A Comparative Study of Photoinduced Isomerizations between 1-*exo*- and 1-*endo*-Cyano-la,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes

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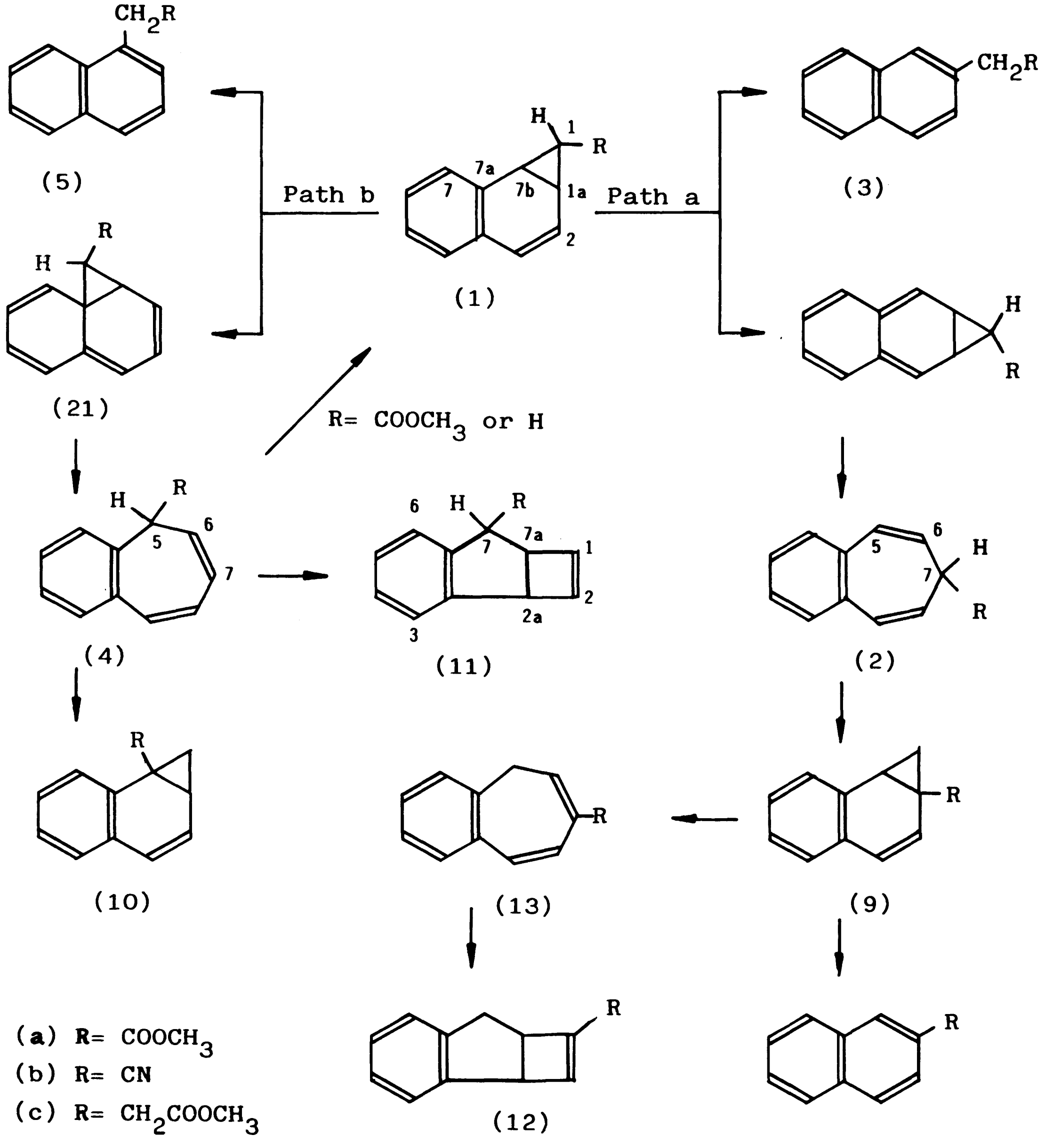
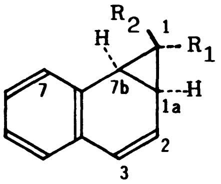
The titled compunds 1-*exo*-Cyano-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes(**8a**), 1-*endo*-Cyano-1a, 7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes(**8b**), were photolyzed in several solvents. The results were: (1) The isomerization proceeded faster in aprotic nonpolar solvents than in polar ones. (2) The 1-*endo* derivative (**8b**) rearranged faster than the 1-*exo*-isomer (**8a**). (3) **8b** was isomerized through Berson-Willcott rearrangement by the fission of bonds C_1–C_{7b} and C_1–C_{1a}, while **8a** gave 1-cyanomethylnaphthalene (**5b**) as a main product. (4) Examination with an optically active 1-*exo* derivative (**8a**) showed that the *exo*-*endo* interconversion occured by the simultaneous two centered (30%) and one centered (70%) epimerization.

