**19**) composed of a part of **20** to be larger than that of *o*-vinylbenzyl radical (**21**) composed of a part of **22**. Thus the cleavage of a bond C-1 to C-1a in **1** is expected to be easier than that of C-1 to C-7b.[32]

The adduct of (1*R*)-(+)-**1c** to furan was found to be optically inactive. We could not detect any of **9b** in the reaction mixture, so the possibility of racemization of an initially formed optically active **3c** under reaction conditions is rather low. The fact that the absolute configuration of C-7b on *exo*-**1c** is conserved in *endo*-**1c** obtained by the sensitized irradiation shows the existence of diradical intermediates **23c** and **24c**[33,34] during the epimerization. But it is difficult to explain why the *endo*-**1c** rearranges to *exo*-**1c** much faster than the *exo*-**1c** does to *endo*-**1c** in the comparative study.[35]

The occurrence of biradical intermediates **23c** and **24c** clarifies the production of **3c** in an optically in-

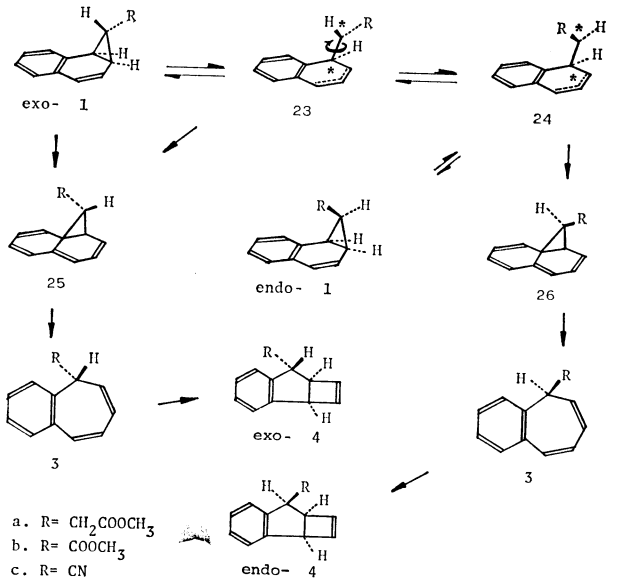


Scheme 6.



$RE(\mathbf{19}) - RE(\mathbf{21}) = -0.09\beta$ (RE = Resonance energy)

Scheme 7.



Scheme 8.

active form.

The stereochemical results of the rearrangement of (+)-**1b** are explained as follows. In this case, as is expected from the fact that **1b** exists solely in its *exo* form and *endo*-**1b**, when it is prepared by photolysis of **3b**,[5] isomerizes readily at room temperature, the steric repulsion between methoxycarbonyl group and π-electrons in the ring **24b** is too large to get close enough to *endo*-**1b**; therefore, the loss of the optical activity of (+)-**1b** is found to be quite small (8%) during irradiation. For the rearrangement to **3b**, the closure of **23b** and **24b** to position C-7a is expected to have the same order of large steric repulsion, because the steric requirement of methoxycarbonyl group is larger than that of cyano group. Therefore, we may obtain **3b** at a rate rather slower than those of **3a** or **3c** and in almost racemic form. However, another explanation for the occurrence of racemic **3b** from (1*R*)-**1b** is possible: that is the racemization of initially formed optically active **3b** under the reaction conditions. This possibility has not been investigated yet.

Next, we must deal with the mechanism of cycloaddition of **1c**, **1a**, and **1f** to furan. Generally, the photochemical [4πs+2πs]-addition is not allowed under the control imposed by the orbital symmetry rule. Two mechanistic alternate pathways may serve to predict the adducts. One is the successive photochemically allowed processes, [2πs+2πs] or [4πs+4πs] cycloaddition, as observed in the photochemical addition of furan to benzene,[36] followed by [1,3]sigmatropic shift to give products. The other is a stepwise biradical or the equivalent process. As the latter cannot explain the regioselectivity of the adduct, the former mechanism assisted by the overlap of the secondary orbitals may satisfactorily predict the selectivity. The stereoselective formation of *exo*-adducts shows that a steric factor is playing an important role as the controlling factor.

Finally, the fact that the *exo-endo* ratio of the cyclization products **4a** formed from **3a** is quite different depending on the irradiation conditions is also interesting. Under direct irradiation, **3a** gives mainly *exo*-**4a** (*exo*:*endo*=95:5) in various solvents, but under sensitized conditions, it gives **4a** in variable ratios of 10:90 to 40:60 (*exo*:*endo*) depending mainly on the reaction temperature. These facts suggest the existence of two different cyclization mechanisms depending on the conditions used. It was reported that, under direct irradiation, such cyclization often proceeds by the concerted disrotatory mode[37] but under the sensitized conditions and/or from easily attained excited triplets, the reaction proceeds with initial *cis-trans* isomerization followed by the thermally allowed conrotatory ring closure.[38,39] It is possible to assume that these two modes of mechanisms might have played a role in the above case, and from each of their favored conformations, they will give the *exo-endo* mixture of **4a** in different ratios following the "accordant rule" discussed by Dauben.[40]

Experimental

General Procedure. UV, IR, H-NMR, and Mass spectra were recorded according to the methods given in the previous paper.[4] C-13 NMR spectra were recorded on a JNM FX-100 spectrometer (25.05 MHz) in $CDCl_3$ and the chemical shifts are expressed in ppm to the middle peak of the solvent-carbon as a standard (δ 77.1 ppm). A Varian Aerograph model 90P was used for the preparative VPC (helium flow rate; 30—40 mL/min) and a Shimazu Gas Chromatograph GC-4BM was used for the analytical purposes (Hydrogen flame ionization detector). The columns used for separation are ϕ 3.2 mm$\times$1.8 m columns charged with: A, 10% Silicone DC QF-1; B, 5% Silicone OV-17; C, 3% Silicone OV-17; D, 5% Silicone SE-30, on Chromosorb WAW.

