November, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *3449—3456 (1983)* 3449

The Solvent Effects on the Photochemical Isomerization of 5-Cyano-5*H*-benzocycloheptene

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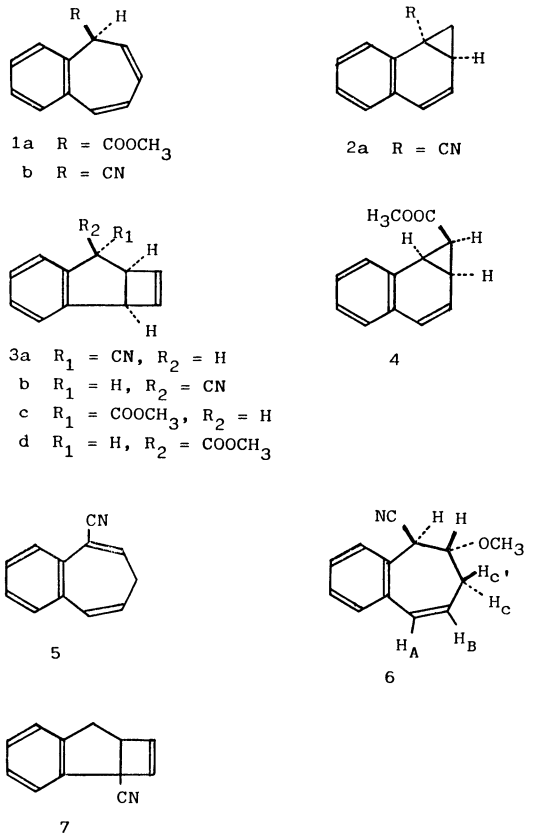
(Received October 18, 1982)

The photochemical reaction of 5-cyano-5*H*-benzocycloheptene (**1b**) has been studied kinetically in various solvents. The main reactions were (1) a 1,7-hydrogen shift, with simultaneous cyclization, to give 7b-cyano-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene and (2) a 4π-electrocyclic ring closure to give cyclobutenes. The former reaction was found to show rather complicated solvent effects, but the latter was accelerated in less polar solvents. The conformational equilibrium between *exo*- and *endo*-forms was also observed in the NMR spectra of **1b** under various conditions. From a consideration of the solvent effects on the product distribution, the ground-state conformations of **1b** could be reflected in the ratio of the *exo* and *endo* forms of the cyclization products.

The photochemistry of 5*H*-benzocycloheptenes (**1**) has been studied by Swenton *et al.*[1] and also by us.[2,3] As a result, it has been found that these molecules are rearranged principally in two directions; *i.e.*, the formation of benzonorcaradienes (**2**) *via* a 1,7-hydrogen shift and the formation of 2a,7a-dihydro-7*H*-cyclobut[*a*]indenes (**3**) by means of an electrocyclic ring closure.

In the case of the 5-methoxycarbonyl derivative (**1a**), a facile 1,7-migration of the substituent took place, instead of the 1,7-hydrogen migration, to give 1-*endo*-methoxycarbonyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) exclusively.[3]

In this paper, we wish to report the photochemistry of 5-cyano-5*H*-benzocycloheptene (**1b**) in order to compare it with that of **1a**. The solvent effects on the conformational equilibrium and on the photochemical isomerization of **1b** have also been studied.



Scheme 1.

Results

The irradiation of **1b** in a methanol solution with the aid of a high-pressure mercury arc (UM-452) through a Pyrex filter for 1 h gave a mixture, **A**—**F**, consisting of **2a** (33%), **3a** (*exo*) (18%), **3b** (*endo*) (9%), **5** (5%), **6** (10%), and **7** (6%). They were separated by successive column and vapour-phase chromatography.

Structure of the Products. Compound **A** showed three signals characteristic of a three-membered ring proton and two olefinic proton signals in the NMR spectrum; it was identical with the known 7b-cyano-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**2a**).[4] Because of the difficulty of separating **B** from **C**, we studied them as a mixture. The NMR spectrum showed two sets of olefinic signals on the cyclobutene ring (**B**, δ 6.42 and 6.15; **C**, δ 6.52 and 6.28 ppm (AX type, J=2.7 Hz)), accompanied by benzylic proton signals characteristic of *exo*- and *endo*-2a,7a-dihydro-7*H*-cyclobut[*a*]indene (**3**) (**B**, δ 4.49 (bd); **C**, δ 4.32 ppm (d)).[5] We deduced **3a** structure for compound **B** and that of **3b** for **C**, because the NMR signals for the benzylic proton in 7-substituted 2a,7a-dihydro-7*H*-cyclobut[*a*]indene are quite indicative of the configuration, whether the substituent occupies the *exo* (broad doublet) or the *endo* position (doublet).[5] These assignments were confirmed by the methanolysis of the mixture to the easily separable corresponding methyl carboxylates, **3c** and **3d**. They were identical with those independently obtained through the sensitized irradiation of 5-methoxycarbonyl-5*H*-benzocycloheptene (**1a**).[6] Compound **D** showed an UV maximum ($\lambda_{\max}$: 229 nm) characteristic of 7*H*-benzocycloheptenes and an IR absorption of the conjugated nitrile ($\nu_{C\equiv N}$: 2220 cm^{-1}). The NMR signals of the three olefinic and two aliphatic protons, together with their coupling patterns, determined the structure to be **5**.[4] Compound **E** had the molecular formula of $C_{13}H_{13}NO$, composed of one molecule each of the starting material and of methanol. This compound showed a UV spectrum similar to that of 6,7-dihydro-5*H*-benzocycloheptene,[7] while the NMR olefinic signals (2H, AB type, J_{AB}=12.2 Hz) showed a strong coupling only with the adjacent methylene protons (J_{AC}=2.2 Hz, $J_{AC'}$=