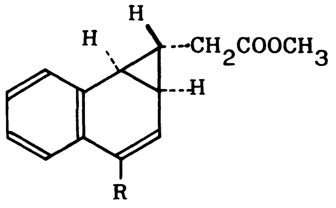
The photochemical isomerization of 1-substituted 1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalenes (**1**) had been found to proceed in two directions (Scheme 1):[1–6] The rearrangements by the fission of the C_1–C_{7b} bond (Path a) to give 7-substituted 7*H*-benzocycloheptenes (**2**) and 2-substituted naphthalenes (**3**) and by the fission of the C_1–C_{1a} bond (Path b) to give 5-substituted 5*H*-benzocycloheptenes (**4**) and 1-substituted naphthalenes (**5**), in addition to the secondary photoproducts originating from **2** and **4**. The difference in photochemical reactivities between 1-*endo* and 1-*exo* substituted derivatives of **1** had been studied in methanol with 1-methoxycarbonylmethyl-3-isopropyl-1a,7b-dihydro-1*H*-cyclopropa[a]naphthalene (**6**), which gave the same products in different proportions.[4] The results were in line with the stereochemical course of the re-



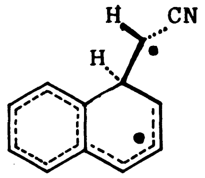
Scheme 1.



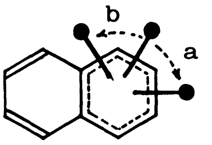
(7a) R_1= $COOCH_3$, R_2= H
(7b) R_1= H, R_2= $COOCH_3$
(8a) R_1= CN, R_2= H
(8b) R_1= H, R_2= CN



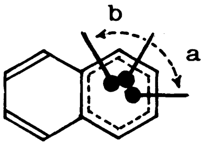
(6) R= i-Pr
(15) R= t-Bu
(16) R= H



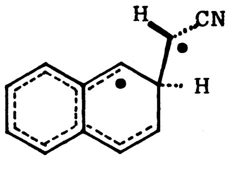
(14a)



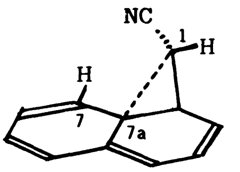
(18a)



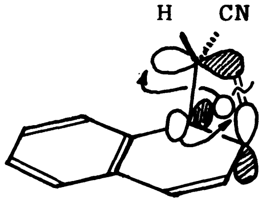
(18b)



(17a)



(19)



(20)

arangement established using optically active substrates.[3,5]