For irradiation of more than 100 mL volume, a solution charged in a vessel fitted with a quartz cooling jacket was purged with dry nitrogen for 5 min and internally irradiated with an Ushio High Pressure mercury arc (UM-452) through a Pyrex filter. For small scale irradiation (less than 15 mL), unless otherwise described, a solution charged in a drum-shaped Pyrex vessel with a ground glass joint fitted with a three-way cock, was purged with dry nitrogen for 5 min and dipped in ice water in a quartz Dewar bottle with a flat quartz window. The solution was then irradiated externally with an Ushio lamp (USH-500D) through a Toshiba filter (UV-31). After irradiation, the solvent was evaporated under reduced pressure and the residue taken in chloroform was chromatographed on silica gel to remove the sensitizer. The product mixture was then purified by the appropriate method.

Photolysis of ***1b***. A solution of **1b** (233 mg, 1.2 mmol) and Michler's ketone (1.31 g, 4.9 mmol) dissolved in benzene (400 mL) was irradiated for 2.5 h. The usual work-up gave a mixture (175 mg, 75% of the starting material) mainly composed of **1b** and **3b**. They were purified by chromatography on silica gel (5 g) using hexane–ether (95:5 *v*/*v*) as an eluent. A mixture (139 mg, 60%) composed of **1b** and **3b** (1:1), in addition to **8a** (23 mg, 10%), was separated and each was identified by direct comparison with the authentic samples.[5] For further identification, the mixture in ethyl acetate was hydrogenated over 10% palladium on carbon at room temperature to give two products (1:1): one was identified with known 2,3-dihydro-**1b**[41] and the other was tetrahydro-**3b**. They were separated by VPC

TABLE 2. PRODUCT DISTRIBUTIONS FOR THE PHOTOLYSIS OF **1b** IN THE PRESENCE OF SEVERAL SENSITIZERS

Sensitizer	E_T / kJ mol^{-1}	Products' ratio				
		1b	**3b**	**8a**	*exo*-**4b**	*endo*-**4b**
Acetophenone	308.3	54.5	Trace	37.0	2.2	6.3
Benzophenone	287.0	84.1	6.9	4.9	2	2
Michler's ketone	259.4	45	30	15	5	5
β-Acetonaphthone	248.5	79	4.7	4.7	3.1	8.2
α-Acetonaphthone	248.5	50	Trace	3.6	3	10.1
Benzil	223.4	100	0	0	0	0
Pyrene	201.2	100	0	0	0	0

(column A, 152 °C: *retention time*; 23.1 min, 14.2 min, respectively). **3b** NMR ($CDCl_3$) δ: 3.62 (1H, d, J=5 Hz), 3.74 (3H, s), 5.9—6.2 (2H, m), 6.38—6.6 (2H, m), 6.9—7.4 (4H, m). Mass *m/e* (rel intensity, %): 200 (M^+, 15), 141 (100), 115 (25). Tetrahydro-**3b** NMR (CCl_4) δ: 2.77 (2H, m), 3.67 (3H, s), 3.78 (1H, d,d, J=2.2, 6.4 Hz), 1.48—2.13 (6H, m), 6.84—7.13 (4H, m). UV (CH_3OH) λ_{max}: 256.5 (sh), 264, 272 nm. Mass *m/e* (%): 204 (M^+, 18), 172 (10), 145 (100), 117 (20), 91 (16). Found: C, 76.41; H, 7.87%. Calcd for $C_{13}H_{16}O_2$: C, 76.44, H, 7.90%.

Photolysis of ***1b****-1*-d_1. A solution of **1b**-1-d_1 (198 mg, 0.99 mmol) and Michler's ketone (1.01 g, 3.8 mmol) dissolved in benzene (400 mL) was irradiated for 3 h at 0—5 °C. After work-up as above, a product mixture (182 mg) was chromatographed on silica gel (6 g, 5% ether–hexane) to give a mixture (151 mg) of **1b**-d_1 and **3b**-d_1 (1.1:1.0). Careful examination of the proton NMR spectrum and comparisons with those of **1b** and **3b** revealed that (1) the area ratio of proton signals for H_1 (δ: 0.74 ppm), H_{1a} (δ: 2.49 ppm, d,d, J=8.2, 4.2 Hz), and H_{7b} (δ: 2.92 ppm, d, J=8.2 Hz) on **1b**-d_1 is equal to 7:100:98, which corresponds to the ratio observed in the starting **1b**-1-d_1 within the experimental error, and that (2) the signal due to H_5 for **3b**-d_1 was very feeble compared with those of olefinic protons (δ: 5.9—6.2 ppm, 2H; δ: 6.38—6.6 ppm, 1H), which fits those for **3b**-5-d_1.

Photolysis of ***1b*** *in Benzene with Several Sensitizers.* The irradiation was carried out in benzene solution (150 mg, 0.75 mmol/300 mL) in the presence of 4 equiv. mol of sensitizer for 2 h. The yields of the products were assayed by VPC (column A, 162 °C; *exo*-**4b** (*retention time*, 9.6 min), *endo*-**4b** (*r.t.*, 12 min), **1b**+**3b** (*r.t.*, 20.8 min), **8a** (*r.t.*, 24.4 min)) and NMR spectroscopy (Table 2).