Table 1. The induced shifts in ^{1}H NMR signals of compound **E** observed upon the addition of Eu(fod)$_3$ (Compound **E** 7 mg/0.4 mL CDCl$_3$)

Added Eu(fod)$_3$ (mg)	Observed proton chemical shifts (δ)						
	H_5	H_6	H_{7a}	H_{7b}	H_8	H_9	OCH_3
0	4.21	3.87	2.55	2.86	5.90	6.51	3.43
6	4.32	3.93	2.66	—	5.93	6.54	3.47
14	4.58	4.08	2.88	2.94	6.00	6.61	3.56
$\Delta\delta H_i/\Delta\delta H_8$	3.7	2.1	3.3	0.8	1.0	1.0	1.3

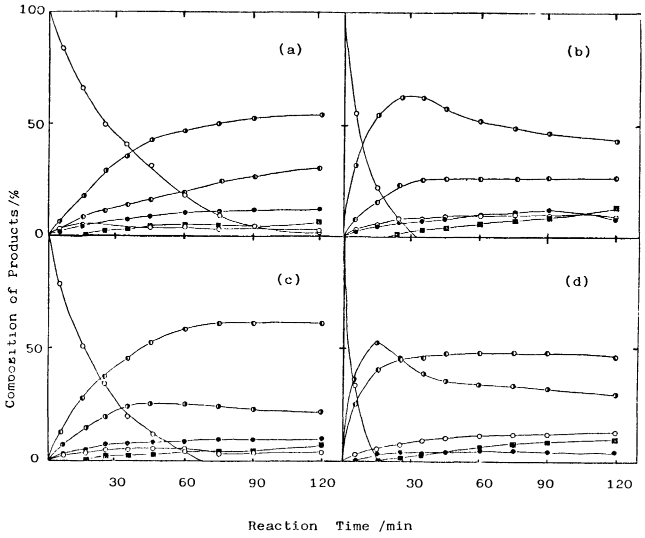


Fig. 1. Plots of the products composition *versus* irradiation time. Solvents; (a) methanol, (b) acetonitrile, (c) *t*-butyl alcohol, (d) benzene. Products; ◑ (**2a**), ◐ (**3a**), ● (**3b**), ○ (**5**), ■ (**7**).

1.5 Hz, J_{BC}=4.4 Hz, $J_{BC'}$=5.4 Hz, $J_{CC'}$=18.3 Hz). Since the proton on C-6 showed a doublet of doublets of doublets (J=9.3, 5.4, 2.2 Hz) at δ 3.87 ppm and the one on C-5, a broad doublet (J=2.2 Hz) at δ 4.21 ppm, the methoxyl and cyano groups must be attached to C-6 and C-5 respectively, or *vice versa*. The structure (**6**) was deduced from the experiment with Siever's reagent on NMR measurements. Thus, in addition to a moderate shift for the signals of H-6, there was an extraordinary lower-field shift for the H-5 and H-7a, which defined the *cis* stereochemistry of both the hydrogens to the methoxyl group (Table 1). Such an enormous shift of the signal of H-7 is expected for the **6** structure.[8] As it had been reported that **2a** gives **5** as a primary photoproduct[4] and that the cyano group rarely migrates under photolytic conditions,[9] **1b** and/or **5** can logically be recognized as a precursor of **6**. Both would then possibly be photochemically isomerized to a constrained *trans*-form. It is well known that the dipolar additions of protic solvents to constrained olefins proceed readily.[10] Compound **F** has a molecular formula, $C_{12}H_9N$ (m/e 167 (M^+)) and shows characteristic olefinic AX-type signals (J_{AX}=2.7 Hz) of cyclobutene in the NMR spectrum. The lack of an NMR signal due to a benzylic proton on C_{2a} defined the structure (**7**) for compound **F**.

Table 2. Relative rate constants for the photoisomerization of **1b** in several solvents[a)]

Solvent	k_r	k_{2a}	k_{3a+3b}	k_{3a} (k_{exo})	k_{3b} (k_{endo})
CH_3OH	0.149	0.062	0.034	0.023	0.011
CH_3CN	0.556	0.384	0.099	0.075	0.024
t-BuOH	0.237	0.059	0.135	0.120	0.015
CH_2Cl_2	0.650	0.221	0.384	0.334	0.050
C_6H_6	1.000	0.480	0.284	0.264	0.020
C_6H_{12}	0.439	0.043	0.393	0.393	0.000
$C_6H_5CH_3$	0.654	0.384	0.169	0.159	0.010

a) Error ±0.005.