It is well known that the substitution with an electron-withdrawing group on the cyclopropane ring will have a strong affect on the bond strengths of the three membered ring under both ground and excited states.[7] Therefore, it was interesting to investigate the difference in photochemical reactivities between *exo* and *endo* isomers of 1-methoxycarbonyl- or 1-cyano-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene and to compare it with the photochemical behavior of *exo* and *endo* isomers of **6**. Swenton *et al.* found that when 1-deuterio-1-*exo*-methoxycarbonyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**7a**-1-d_1) was irradiated, though the typical products *via* path b were not detected, the deuterium atom on C_1 scrambled into the hydrogens on C_{1a} and C_{7b} of recovered **7a**,[2] which suggested that the rearrangement occurs in two directions. Later on, we reported that the direct irradiation at low temperature of 5-methoxycarbonyl-5*H*-benzocycloheptene (**4a**), which is assumed to be one of the primary photoproducts of the skeletal rearrangement of **7a**, gave exclusively 1-*endo*-methoxycarbonyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene(**7b**).[8] Beacause of the thermal instability of **7b** (facile Cope rearrangement),[8] comparison of the reactivities between exo and endo isomers of **7** was difficult.

Recently, the cyano derivatives (**8a** and **8b**) were obtained in stable crystalline forms,[6] therefore, we studied concurrently their photochemistry under direct irradiation in several solvents. The results were different from their isomerization under sensitized irradiation,[6] and also from the results obtained with **6**.[4]

Results

Irradiation of **8b** (*endo*) in benzene for 30 min resulted in a 94.3% recovery of the material. The mixture was composed of **8a** (yield, 2%), **8b** (35%), **9b** (11%),[10] **10b** (15%),[9] 7-cyano-[9] and 1-cyano-2a,7a-dihydro-7*H*-cyclobut[*a*]indene[9] (**11b**, 18%; **12b**, 8%). They were identified by direct comparison with the authentic samples obtained through direct irradiation of **4b**[9] and of 7-cyano-5*H*-benzocycloheptene (**13b**).[10]

The preparative photochemistry of **8a** has also been examined with an optically active isomer (see below) and **5b** was obtained as the main product, which was identical with an authentic sample prepared according to the known procedure.[11]

In order to uncover the effect of the solvent polarity on the product composition,[9] the rearrangement of **8a** and **8b** was carried out in several solvents. The results are shown in Table 1. It is observed that the rates for disappearance of **8a** and **8b** are faster in aprotic nonpolar solvents than in polar ones. In every solvent, **8b** was consumed somewhat faster than **8a** and,