Characterization of ***4b***: After evaporation of the solvent, the residue taken in methanol was treated with sodium borohydride (4 equiv. mol) to make separation of the products from ketonic sensitizer easier. The usual work-up followed by chromatography (silica gel/10% ether–hexane) gave *exo*- and *endo*-***4b*** together with **8a**. They were further purified by preparative VPC (column A, 162 °C) as mentioned above. *exo*-**4b** NMR (CCl_4) δ: 3.65 (3H, s), 3.78—3.95 (2H, m), 4.31—4.40 (1H, m), 6.12 and 6.31 (2H, AB type d, J=2.8 Hz), 7.07—7.38 (4H, m). UV (cyclohexane) λ_{max} (log ε): 255.5 (2.71), 262 (2.89), 268 (3.06), 275 (3.11) nm. IR (liq. film) ν_{max}: 1731, 1486, 1442, 1251, 1178, 772, 747 cm^{-1}. Mass *m/e* (rel intensity, %): 200 (M^+, 12), 185 (11), 174 (7), 141 (100), 115 (10). Found: C, 77.91; H, 6.15%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%. *endo*-**4b** NMR (CCl_4) δ: 3.73 (3H, s), 3.89, 4.04 (AB part of ABX, J_{ab}=10, J_{ax}=3.6 Hz), 4.24 (1H, X part of ABX, J_{ax}=3.6 Hz), 6.04 and 6.38 (2H, AB type, J=2.8 Hz), 7.08—7.36 (4H, m). UV (cyclohexane) λ_{max}: 263, 268, 275.5 nm. Found: C, 77.96; H, 6.12%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

*Photolysis of (1*R*)-****1b****.* A solution of (1*R*)-**1b** ($[\alpha]_D^{14}$ +124° (*c* 1.16, CH_3OH); 228 mg, 1.14 mmol), prepared from (1*R*)-**1d** ($[\alpha]_D$ +143°), and Michler's ketone (1.84 g, 6.84 mmol) dissolved in benzene (120 mL) was irradiated under ice-cooling for 2 h. The usual work-up gave a mixture (102 mg, 45%) composed of mainly **3b** and **1b**, in addition to small amounts of *exo*- and *endo*-**4b** and **8a** (VPC, column C, 165 °C). The mixture was separated by medium pressure liquid chromatography (Kieselgel 60, 23 g/5% ether–hexane) into 60 fractions of 5 ml each. Fractions 20—23 contained **3b** (22.7 mg, $[\alpha]_D^{14}$ −2.82° (*c* 1.13, 95% C_2H_5OH)) and fractions 27—30 contained recovered **1b** (23.3 mg, $[\alpha]_D^{15}$ +114° (*c* 1.16, CH_3OH)).

Synthesis of Optically Active ***1a****.* (1*R*)-**1d** (522 mg, $[\alpha]_D$ +143°, optical purity >95%) was transformed to the corresponding diazo ketone (yellow silky crystals, 578 mg, 98%; ν_{max}: 2120, 1600 cm^{-1}), *via* the acid chloride (solid, 599 mg; $\nu_{C=O}$ 1760 cm^{-1}) by the usual method.[8] The diazo ketone dissolved in anhydrous methanol was irradiated at *ca.* 2 °C until 80% of the theoretical amount of nitrogen had evolved (22 min) and then concentrated below 3 °C under reduced pressure. The residue taken in cold chloroform was chromatographed on silica gel below 5 °C to give an optically active 1-*exo*-(+)-**1a** (300 mg; no contaminants other than **1a**, by TLC).

For the synthesis of *exo-endo* mixture (2:1) of (1*R*)-**1a**, the above photolysate was purified by chromatography on silica gel at room temperature with 10% ether–hexane as an eluent. Then the product (393 mg, 65% of the theoretical amount) was thermally equilibrated by heating it at 95 °C for 5 min ($[\alpha]_D^{31}$ +24.7° (*c* 1.2, CH_3OH)).

Photolysis of exo-endo *Mixture of (1R)-****1a****.* A solution of (1*R*)-**1a** ($[\alpha]_D$ +24.7°; 118 mg, 0.55 mmol) and Michler's ketone (888 mg, 3.31 mmol) dissolved in dichloromethane (130 mL) was irradiated under nitrogen below 5 °C for 30 min. After the usual work-up, the product was rechromatographed on silica gel (12 g/benzene) to give an *exo-endo* mixture of **4a** (43.6 mg). VPC separation (column B, 150 °C) of it gave (−)-*endo*-**4a** ($[\alpha]_D^{25.5}$ −28° (*c* 0.35, $CHCl_3$) 19% enantiomer excess) and (+)-*exo*-**4a** ($[\alpha]_D^{23}$ +56° (*c* 0.35, $CHCl_3$)).[8]

Similarly, a solution of (1*R*)-**1a** (228 mg, 1.07 mmol) and Michler's ketone (1.72 g, 6.42 mmol) in benzene (110 mL) was irradiated at 40±1 °C for 5 min. The usual work-up and repeated chromatography gave a mixture (182 mg, 80%), which was estimated to be composed of **1a** (80%) and **3a** (20%), in addition to a minor amount of **4a**. A pure sample (3.5 mg) of **3a** was isolated by medium pressure liquid chromatography (Kieselgel 60, 23 g) and estimated to be 16% enantiomer excess by NMR measurement in the presence of tris[3-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutylidene)-*d*-camphorato]europium (III).

*Photolysis of (1R)-exo-**1a**.* (1*R*)-*exo*-**1a**, obtained above, was photolyzed in dichloromethane (5 min) below 3 °C as described in the case of (1*R*)-**1a** (*exo-endo* mixture) and gave (+)-**3a**[1] ($[\alpha]_D^{18}$ +65° (*c* 0.63, 95% C_2H_5OH); 76% enantiomer excess (chiral NMR shift reagent)) and *endo*-**4a**[1] ($[\alpha]_D^{18}$ −81° (*c* 0.21, $CHCl_3$); 76% enantiomer excess) in addition to a recovery of **1a** ($[\alpha]_D^{23}$ −3.1° (*c* 1.04, CH_3OH).