*Kinetic Studies of Photochemical Reactions of **1b** in Several Solvents.* In order to obtain further information about how the photochemical behavior of **1b** is changed by the solvents used in photolysis, we studied it comparatively in a merry-go-round apparatus in several solvents; methanol, *t*-butyl alcohol (protic polar), acetonitrile, dichloromethane (aprotic polar), and cyclohexane, benzene (aprotic nonpolar). Two runs were carried out for every solvent. With a longer period of irradiation, we obtained the product distributions shown in Fig. 1, while the results of the shorter-period irradiation are summarized in Table 2. From Fig. 1 it is obvious that the formation of **5** and **7** at the initial stage was so trivial that they were omitted from the table.

Among the solvents studied, the rate of the disappearance of **1b** (k_r) was the fastest in benzene, and the rates were almost all consistent with the first-order kinetics at the initial stage. Therefore, we related them to the decreasing rate of **1b** in benzene.

Discussion

Table 2 shows that, though there is no parallel relationship between the relative rates for the formation of **2a** and the solvent polarities, in all aprotic solvents except benzene and toluene the reaction proceeds faster as the polarities of the solvents increase, while the reaction is retarded in protic solvents.

On the other hand, it is obvious that the electrocyclic reaction to **3a** and **3b** proceeded faster as the polarity of the solvents decreased. The solvent effect observed here suggests the existence of different transition states (or energy surfaces) between the 1,7-hydrogen shift and the 4π-electrocyclic ring closure.

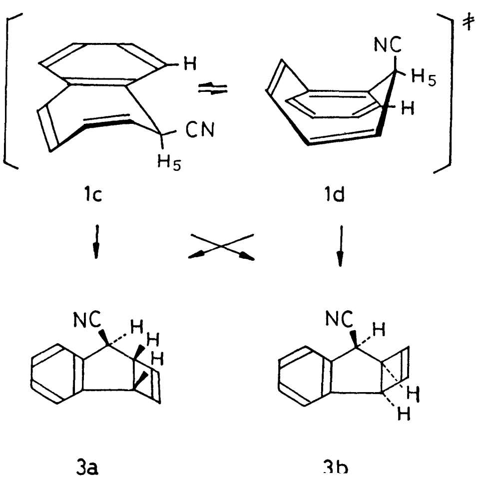
It is interesting to note that the ratio of k_{3b}/k_{3a} decreases gradually as the solvent polarities decrease.

This was not seen in the case of the cyclization of 5-methoxycarbonylmethyl-5*H*-benzocycloheptene, which gives an almost constant ratio of cyclization products in various solvents (*exo*:*endo*=95:5).[6]

It is well established that cycloheptatrienes exist in an equilibrium mixture of two tub conformations;[11] for example, the two conformers of 5-methoxy-6,7,8-triphenyl-5*H*-benzocycloheptene are separated by an energy barrier of 71 kJ/mol.[12] We estimated, by means of the ^1H and ^{13}C NMR spectra in dideuteriodichloromethane, that the energy barrier of the conformational flipping of the seven-membered ring of **1b** is equal to ΔG^* 40.2 kJ/mol at −73 °C and that the equilibrium between the two conformers with the cyano group in either the *quasi*-equatorial (**1c**) or the *quasi*-axial position (**1d**) is approximately equal to 81:19.[3]

The increase in the ratio of the *quasi*-equatorial form in **1b** compared with that of **1a** (52:48)[3] reflects the fact that the equilibrium is sensitive to the bulkiness of the substituents on C-5. **1c** and **1d** should interact with a polar solvent more strongly at the polar site than at any other part of the molecule. This interaction can be expected to affect the equilibrium between **1c** and **1d** by the increase in the steric repulsion between H-4 and cyano group and/or by the decrease in the solvation energy in **1d** compared with that in **1c**. The *quasi*-axial cyano group of **1d** is opened to solvation in every direction, but the *quasi*-equatorial cyano group of **1c** is blocked at the side facing a hydrogen on C-4. The solvation energy gained by **1d** must be much larger than that won by **1c**; therefore, the equilibrium between **1c** and **1d** moves toward **1d** as the polarity of the solvent increases (Scheme 2).

The photochemical reaction from its excited singlet is expected to proceed much faster than the ring inversion;[13] therefore, the ring closure of **1c** can be discriminated from that of **1d**. There are two possible disrotatory modes of 4π-electrocyclic-ring closure for the conformations. When we write the boat form in the upper concave, as is shown by **1d** in Scheme 2, one mode is a ring closure with the rotation of the bonds, from C-8 to C-9 and from C-7 to C-6, in the opposite and outer directions to give the cyclobutene, while the other is the ring closure with the rotation of the same bonds in the inner directions. In the former mode, the axial substituent in **1d** is transformed to the *endo* substituent, and the equatorial one, to the *exo* substituent. In the latter mode, the axial substituent is transformed to the *exo* substituent, and the equatorial one, to the *endo* substituent. Considering the energy relation along the reaction coordinate, it is possible that one of these cyclization modes is to be preferred to the other. Then the ring closure to either the pair of **3a** (*exo*) from **1c** and **3b** (*endo*) from **1d**, or the pair of **3a** from **1d** and **3b** from **1c**, will proceed easier than the other pair.[14] Then, if we could determine the ratio of the conformers in equilibrium, we would be able to evaluate k_{endo} using the ratio and k_{exo}. It seemed difficult, however, to estimate the conformer's ratio of **1b** by NMR at the low temperatures in the solvents used, other than dichloromethane-d_2, because of their higher melting points or of their increasing viscosities at low temperatures.



Scheme 2.