Table 1. Photochemical reactions of **8a** and **8b** in various solvents

a) in Methanol

Irradiation time/h	Compounds[a]									
From **8a**	**8**[b]	**11b**	**12b**	**4b**	**10b**	**9b**	**5b**	A[c,d]	B[c,d]	C[c,d]
1	92.6	0.0	0.0	0.0	0.0	0.6	6.0	0.34	—	—
2	80.0	1.05	0.95	1.4	1.3	3.4	8.9	0.35	0.70	0.86
3	70.7	1.05	1.35	1.1	1.3	4.6	13.4	0.35	0.80	0.58
4	67.4	1.8	1.8	1.6	2.6	6.0	16.5	0.35	0.73	0.77
5	59.0	2.25	2.55	2.1	3.3	8.6	19.4	0.41	0.72	0.68
							mean[d]	0.37	0.74	0.72
From **8b**										
1	82.5	1.8	0.4	6.2	4.4	3.1	0.0	0.28		
2	72.2	3.6	1.9	6.8	7.2	5.7	0.0	0.43		
3	61.9	6.9	2.1	5.6	11.2	9.0	0.0	0.47		
4	51.7	11.3	3.4	3.8	14.3	11.7	0.0	0.52		
5	41.7	18.9	3.7	3.0	18.2	13.2	0.0	0.42		
							mean	0.46		
b) in Acetonitrile										
From **8a**	**8**	**11b**	**12b**	**4b**	**10b**	**9b**	**5b**	A[c,d]	B[c,d]	C[c,d]
1	86.9	1.2	0.3	0.5	1.0	2.3	7.0	0.27		
2	78.3	1.3	1.0	0.7	1.9	5.1	10.7	0.42	0.73	0.64
3	73.7	2.3	1.3	0.8	2.8	6.0	12.5	0.35	0.68	0.81
4	64.7	3.1	2.0	1.2	4.0	9.0	13.7	0.50	0.62	0.81
5	59.5	4.6	2.7	1.2	5.6	10.8	14.5	0.52	0.56	0.85
							mean	0.45	0.65	0.78
From **8b**										
1	78.7	3.9	1.2	1.7	6.9	5.3	0.0	0.52		
2	67.7	6.0	2.3	1.2	10.8	9.1	0.0	0.63		
3	59.4	7.3	2.3	0.8	13.7	12.4	0.0	0.67		
4	51.7	10.4	3.5	0.0	16.7	12.4	0.0	0.59		
5	41.9	12.4	4.7	0.0	17.7	16.2	0.0	0.69		
							mean	0.65		
c) in *t*-Butyl alcohol										
From **8a**	**8**	**11b**	**12b**	**4b**	**10b**	**9b**	**5b**	A[c,d]	B[c,d]	C[c,d]
1	86.7	1.2	0.4	1.4	0.8	2.6	6.7	0.30	—	—
2	78.6	2.1	1.1	1.6	1.3	5.0	10.2	0.40	0.67	0.82
3	72.1	3.5	1.7	1.5	1.6	5.2	13.7	0.34	0.67	0.95
4	63.1	5.2	2.7	1.6	2.6	7.1	17.0	0.37	0.64	0.96
5	59.5	6.2	2.9	1.6	3.3	7.8	18.0	0.37	0.62	1.04
							mean	0.37	0.65	0.94
From **8b**										
1	80.4	5.0	1.3	5.1	3.0	4.4	0.0	0.44		
2	70.3	9.1	1.9	5.2	4.8	7.3	0.0	0.48		
3	62.5	15.3	3.7	4.9	10.5	10.5	0.0	0.46		
4	49.5	17.6	4.6	3.5	10.2	11.2	0.0	0.50		
5	44.9	21.6	5.3	2.6	10.3	10.8	0.0	0.47		
							mean	0.48		
d) in Benzene										
From **8a**	**8**	**11b**	**12b**	**4b**	**10b**	**9b**	**5b**	A[c,d]	B[c,d]	C[c,d]
1	72.2	2.9	1.4	1.0	2.7	6.0	12.1	0.40	—	—
2	58.4	4.1	2.9	1.1	4.1	9.4	19.2	0.43	0.67	0.76
3	46.3	6.1	4.8	0.0	5.0	12.3	23.6	0.49	0.68	0.65
4	38.3	6.3	6.8	0.0	5.6	13.5	27.3	0.51	0.70	0.59
5	32.9	8.6	7.4	0.0	5.5	15.3	27.6	0.54	0.66	0.62
							mean	0.49	0.68	0.66

From **8b**

1	72.1	9.7	2.4	1.2	9.9	2.2	0.0	0.22
2	52.1	13.8	3.9	1.1	14.2	9.6	0.0	0.46
3	39.8	17.9	6.4	0.0	18.5	11.6	0.0	0.49
4	31.7	19.8	8.8	0.0	19.0	11.7	0.0	0.52
5	22.2	23.3	10.7	0.0	19.2	13.3	0.0	0.56
							mean	0.51