*Synthesis of Optically Active **3a**.* (5*S*)-(+)-**3a** ($[\alpha]_D^{17}$ +86° (*c* 0.88, 95% C_2H_5OH)) was prepared from benzotropylium tetrafluoroborate as described previously.[2]

*Photolysis of (+)-**3a**.* A solution of (+)-**3a** (128 mg, 0.60 mmol; $[\alpha]_D$ +86°, 95% optically pure) and Michler's ketone (802 mg, 2.99 mmol) dissolved in benzene (110 mL) was irradiated under nitrogen for 40 min at 40 °C. After the usual work-up, an *exo-endo* mixture (1:4.8; 39 mg) of **4a** was obtained. VPC separation (column B, 150 °C) of the mixture gave (−)-*endo*-**4a** ($[\alpha]_D^{27}$ −107° (*c* 0.38, $CHCl_3$)) and (+)-*exo*-**4a** ($[\alpha]_D^{27}$ +180° (*c* 0.08, $CHCl_3$)).

*Synthesis of Optically Active **1e**.* Into the acid chloride, obtained from (1*R*)-(+)-**1d** ($[\alpha]_D$ +143°, optical purity >95%; 1.16 g, 6.24 mmol) and dissolved in anhydrous ether (170 mL), was passed gaseous ammonia at 0 °C for 25 min until the pH of the solution reached 10 against a wet test paper. After stirring for 1 h at room temperature, water (150 mL) was added to the solution. The aqueous solution was separated and extracted three times with dichloromethane and the combined organic layer was washed successively with water and saturated brine, and then dried. The crude amide (1.11 g, 96%) was recrystallized from methanol. **1e** colorless crystals (775 mg, 67%), mp 261—262 °C; $[\alpha]_D^{15}$ +201° (*c* 0.51, dioxane). IR (Nujol mull) ν_{max}: 3420, 3230, 1645, 1605, 775, 735 cm^{-1}. NMR (DMSO-d_6) δ: 0.72 (1H, t, J=4.0 Hz), 2.5 (H_{1a}, m), 2.83 (1H, d,d, J=8.3, 4.0 Hz), 6.2—6.5 (2H, m) 7.0—7.5 (4H, m). Found: C, 77.76; H, 5.99; N, 7.52%. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56%.

*Synthesis of Optically Active **1c**.* To a solution of the amide ($[\alpha]_D$ +201°; 519 mg, 2.81 mmol) and anhydrous pyridine (445 mg, 5.62 mmol) in anhydrous dioxane (12 mL) was added dropwise a solution of trifluoroacetic anhydride (649 mg, 3.1 mmol) in dioxane (5 mL) in a period of 25 min. After stirring for 3 h at room temperature, chloroform (50 mL) was added to the mixture. The organic layer was then washed successively with water (three times), and with saturated brine and dried. Evaporation of the solvent gave a crude nitrile (487 mg, 100%). Chromatographic separation (silica gel (12 g)/10% ether–hexane), followed by recrystallization from hexane gave **1c** as colorless crystals (280 mg, mp 76.5 °C; $[\alpha]_D^{15}$ +103° (*c* 0.95, CH_3OH)). *exo*-**1c** IR (Nujol mull) ν_{max}: 2225, 770, 730 cm^{-1}. UV (CH_3OH) λ_{max} (log ε): 273 nm (3.89): (cyclohexane) λ_{max}: 273 nm (3.89). H-NMR ($CDCl_3$) δ: 0.69 (1H, t, J=4.3 Hz), 2.69 (1H, d,d,d, J=8.3, 4.3, 4.2 Hz), 3.10 (1H, d,d,d, J=8.3, 4.3, 0.7 Hz), 6.25 (1H, d,d,d, J=9.8, 4.2, 0.7 Hz), 6.39 (1H, d, J=9.8 Hz), 7.0—7.5 (4H, m). C-13 NMR ($CDCl_3$) δ: 130.5 (s), 130.0 (s), 129.0 (d), 128.4 (d), 128.1 (d), 127.7 (d), 126.8 (d), 123.9 (d), 121.5 (s), 28.8 (d, J=168 Hz), 25.7 (d, J=171 Hz), 7.6 (d, J=178 Hz). Found: C, 86.32; H, 5.48; N, 8.36%. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38%.

*Thermal Conversion of (+)-exo-**1c** to endo-**1c**.* (+)-*exo*-**1c** ($[\alpha]_D^{18}$ +103°; 16.6 mg) dissolved in DMSO-d_6 (0.4 mL) was heated in an NMR tube at 130 °C for 20 min. The mixture (*exo*:*endo*=2:3) was separated by chromatography on silica gel (10 g) and 37 fractions (fr. 1—30; 10% ether–hexane: fr. 31—37; CH_2Cl_2) of 8 mL each were collected. Fractions 6—10 contained 8 mg of (+)-*exo*-**1c**, mp 76.5 °C, $[\alpha]_D^{18}$ +103° (*c* 0.21, CH_3OH), and fraction 35, (−)-*endo*-**1c**, mp 153 °C, $[\alpha]_D^{16}$ −579° (*c* 0.17, CH_3OH). IR (Nujol mull) ν_{max}: 2217 cm^{-1}. UV (CH_3OH) λ_{max} (log ε): 270 nm (3.89): (cyclohexane) λ_{max} 270 nm (3.88). NMR ($CDCl_3$) δ: 2.19 (H_1, t, J=8.3 Hz), 2.63 (H_{1a}, d,t, J=8.3, 5.1 Hz), 3.03 (H_{7b}, t,d, J=8.3, 0.7 Hz), 6.12 (H_2, d,d,d, J=9.7, 5.1, 0.7 Hz), 6.70 (H_3, d, J=9.7 Hz), 7.2—7.4 (4H, m).