In order to clarify the conformational aspect, the NMR spectra of **1b** were measured in several solvents at room temperature. The chemical shifts of H-5 and H-9 are listed in Table 3, while the plots of $\delta H_9 - \delta H_5$ *versus* k_{exo} are shown in Fig. 2. We noticed a rough trend for the less polar solvents to favor a larger separation of $\delta H_9 - \delta H_5$ and a bigger k_{exo}, while the more polar ones favor less separation and a smaller k_{exo}.

TABLE 3. THE CHEMICAL SHIFTS OF H_9 AND H_5, AND THEIR DIFFERENCES

Solvent	δH_9	δH_5	$\delta H_9 - \delta H_5$	
CD_3OD	7.33±0.2	4.34±0.2	2.99±0.4	(48.4%)[a]
CD_3CN	7.31	4.30	3.01	(46.7%)
t-BuOH	7.21	4.01	3.20	(31.1%)
CH_2Cl_2	7.14	3.79	3.35	(19.0%)
C_6H_6	6.82	3.37	3.45	(10.7%)
C_6H_{12}	7.13	3.65	3.48	(7.9%)

a) The estimated percentages of **1d** are shown in parentheses..

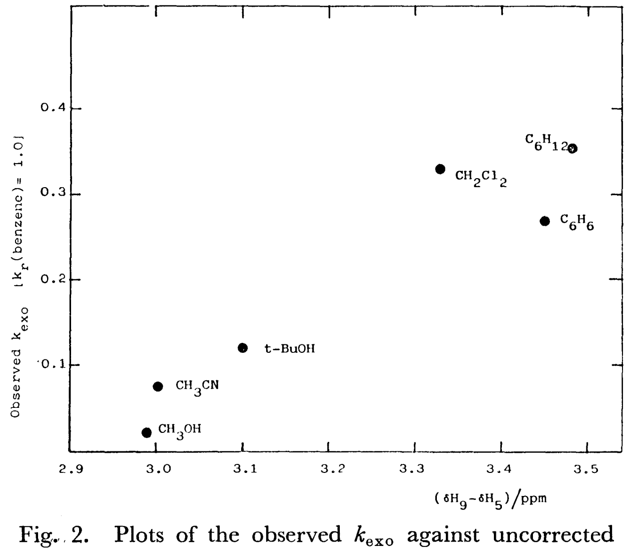


Fig. 2. Plots of the observed k_{exo} against uncorrected $\delta_{H_9} - \delta_{H_5}$.

TABLE 4. THE PERCENTAGES OF **1d** IN THE EQUILIBRIA FOR SEVERAL SOLVENTS, AND THE POLARITY PARAMETERS OF THE SOLVENTS

Solvent	Method I[a] (%)	Method II[a] (%)	$(J_{H_5-H_6})$ / Hz	Mean value / %	$E_{T_{30}}$ / kJ mol^{-1}
CH_3OH[b]	48.4±5	46.5±5	(6.74±0.2)	47.5	232
CH_3CN	46.7	48.5	(6.79)	47.6	192
t-BuOH	31.1	26.0	(6.25)	28.6	184
CH_2Cl_2	19.0	26.0	(6.25)	22.5	172
C_6H_6	10.7	15.0	(5.99)	12.9	144
C_6H_{12}	7.9	7.0	(5.79)	7.5	142

a) Methods I and II are referred to the estimation methods, *i.e.*, the use of the chemical shifts (Method I) and the coupling constants, $J_{H_5-H_6}$ (Method II). b) The full deuterated solvents were used for NMR measurements.

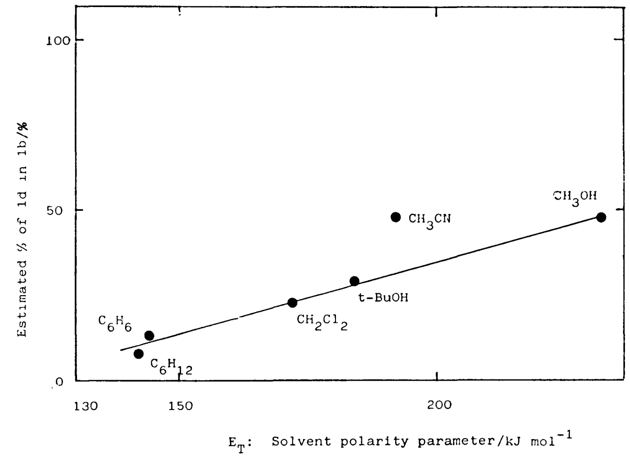


Fig. 3. Plots of the estimated percentage of **1d** against solvent polarity.

Günther *et al.* reported the determination by means of ^{13}C NMR spectroscopy, of the ratio of the *quasi*-equatorial to the *quasi*-axial conformer of 7-cyano-1,3,5-cycloheptatriene in equilibrium as 79:21. Here, the chemical shifts of C-3 (or C-4) in the two conformers are identical with each other in the temperature range from −2.5 to −123 °C.[11)] If we use the chemical shift of H-9, which is far from the cyano group, as the standard, the $\delta H_9-\delta H_5$ becomes a chemical shift of H-5 from this standard, which has already been cancelled in the same magnitude as the solvent effect influencing H-9. As has been mentioned above, this chemical shift of H-5 is equal to a weight average of the chemical shifts of H-5 existing in **1c** and **1d**.[15)] In order to check the propriety of this method, the difference in the chemical shifts between aromatic and benzylic protons of benzyl cyanide were examined and found to show satisfactory similarities (±0.1 ppm), except in benzene (+0.58 ppm).