*Photolysis of 1-exo-**1c** in Benzene.* A solution of *exo*-**1c** (64.5 mg, 0.39 mmol) and Michler's ketone (486 mg, 1.81 mmol) in benzene (40 mL) was irradiated with HPL (100 W) through a Pyrex filter under ice cooling for 15 min. The usual work-up gave a mixture (44.0 mg, 68.2%), which was separated by column chromatography into *endo*-**1c** (4.0 mg, 6.2%) and a mixture (7:5) of *exo*-**1c** and **5a** (39 mg, 60%). The latter was estimated by VPC (column C, 165 °C: *retention time*; **5a**, 3.5 min; **1c** 5.7 min).

Photolysis of endo-*1c in Benzene.* The same experiment as that of *exo*-**1c** was carried out using *endo*-**1c** (63.6 mg, 0.38 mmol). We obtained a mixture of products (55.7 mg, 88%) which was revealed by VPC and NMR spectroscopy to contain *endo*-**1c** (10 mg, 15.7%), *exo*-**1c** (28.5 mg, 44.8%), and **5a** (15.9 mg, 25.0%).

Photolysis of Optically Active exo-*1c in Furan.* A solution of (+)-*exo*-**1c** ($[\alpha]_D$ +103°, 133 mg, 0.80 mmol) and Michler's ketone (1.28 g, 4.77 mmol) dissolved in furan (110 mL) was irradiated below 5 °C under nitrogen for 15 min. After furan was recovered by distillation, the residue was chromatographed on silica gel (90 g/chloroform) to give an *adduct*-1 (12.1 mg), (−)-*endo*-**1c** (17.2 mg), and **5a** (10.8 mg) in addition to the recovered (+)-*exo*-**1c** (50.9 mg, $[\alpha]_D^{20}$ +110°, mp 74.5 °C). (−)-*endo*-**1c** Colorless needles, mp 153 °C; $[\alpha]_D^{16}$ +572° (*c* 0.8, CH_3OH). NMR ($CDCl_3$) δ: 2.19 (1H, t, J=8.3 Hz), 2.63 (1H, t,d, J=8.3, 5.1 Hz), 3.03 (1H, t,d, J=8.3, 0.7 Hz), 6.12 (1H, d,d,d, J=9.7, 5.1, 0.7 Hz), 6.70 (1H, d, J=9.7 Hz), 7.4—7.21 (4H, m). *Adduct*-1 Colorless needles, mp 107—109 °C; $[\alpha]_D^{16}$ −0.8° (*c* 0.25, $CHCl_3$). IR (Nujol mull) ν_{max}: 2230, 1615, 1140, 1070, 1015 cm^{-1}. NMR ($CDCl_3$) δ: 3.42 (1H, d,d, J=6.8, 2.9 Hz), 3.51 (1H, broad d, J=2.4 Hz), 3.62 (1H, m), 4.43 (1H, t, J=2.3 Hz), 4.56 (1H, d, J=3.2 Hz), 5.00 (1H, d,d, J=11.7, 6.8 Hz), 6.08 (1H, d,d, J=2.9, 2.0 Hz), 6.21 (1H, d, J=7.1 Hz), 6.72 (1H, m), 7.35—6.9 (4H, m). Found: C, 81.66; H, 5.53; N, 5.88%. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95%. Mass *m/e* (rel intensity): 235 (M^+, 0.38), 206 (2.73), 168 (46.9), 167 (100). **5a** IR (liq. film) ν_{max}: 3030, 2920, 2235, 1490, 1455, 1215, 1045, 955, 900, 855, 778, 740 cm^{-1}.

*Photolysis of **3c**.* A solution of **3c** (58 mg, 0.35 mmol) and Michler's ketone (465 mg, 1.73 mmol) in benzene (13 mL) was irradiated externally for 3 h under ice-cooling to give, in addition to **3c** (7.5 mg, 13%), **5a** (19.5 mg, 34%) after chromatographic separation followed by preparative VPC (column A, 150 °C: *retention time*; **3c**, 10.3 min; **5a**, 11.4 min).

*Photolysis of **3c** in Furan.* A solution of **3c** (17 mg, 0.1 mmol) and Michler's ketone (136 mg, 0.81 mmol) dissolved in furan (13 mL) was irradiated externally for 2 h. The solution was concentrated and the residue taken in benzene was chromatographed on silica gel to give 10 mg of material composed of **5a** (52%) and *adduct*-1 (48%) estimated by VPC (column D, 169 °C: *retention time*; **5a**, 2.4 min; *adduct*-1, 9.6 min).

Synthesis of 1a,2,3,7b-Tetrahydro-1H-cyclopropa[a]naphthalene-1,1-d_2. To a stirred solution of 1,2-dihydronaphthalene containing 20% of naphthalene (12 g, 92 mmol) dissolved

in tribromomethane (60 g, 0.24 mol) was added dropwise 50% aq sodium hydroxide (20 mL) in the presence of tetrabutylammonium iodide (0.35 g, 0.95 mmol) under ice-cooling in a period of 10 min. Then the solution was vigorously stirred for 0.5 h. Then it was gradually warmed and stirred for 24 h at 40 °C. After cooling, water was added to the mixture and the aqueous layer was extracted with chloroform. The combined organic layer was washed with water and dried. Separation by chromatography (silica gel/hexane) of the product gave 1,1-dibromo-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (17.3 g, 63%) as a yellow oil. A mixture of the bromide (5.8 g, 19 mmol), 40% tributyltin deuteride (32 g; contaminated by tributyltin chloride) and a catalytic amount of 2,2′-azobis(2-methylpropionitrile) (60 mg) was stirred at 95±5 °C for 26 h. The mixture was separated by column chromatography (Woelm neutral aluminium oxide, 300 g/hexane) to give 2,3-dihydro-**1f**-1,1-d_2 (2.5 g, 17 mmol, 89%). For analysis, it was purified by preparative VPC (column A, 99 °C; *retention time*, 12 min). Found: C, 90.36; H, 8.44% (H_2O as D_2O). Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65%: for $C_{11}H_{10}D_2$: C, 90.35; H, 8.27%. NMR (CCl_4) δ: 1.7—2.85 (6H, m), 6.85—7.5 (4H, m).

Synthesis of ***1f****-1,1-*d_2. A solution of 2,3-dihydro-**1f**-1,1-d_2 (1.1 g, 7.7 mmol) and *N*-bromosuccinimide (1.4 g, 7.9 mmol) in carbon tetrachloride (70 mL) was refluxed in the presence of 2,2′-azobis-(2-methylpropionitrile) (60 mg) for 2.5 h. The solution was filtered and the filtrate was concentrated to dryness to give a yellow liquid, which was taken in *N,N*-dimethylformamide (40 mL). The solution was stirred with calcium hydrogen phosphate (1.38 g, 10.1 mmol) at 80—90 °C for 16 h. After cooling, the solution was diluted with water (100 mL) and extracted with ether. The combined ether solution was washed with water and dried. Evaporation of the solvent in vacuo left a crude product, which was purified by column chromatography (silica gel, 15 g/hexane). **1f**-1,1-d_2 (626 mg, 44%) was obtained as a colorless liquid. For photolysis, it was further purified by preparative VPC (column A, 100 °C; *retention time*, 14 min). NMR (CCl_4) δ: 1.93 (1H, broad; when irradiated on 6.18 ppm it becomes a broad doublet, J=8 Hz), 2.36 (1H, broad d, J=8 Hz), 6.18 (2H, two sharp signals), 6.9—7.35 (4H, m). The proton area ratio of *exo*-H_1 to olefinic 2H is 2:167=1:83.5 (purity 97%).

The same experiments as above were carried out using 1,1-dibromo-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene and tributyltin hydride in place of tributyltin deuteride. We obtained **1f** as a colorless liquid. UV (95% C_2H_5OH) λmax (log ε): 274.5 (3.87), 306 (3.11). H-NMR (CCl_4) δ: −0.3 (1H, d,t, J=3.8, 5 Hz), 1.50 (1H, d,t, J=3.8, 9 Hz), 1.96 (1H, m), 2.40 (1H, d,d,d, J=9, 7, 5 Hz), 6.20 (2H, m), 6.9—7.4 (4H, m). C-13 NMR ($CDCl_3$) δ: 9.45 (t, J_{CH}=164 Hz), 17.7 (d, J_{CH}=165 Hz), 20.6 (d, J_{CH}=163 Hz), 123.6, 125.7, 127.1, 127.7, 128.2, 129.0, 130.7, 135.5.

Photolysis of ***1f****.* A solution of **1f**(34 mg, 0.24 mmol) and Michler's ketone (318 mg, 1.9 mmol) dissolved in benzene (130 mL) was irradiated under ice-cooling for 30 min. The usual work-up and VPC separation left a mixture of products (6 mg). Careful examination of the NMR spectrum revealed that the mixture contained mainly 5*H*-benzocycloheptene (**3f**) in addition to a minor amount of **1f**. **3f** NMR (CCl_4) δ: 3.02 (2H, d, J=6.5 Hz), 5.73 (1H, m), 6.03 (1H, m), 6.43 (1H, d,d, J=11, 6 Hz), 7.04 (1H, d, J=11 Hz).

Photolysis of ***1f****-1,1-*d_2. A solution of **1f**-1,1-d_2 (23 mg, 0.16 mmol) and Michler's ketone (230 mg, 0.86 mmol) dissolved in benzene (100 mL) was irradiated for 15 min. The NMR spectrum of the isolated mixture (12 mg) was compared with that of the products from **1f**. They were quite similar, but in the former, the signal due to H_5 of **3f** were very weak and that of H_6 appeared as a broad doublet at 5.8 ppm. Further, the signal due to H_1 of **1f** appeared as weak as that of H_5 on **3f**. VPC (column A, 100 °C) of the mixture showed 4 peaks: peak-1 (unknown; *retention time*, 18.4 min; 7.1%), peak-2 (**3f**; 21.6 min; 39.4%), peak-3 (**1f**; 25.6 min; 49.1%), and peak-4 (**8b**-d_2; 33.2 min; 4.4%). In the NMR spectrum of peak-3, the peak area ratio for H_{7b}:H_{1a}:*endo*-H_1:H_2+H_3 is equal to 32:42:5:83. These results define unambiguously that **1f**-d_2 is composed of **1f**-1,1- and 1,7b-d_2 in a ratio of 3.2:1.

Photolysis of ***9a****.* A solution of **9a** (33.5 mg, 0.24 mmol) and Michler's ketone (31.9 mg, 1.18 mmol) dissolved in benzene (100 mL) was irradiated for 30 min. The product (9 mg), isolated as above, showed 5 peaks in the VPC (column A, 100 °C) with a area ratio for an unknown, naphthalene, a mixture (1:2) of **3d** and **9a**, **1f**, and **8b** was 1:6:125:96:2, respectively. The NMR spectrum of the mixture also supports these assignments.

Photolysis of ***1a*** *in Furan.* A solution of **1a** (15 mg) and Michler's ketone (80 mg) dissolved in furan (12 mL) was irradiated externally for 3 h. The product was separated as above by chromatography (silica gel 5 g/benzene followed by benzene–ethyl acetate (9:1 v/v)) to give a product mixture (6.5 mg). This was estimated by VPC (column B, 165 °C) to contain the *adduct*-3 (30%).