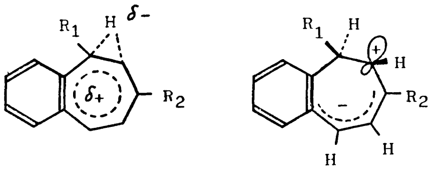
When the chemical shifts at δ 3.56 (H-5 for **1c**) and δ 4.78 ppm (H-5 for **1d**) observed at a low temperature in CD_2Cl_2 are in effect as the standard at room temperature in CH_2Cl_2, the percentage of **1d** in the equilibrium in several solvents can be roughly estimated as is shown in Table 3 (Method I).

Another approach[16)] to determine the equilibrium has been done by taking advantage of the difference in the spin-spin coupling constants of C-5 protons between **1c** (equatorial-CN) and **1d** (axial-CN). From the low-temperature NMR spectrum of **1b** in CD_2Cl_2, the signals due to equatorial H-5 (**1d**) (lower field) and to axial H-5 (**1c**) (higher field) are seen as broad doublets. Applying the computer program for the resolution of the overlapping peak into their components (Gaussian function) to those bands,[17)] we obtained the coupling constants; $J_{endo-5,6}=5.63\pm0.2$, $J_{exo-5,6}=8.02\pm0.2$ Hz for **1b**.[18)] From the NMR spectra of **1b** in several solvents, we get the weight-averaged coupling constants for the equatorial and for the axial H-5 of **1b**. We can then calculate the percentages of **1c** in **1b** from the coupling constants in several solvents (Table 4, Method II). The percentages thus obtained were parallel with those obtained from the chemical shifts; we used the mathematical mean values for the following calculations. The plots of the percentages of **1d** in **1b** *versus* the solvent polarity parameters, E_T,[19)] in various solvents are shown in Fig. 3. A linear correlation was observed for every solvent except acetonitrile, in which the cyano group of **1b** may have a strong affinity to the same group of the solvent.

As the conformers' ratios are obtained based on NMR data in CD_2Cl_2 at low temperatures, we used the kinetic data in dichloromethane as a standard. When the observed values of k_{exo} are divided by each respective molar fraction of **1c** in the same solvent, we obtain the values of k°_{exo}; the values of k_{exo} from pure **1c**. Similarly, if the observed value of k_{endo} (CH_2Cl_2) is divided by the molar fraction of **1d** in dichloromethane, we obtain the value of k°_{endo} (CH_2Cl_2): the value of k_{endo} from pure **1d** in dichloromethane. If we assume that the ratios of the reaction rate, $k^{\circ}_{endo}/k^{\circ}_{exo}$, were constant in every solvent, we can calculate the values of k°_{endo} for every solvent using the values of k°_{exo} and the ratio in CH_2Cl_2 (0.515). Further, we will be able to evaluate k_{endo} (calcd) in a solvent by the use of the k°_{endo} (calcd) and the molar fraction of **1d** in the same solvent. The calculated values of k_{endo} (calcd), listed in Table 5, are in satisfactory agreement with the observed values of k_{endo}. Therefore, it seems reasonable that the photochemical progenitors of **3a** (*exo*) and **3b** (*endo*) are **1c** and **1d** respectively. In other words, the interrelation between the estimated conformer ratio of the starting material in the equilibrium and the experimental product-ratio supports the allowed disrotatory ring closure with rotation at the conjugated double

TABLE 5. COMPARISON OF THE OBSERVED AND THE CALCULATED PARAMETERS

Solvent	k_{exo}	k_{endo}	k°_{exo}	$k^{\circ}_{\mathrm{endo}}$	k_{endo} (Calcd)
CH_3OH	0.023	0.011	0.044	0.023	0.011
CH_3CN	0.075	0.024	0.143	0.074	0.035
t-BuOH	0.120	0.015	0.168	0.087	0.025
CH_2Cl_2	0.334	0.050	0.431	0.222	0.050
C_6H_6	0.264	0.020	0.303	0.156	0.020
C_6H_{12}	0.393	0.000	0.425	0.219	0.016



8a R_1 = CN, R_2 = H
b R_1 = H, R_2 = CN

9

Scheme 3.

bond in a 7-membered-ring tub conformation to the outer direction. This process corresponds to the pathway with the least torsional energy around the $C_5(sp^3)$–$C_6(sp^2)$ bond.

A clear solvent effect on the *anti-syn* ratio in the formation of the [2+2] adducts was seen in the case of the photochemical dimerization of 2-cyclopentenone.[20] The photochemical reactions which proceed under the control of the ground-state geometries have previously been observed in the ring opening of 1,3-cyclohexadiene derivatives;[21] the present case is the first example of such a reaction for a seven-membered ring analogue.