Photolysis of ***3a*** *in Furan.* A solution of **3a** (40 mg, 0.19 mmol) and Michler's ketone (450 mg, 1.68 mmol) dissolved in furan (75 mL) was irradiated with a medium pressure mercury lamp (500 watts) for 0.5 h in a Pyrex jacket. After separation of the mixture by the usual method, the products were purified by preparative TLC (silica gel/20% ether–hexane) to give *adduct*-3 (23 mg, 43%). *Adduct*-3 IR (liq. film) ν_{max}: 3050, 2925, 1735, 1616, 1250, 1140, 1075, 760, 740, 725 cm^{-1}. UV (95% C_2H_5OH) λ_{max} (ε): 220 (end absorp., 9990), 260 (648), 267 (678), 275 (617) nm. NMR ($CDCl_3$) δ: 2.5—2.9 (2H, m), 3.0—3.56 (3H, m), 3.82 (3H, s), 4.47 (1H, t, J=2.5 Hz), 5.10 (1H, d,d, J=7, 11 Hz), 6.1—6.3 (2H, m), 6.78 (1H, d,d, J=7, 8 Hz), 6.9—7.4 (4H, m). C-13 NMR ($CDCl_3$) δ: 36.7 (d), 38.6 (d), 41.9 (t), 45.6 (d), 49.3 (d), 51.8 (q), 82.5 (d), 101.4 (d), 125.9 (d), 126.6 (d), 128.3 (d), 129.6 (d), 131.0 (d), 138.4 (d), 138.6 (s), 140.8 (s), 146.6 (d), 173.0 (s). Mass *m/e* (rel intensity): 250 (1.78, M^+-OCH_4), 215 (11.3), 214 (64.3, M^+−furan), 155 (14.9), 154 (59.5), 142 (12.5), 141 (100). Found: C, 77.04; H, 6.52%. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%.

Photolysis of ***1f*** *in Furan.* Irradiation of **1f** (94 mg, 0.67 mmol) and Michler's ketone (888 mg, 3.3 mmol) in furan (80 mL) for 45 min gave a product (76 mg) after chromatography (silica gel, 20 g/hexane). VPC separation (column D, 170 °C) of the product gave **1f** (23.5 mg; *retention time*, 1 min) and *adduct*-4 (5.2 mg; *r.t.*, 4.8 min). *Adduct*-4 UV (95% C_2H_5OH) λ_{max} (ε): 220 (end absorp. 8900), 260 (599), 267 (751), 275 (723) nm. IR (liq. film) ν_{max}: 3050, 2925, 1616, 1140, 1075, 1017, 745, 720, 710 cm^{-1}. NMR ($CDCl_3$) δ: 2.83 (*exo*-H_{10}, d,d, J=4, 20 Hz), 2.9—3.15 (H_6, m), 3.3—3.8 (*endo*-H_{10}, H_7, H_1, m), 4.27 (H_5, t, J=2.5 Hz), 5.0 (H_2, d,d, J=6.5, 10.5 Hz), 6.10 (H_{11}, d,d, J=6, 8 Hz), 6.22 (H_4, t, J=2.5 Hz), 6.6 (H_{12}, d,d, J=6, 8 Hz), 6.86—7.2 (4H, m). Mass *m/e* (rel intensity): 210 (M^+, 0.55), 165 (3.1), 142 (100, M^+−furan). Found: C, 86.00; H, 6.78%. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71%.

The authors wish to thank Mr. Jun-Ichi Goda of our University for the elementary analyses and Mr. Tadasu Tahara of the Nitto Kasei Chemical Co. for a generous supply of tributyltin chloride.

References

1) This paper is dedicated to Emeritus Professor Takeo Sakan on the occasion of his 70th birthday.

2) M. Kato, M. Funakura, M. Tsuji, and T. Miwa, *J. Chem. Soc., Chem. Commun.*, **1976**, 63.

3) F. -G. Klärner and S. Yaslak, *Chem. Ber.*, **112**, 2286 (1979).

4) M. Kato, K. Takatoku, S. Ito, M. Funakura, and T. Miwa, *Bull. Chem. Soc. Jpn.*, **53**, 3648 (1980).

5) M. Kato, K. Takatoku, S. Ito, and Miwa, *Tetrahedron Lett.*, **1979**, 867.

6) H. Günther, *Tetrahedron Lett.*, **1970**, 5173; S. W. Stayley, M. A. Fox, and A. Cairncross, *J. Am. Chem. Soc.*, **99**, 4524 (1977).

7) H. Meier, J. Heiss, H. Suhr, and E. Muller, *Tetrahedron*, **24**, 2307 (1968).

8) M. Kato, M. Kawamura, Y. Okamoto, and T. Miwa, *Tetrahedron Lett.*, **1972**, 1171.

9) D. Wendisch and W. Metzner, *Chem. Ber.*, **101**, 4106 (1968).

10) F. Campagna, A. Carotti, and G. Casini, *Tetrahedron Lett.*, **1977**, 1813.

11) J. S. Swenton, K. A. Burdett, D. M. Madigan, and P. D. Rosso, *J. Org. Chem.*, **40**, 1280 (1975).

12) N. F. Chamberlain, "The Practice of NMR Spectroscopy," Plenum Press, New York and London (1974), p. 299.

13) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *J. Am. Chem. Soc.*, **91**, 6856 (1969).

14) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *J. Am. Chem. Soc.*, **91**, 6858 (1969).

15) D. I. Schuster, R. H. Brown, and B. M. Rosnick, *J. Am. Chem. Soc.*, **100**, 4504 (1978).

16) J. S. Swenton, K. A. Burdett, D. M. Madigan, T. Johnson, and P. D. Rosso, *J. Am. Chem. Soc.*, **97**, 3428 (1975).

17) A. G. Anastassiou, E. Reichmanis, S. J. Girgenti, and M. Schaefer-Ridder, *J. Org. Chem.*, **43**, 315 (1978).

18) G. W. Gruber and M. Pomerantz, *J. Am. Chem. Soc.*, **91**, 4004 (1969); *J. Org. Chem.*, **33**, 4501 (1968).

19) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962); H. G. Kuivila, *Acc. Chem. Res.*, **1**, 299 (1968); E. J. Corey and J. W. Suggs, *J. Org. Chem.*, **40**, 2554 (1975).