As has been mentioned above, rather complicated solvent effects on the formation of **2a** can not be understood from the control of the ground-state geometries of the starting material. It is possible to assume that the electronic polarization of **1b** to **8a** or **9** may have played a role in the transition state. The former (**8b**) was suggested by Swenton and his co-workers to explain the solvent effect on the same rearrangement of 7-substituted 5*H*-benzocycloheptenes,[1] and a similar polarization to the latter was proposed by Tezuka and Houk to clarify the substituent effects on the cyclization and 1,7-sigmatropic hydrogen shift of substituted cycloheptatrienes.[22] Interaction with protic solvents can be expected to retard the reaction, and enhancement of the charge separation by aprotic polar and benzenoid solvents may accelerate the reaction.[23]

Thus, we found that the photochemical isomerization of **1b** under direct irradiation was quite different from that of 5-methoxycarbonyl-5*H*-benzocycloheptene, which gave **4** exclusively.[3]

Experimental

General Procedure. The UV, IR, ^1H NMR, ^{13}C NMR, and mass spectra were recorded according to the methods given in the previous paper. A Varian Aerograph, model 90P, was used for the preparative VPC (Helium flow rate; 30—40 mL/min), while a Shimadzu Gas Chromatograph GC-4BM was used for the analytical purposes (Hydrogen flame detector). The columns used for separation were ϕ3.2 mm × 1.8 m columns charged with: A, 3% Silicone OV-17; B, Silicone SE-30, on Chromosorb WAW.

For irradiation of a volume of more than 100 mL, a solution charged in a vessel fitted with a quartz cooling jacket was purged with dry nitrogen for five min and then 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 five min and then dipped in ice water in a quartz-made 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).

*Synthesis of **1b**.* Benzotropylium tetrafluoroborate, which had been derived from 2,3-benzotropone (3.24 g, 20.7 mmol),[2] in anhydrous acetonitrile (18 mL), was added, drop by drop, to sodium cyanide (910 mg, 18.6 mmol) in acetonitrile (12 mL) at 0 °C under a nitrogen atmosphere, and then the mixture was stirred for 30 min at room temperature. The mixture was filtered through Hyfrosupercel (a filter aid), and the filtrate was concentrated under reduced pressure. The residue taken up in ether (100 mL), washed successively with water and saturated brine, and dried. After the evaporation of the ether, the remaining oily products (2.88 g, 81%) were separated by column chromatography (silica gel 90 g/benzene), followed by preparative TLC with a multiple-developing technique (10% ether–hexane) to give **1b** (1.41 g, 8.43 mmol; 41%) and a mixture of 7-cyano-7*H*- and 7-cyano-5*H*-benzocycloheptene (*ca.* 95:5, 0.81 g, 4.84 mmol; 23%). The latter mixture was converted quantitatively into 7-cyano-5*H*-benzocycloheptene by passing it through a column of basic alumina (Merk; activity I/benzene). **1b** IR (liq film) ν_{max}: 3030, 2260, 1589, 1493, 893, 822 cm^{-1}. UV (95% C_2H_5OH) λ_{max} (log ε): 274.5 (3.89) nm. NMR (CCl_4) δ=3.76 (1H, dd, *J*=6.0, 1.3 Hz), 5.75 (1H, dd, *J*=9.5, 6.0 Hz), 6.19 (1H, ddd, *J*=9.5, 5.3, 1.3 Hz), 6.55 (1H, dd, *J*=11.8, 5.3 Hz), 7.20 (1H, d, *J*=11.8 Hz), 7.2—7.7 (4H, m). ^{13}C NMR ($CDCl_3$) δ=35.6, 119.1, 123.1, 125.3, 127.3, 128.0, 128.7, 129.9, 130.7, 134.3, 134.6 ppm. Found: C, 86.00; H, 5.41; N, 8.43%. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38%. *7-Cyano-7H-benzocycloheptene.* IR (liq film) ν_{max}: 3040, 2260, 1638, 1492, 1445, 800, 770, 712 cm^{-1}. UV (95% C_2H_5OH) λ_{max}: 227 nm. NMR (CCl_4) δ=3.25 (1H, tt, *J*=6.0, 1.0 Hz), 5.76 (2H, dd, *J*=10.0, 6.0 Hz), 6.64 (2H, dd, *J*=10.0, 1.0 Hz), 7.25 (4H, s).

*Photolysis of **1b** in Methanol.* A solution of **1b** (171 mg, 0.99 mmol), dissolved in methanol (130 mL), was irradiated with a HPL through a Pyrex filter under a nitrogen atmosphere for 1 h. The usual work-up gave a mixture, which was then separated using preparative thin-layer chromatography with a multiple-development technique to give **1b** (28 mg, 16%), a mixture (2:1) of **3a** and **3b** (47 mg, 27%), and **6** (10 mg, 5%), in addition to a mixture of **2a**, **5**, and **7** (78 mg, 33, 5, 6%, respectively). The latter was further separated by preparative VPC (column B, 145 °C: retention time; **7**, 4.4 min; **2a**, 7.0 min; **5**, 8.4 min). The spectroscopic data of **2a** and **5** were identical with those of the authentic sample reported by Swenton.[4] **3a** NMR ($CDCl_3$) δ=3.9 (1H, m), 4.0 (1H, m), 4.49 (1H, bd), 6.15 (1H, dd, *J*=2.7, 0.7 Hz), 6.42 (1H, dd, *J*=2.7, 0.7 Hz), 7.25—7.46 (4H, m). **3b** NMR ($CDCl_3$) δ=3.8 (1H, m), 4.0 (1H, m), 4.32 (1H, d, *J*=3.0 Hz), 6.28 (1H, d, *J*=2.7

TABLE 6. THE RELATIVE CONCENTRATIONS OF THE STARTING **1b** AND PRODUCTS AS ESTIMATED BY GLC DURING IRRADIATION[a)]

a) The relative recovery yields of **1b**.[b)]

Time min	Solvent					
	CH_3OH	CH_3CN	*t*-BuOH	CH_2Cl_2	C_6H_6	C_6H_{12}
2	—	86.8	—	81.8	80.0	89.9
4	—	77.5	—	72.3	61.3	82.9
5	93.2	74.6	89.2	—	54.5	—
6	—	70.7	—	62.5	51.1	76.9
9	—	60.6	—	56.7	39.2	66.3
12	—	50.4	—	46.1	33.5	57.8
15	70.8	41.4	57.5	37.3	31.9	47.5

b) The relative yields of **2a**.[b)]

Time min	Solvent					
	CH_3OH	CH_3CN	*t*-BuOH	CH_2Cl_2	C_6H_6	C_6H_{12}
2	—	10.5	—	5.1	12.0	1.0
4	—	16.0	—	10.3	23.1	1.6
5	3.8	17.8	4.3	—	21.6	—
6	—	18.4	—	14.0	29.2	3.0
9	—	25.4	—	14.2	32.5	5.1
12	—	32.5	—	15.6	35.4	5.0
15	9.8	37.5	7.5	15.0	30.2	6.6

c) The relative yields of **3a** and **3b**.[b)]

Time min	Solvent					
	CH_3OH	CH_3CN	*t*-BuOH	CH_2Cl_2	C_6H_6	C_6H_{12}
2	— (—)[c)]	1.9 (0.0)	— (—)	8.6 (12.8)	6.5 (7.7)	9.0 (0.0)
4	— (—)	3.85 (22.0)	— (—)	17.4 (16.7)	12.7 (7.9)	15.5 (0.0)
5	2.04 (24.5)	5.7 (26.3)	7.6 (14.5)	— (—)	14.3 (7.7)	— (—)
6	— (—)	7.3 (26.0)	— (—)	23.5 (13.6)	18.3 (9.3)	23.1 (0.0)
9	— (—)	11.3 (25.7)	— (—)	32.1 (12.5)	24.3 (8.2)	28.6 (0.0)
12	— (—)	14.2 (34.5)	— (—)	38.4 (15.4)	28.3 (7.1)	38.8 (0.0)
15	6.7 (34.3)	17.0 (28.2)	17.8 (14.6)	50.7 (13.2)	23.9 (8.4)	45.9 (0.0)

a) All data are calibrated with the data obtained concurrently in benzene. b) All irradiations were carried out in the same concentration (1.0 mmol dm^{-3}) of **1b**. The initial concentrations of **1b** are expressed as 100. c) The contents (%) of **3b** are shown in parentheses.

Hz), 6.52 (1H, d, J=2.7 Hz), 7.2—7.4 (4H, m). A mixture of **3a** and **3b** UV (95% C_2H_5OH) λ_{max}: 250.5, 266, 273 nm. Mass *m/e* (%): 167 (100, M$^+$), 166 (70), 141 (71), 140 (47). Found: C, 86.15; H, 5.43; N, 8.25%. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.45; N, 8.38%. **6** UV (95% C_2H_5OH) λ_{max} (log ε): 252 (4.14). IR ($CHCl_3$) ν_{max}: 3010, 2930, 2830, 2260, 1100 cm^{-1}. NMR ($CDCl_3$) δ=2.55 (1H, dddd, J=18.3, 9.3, 4.4, 2.2 Hz), 2.86 (1H, dtd, J=18.3, 5.4, 1.5 Hz), 3.43 (3H, s), 3.87 (1H, ddd, J=9.3, 5.4, 2.2 Hz), 4.21 (1H, d, J=2.2 Hz), 5.90 (1H, ddd, J=12.2, 5.4, 4.4 Hz), 6.51 (1H, ddd, J=12.2, 2.2, 1.5 Hz), 7.2—7.48 (4H, m). Mass *m/e* (%): 199 (76.2, M$^+$), 184 (14.4), 168 (100), 167 (74.4), 159 (15.8), 141 (39.0), 129 (39.6). Found: C, 78.24; H, 6.54; N, 6.86%. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%. **7** mp 41.5—42.5 °C. UV (95% C_2H_5OH) λ_{max}: 261.5, 267.5, 274 nm. IR (liq film) ν_{max}: 3050, 2920, 2840, 2250, 1483, 1270, 987, 778, 755 cm^{-1}. NMR (CCl_4) δ=3.0 (2H, m), 3.95 (1H, dd, J=10.0, 2.7 Hz), 6.25 (1H, dd, J=2.7, 1.0 Hz), 6.42 (1H, d, J=2.7 Hz), 7.0—7.5 (4H, m). Mass *m/e* (%): 168 (12.7), 167 (100, M$^+$), 166 (94), 141 (36.4), 140 (40.4), 139 (19.2).