20) D. E. Applequist, M. R. Johnston, and F. Fisher, *J. Am. Chem. Soc.*, **92**, 4614 (1970).

21) K. A. Burdett, F. L. Shenton, D. H. Yates, and J. S. Swenton, *Tetrahedron*, **30**, 2057 (1974).

22) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1458 (1968).

23) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971).

24) J. Eriksen, K. Krogh-Jespersen, M. A. Ratner, and D. I. Schuster, *J. Am. Chem. Soc.*, **97**, 5596 (1975).

25) P. S. Mariano and J. -K. Ko, *J. Am. Chem. Soc.*, **95**, 8670 (1973).

26) J. S. Swenton, R. M. Blankenship, and R. Sanitra, *J. Am. Chem. Soc.*, **97**, 4941 (1975).

27) We confirmed the optical yields for the rearrangement under direct irradiation[8] as follows: **1a** obtained from **1d** ($[\alpha]_D$ +143°) below 5 °C gave *exo*-**4a** ($[\alpha]_D$ −122° (*c* 0.65, $CHCl_3$)) and the thermally equilibrated *exo-endo* mixture (2:1) of **1a** ($[\alpha]_D$ +29° (*c* 0.98, $CHCl_3$)) obtained from the same acid gave *exo*-**4a** ($[\alpha]_D$ −120° (*c* 0.65, $CHCl_3$)). The enantiomer excesses of both *exo*-**4a** were found to be 60% by NMR measurements using tris[3-(2,2,3,3,4,4,4-heptafluoro-1-hydroxybutylidene)-*d*-camphorato]europium-(III) as a chiral shift reagent.

28) J. Hine, *J. Am. Chem. Soc.*, **88**, 5525 (1966); O. S. Tee and Y. Yates, *ibid.*, **94**, 3074 (1972).

29) W. T. Borden, J. G. Lee, and S. D. Young, *J. Am. Chem. Soc.*, **102**, 4841 (1980).

30) M. Kato, M. Tsuji, and T. Miwa, *Bull. Chem. Soc. Jpn.*, **51**, 1450 (1978).

31) The determination of optical purity with chiral NMR shift reagent was unsuccessful but the absolute value of the specific rotation was the same as the one thermally obtained from (1*R*)-*exo*-**1c**.

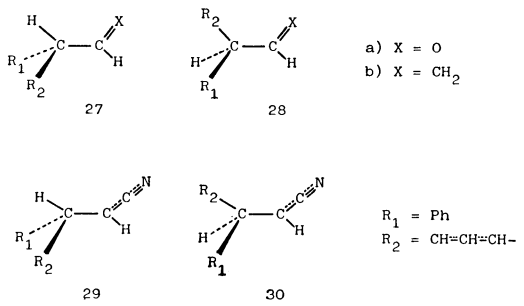
32) These facts are parallel with the thermal behavior of **1a**. When **1a** was heated above 250 °C for 1.5 h, it gave, in addition to a trace amount of naphthalene, methyl 3-(1-naphthyl)acrylate (29%) and methyl 3-(1-naphthyl)propanoate (53%). The latter was identified by direct comparison with an authentic sample and the former was confirmed by the spectral data (NMR ($CDCl_3$) olefinic protons δ: 8.2 (1H, d, J=16 Hz), 6.2 (1H, d, J=16 Hz): UV λ_{max}: 330 nm. IR ν_{max}: 1710, 1635 cm^{-1}) and by quantitative transformation to the latter under catalytic hydrogenation (H_2 (10% Pd-C, CH_3OH)).

33) N. H. Fischer and H.-N. Lin, *J. Org. Chem.*, **38**, 3073 (1973).

34) M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970); M. J. Jorgenson, *J. Am. Chem. Soc.*, **91**, 6432 (1969).

35) In a rough approximation, the rotamer relationships about the sp^2–sp^3 bond of **23** or **24** (C_{7b}–C_1) are similar to those of substituted acetaldehydes or 3-substituted propenes.[42] Karabatsos described that, of the two minimum energy-tautomers, **27a** has an advantage over **28a** by 250 cal/mol when two ethyl groups are attached to the α-carbon of acetaldehyde. Further, **27a** increases its stability about 350 cal/mol by the phenyl substitution in place of ethyl group in butanal.[42] Therefore, in 2-phenylbutanal, **27a** might be estimated to be more stable (250—600 cal/mol) than **28a**. Similar trends are seen in the substituted propenes (**27b** and **28b**). In the conformers, **23c** and **24c**, because the substituents are regarded as a phenyl and a vinylmethinyl group (**29** and **30**), the steric requirement is supposed to be of the same order as the one substituted with a phenyl and an ethyl group. If we assume the conformer **23c** related to **29** is more stable and hence more populated than **24c** related to **30** and that there is little difference in steric requirement for reconversion processes of **23c** to *exo*-**1c** and of **24c** to *endo*-**1c**, the rates of ring closure might be governed mainly by the population of **23c** against that of **24c**.

36) J. C. Berridge, D. Bryce-Smith, A. Gilvert, and T.



27 28 29 30

Scheme 9.

S. Cantrell, *J. Chem. Soc., Chem. Commun.*, **1975**, 611.
37) R. S. Lie, *J. Am. Chem. Soc.*, **89**, 112 (1967).
38) K. Schafner and M. Demuth, "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 3, p. 334.
39) D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, **35**, 3190 (1970).
40) W. G. Dauben and M. S. Kellog, *J. Am. Chem. Soc.*, **102**, 4456 (1980).
41) R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961).
42) G. J. Karabatsos and D. J. Fenoglio, "Topics in Stereochemistry," ed by E. L. Eliel and N. L. Allinger, Wiley-Interscience, New York (1970), Vol. 5, p. 167.