*Identification of the Mixture of **3a** and **3b**.* Into a solution of a mixture of **3a** and **3b** (2:1, 31 mg, 0.19 mmol), dissolved in anhydrous ether (1 mL) and methanol (1 mL), we passed dry hydrogen chloride at 0 °C for 2.5 h. After stirring further for 1 h at room temperature, water (5 mL) was added slowly to the solution under cooling. After sweeping off the hydrogen chloride by passing nitrogen into the solution, the solution was filtered and the filtrate concentrated to a small volume. The residue was extracted with ether, and the ethereal extracts were washed successively with water and saturated brine, and then dried. The ether was evaporated, and the remaining crude product (30 mg) was purified by preparative TLC (10% ether–hexane) to give **3c** (20 mg, 53%) and **3d** (10 mg, 26%). The spectral data were identical with those of authentic samples of **3c** and **3d** described previously.[6] As a result, the structures of compounds **B** and **C** were established as **3a** and **3b** respectively.

*Photolysis of **1b** in Benzene.* A solution of **1b** (51 mg, 0.3 mmol), dissolved in benzene (11 mL), was irradiated externally for 4.8 h. The resulting solution was concentrated, and the residue (50 mg) was separated by preparative TLC (10% ether–hexane) to give **2a** (17.4 mg, 34%) and **3a** (11 mg, 21.5%). **3a** IR (liq film) $\nu_{\max}$: 3045, 2250, 1484, 1279, 830, 770, 740 cm^{-1}.

*Photolysis of a Mixture of **3a** and **3b** in Benzene.* A solution of a mixture (5 mg, 2:1) of **3a** and **3b** in benzene (11 mL) was irradiated externally for 2.5 h. The solution was then concentrated, and the residue (4.8 mg) was examined in terms of its NMR spectrum, which was found to be identical with that of the starting mixture.

*Photolysis of **3a** in Methanol.* A solution of **3a** (11 mg, 0.06 mmol), dissolved in methanol (11 mL), was irradiated externally for 3 h under ice cooling. After the evaporation of the solvent, the isolated material (8.4 mg) was examined in terms of its NMR spectrum. The spectrum revealed that it consists solely of **3a**.

*Kinetic Measurement of Photochemical Reaction of **1b**. Solvents*: The solvents used for photolysis were as follows. Methanol: The UV spectrum of a special-grade one was checked to confirm it to be transparent above 205 nm and was used without purification. Cyclohexane: A spectrophotometric grade of Merk's cyclohexane was used directly. Acetonitrile: A first-grade specimen was distilled over phosphoric pentoxide, then let stand over anhydrous potassium carbonate for more than one day, and distilled before use. Dichloromethane: A first-grade specimen was distilled over phosphoric pentoxide before use. Benzene: A first-grade substance was washed successively with concentrated sulfuric acid and water. This was dried over anhydrous calcium chloride and then distilled. After being dried over sodium wire, it was distilled before use. *t*-Butyl alcohol: A first-grade specimen was distilled over sodium before use.

Measurement: Each 1.0 mmol/dm^3 solution of **1b** was prepared in an appropriate solvent containing 0.10 mmol/dm^3 of hexadecane as an internal standard. Each test tube (ϕ1.5 cm × 16 cm) with a ground-glass male joint at the top was fitted with a cap made of female joint of the same size connected to a two-way cock and was then used for photolysis. Five of the tubes containing the same solution (5 mL) and two containing the benzene solution (5 mL) were arranged cylindrically in a circle (ϕ16.5 cm for short-period irradiation and ϕ11.5 cm for longer-period irradiation) at the same distance from the light source placed at the center (merry-go-round apparatus).[24] Before irradiation, purified nitrogen was passed through every solution for five minutes and the cocks were shut off. The photolysis was carried out with a high-pressure mercury lamp (UM-452) mounted in a quartz cooling jacket through a Pyrex filter under cooling (ice water; care must be taken not to keep the samples too cold; otherwise, they freeze). During irradiation, a test tube was taken out every definite number of minutes (see the text), and each 10 μL of the solution was examined by VPC (Column A, 130 °C; nitrogen-flow rate, 40 mL/min: retention time; hexadecane, 1.6 min; **7**, 3.2 min; **3a**, 3.6 min; **3b**, 4.15 min; **1b**, 4.8 min; **2a**, 5.0 min; **5**, 7.25 min). The product ratios were obtained by comparing the integrated curve areas as estimated using this equation: S = the height times the half-width of the curve. In some runs, uniform paper was cut into the curved areas, and their weights were compared. Both methods gave satisfactorily similar results within a 3% margin of error. The calibration curves for the pure samples, **1b**, **2a**, and **3a**, as separated by preparative VPC, was obtained similarly, and a linear relationship between the sample amounts and the integrated areas of the peaks was obtained. The ratio of the VPC intensities for **1b**, **2a**, and **3a** for samples of the same amount was 100:91:109 (including a 5% margin of error). As we could not obtain **3b** in the pure state, we assumed the intensity in VPC was the same as that of **3a**. The other materials in the product were not calibrated to their standards, but their VPC areas were directly compared with that of **1b**. Each datum was recalculated against that of the standard (hexadecane) as unity, and the two values were compared with each other. Two runs were carried out, one for a longer period of irradiation (up to 2 h) and the other for a shorter period of irradiation (up to 15 min). The results are summerized in Fig. 1 (longer-period irradiation) and Tables 2 and 6 (shorter-period irradiation).

This paper is dedicated to Emeritus Professor Takeo Sakan on the occasion of his 70th birthday. The authors wish to thank Dr. Yoshimasa Fukazawa of Tohoku University for valuable discussion and Mr. Jun-ichi Goda of our University for the elementary analysis.

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