e) in Cyclohexane

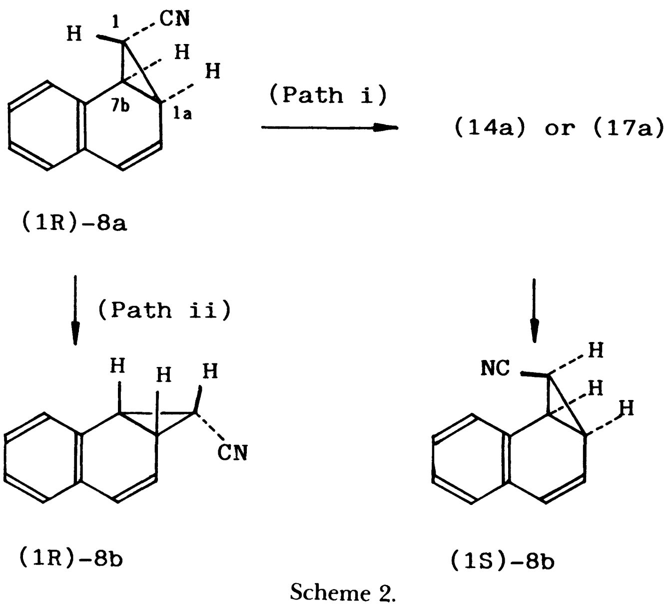
From **8a**	**8**	**11b**	**12b**	**4b**	**10b**	**9b**	**5b**	$\mathbf{A}^{c,d)}$	$\mathbf{B}^{c,d)}$	$\mathbf{C}^{c,d)}$
1	78.1	4.0	1.9	1.5	0.6	4.4	8.6	0.43	—	—
2	65.5	7.3	3.7	2.0	1.0	6.7	12.9	0.45	0.56	1.00
3	58.3	10.0	4.3	1.8	1.6	8.3	14.5	0.45	0.52	1.1
4	48.1	13.4	5.8	2.1	1.9	10.0	17.3	0.46	0.50	1.1
5	43.5	16.9	6.7	1.6	1.6	10.9	19.8	0.44	0.50	1.1
							mean	0.45	0.52	1.1
From **8b**										
1	77.5	10.0	2.5	3.3	2.0	4.1	0.0	0.43		
2	63.2	18.2	4.2	3.2	3.2	6.8	0.0	0.45		
3	51.0	25.9	5.4	2.7	3.9	7.5	0.0	0.40		
4	44.2	32.0	6.1	1.9	4.6	8.2	0.0	0.37		
5	32.9	34.4	9.4	1.9	5.2	11.5	0.0	0.50		
							mean	0.43		

a) The concentrations of **8a** and **8b** were kept constant throughout and their initial concentration was set equal to 100. All figures are normalized to those obtained in benzene. b) Compounds **8a** and **8b** were not distinguishable by GLC because of their thermal interconversion. c) Following product ratios are shown as **A**, **B**, and **C**: **A**=(**9b**+**12b**)/(**4b**+**10b**+**11b**+**5b**); **B**=**5b**/(**4b**+**10b**+**11b**+**5b**); **C**=(**4b**+**10b**+**11b**)/(**9b**+**12b**). d) To calculate the mean values of **A**, **B**, and **C**, the data of 1h-irradiation were omitted, where some of the products were formed in small amounts, hence, the margins of the error in **A**, **B**, and **C** seemed to be large.

although **5b** was not detected in the products from **8b**, it was the main product from **8a**.

Discussion

It was found that, in every solvent studied, **8a** produced **5b** in the largest quantity along with **9b** and **11b**, while **8b** gives mainly **11b** and **10b** (or **9b**). Dissimilar to the results of the direct irradiation of *exo*-**6** and *endo*-**6**,[4] the *exo*-*endo* interconversions of **8** were found to occur during irradiation, though the rates were very slow. To test the mechanism of the isomerization from **8a** to **8b** under direct irradiation, (+)-(1R)-**8a** ($[\alpha]_D$ +103°) was photolyzed in benzene and the following compounds were isolated: **8b** (6%, $[\alpha]_D$ +259° ±40°), **9b** (13%), and **3b** (19%), in addition to the recovered **8a** (48%, $[\alpha]_D$ +94.2°±2°). This result indicates that the racemization of the starting material was 8.6±0.2% and the retention of optical activity for isomerization of **8a** was 45±7%. Thus, it is estimated that the one-centered epimerization (Scheme 2, Path i) in (1R)-**8a** was contaminated with the two-centered epimerization (Path ii) to an extent of 30%. This result was quite different from that under sensitized irradiation where the very fast one-centered epimerization was observed.[6] Under the sensitized conditions, a triplet biradical species (**14a**) could solely be the convincing intermediate, and hence no racemization of both carbon centers C_{1a} and C_{7b} was observed.



Scheme 2.

In order to discover if **5b** was formed through a biradical intermediate derived from **8a**, **8a** was irradiated in the presence of tributyltin hydride, a good hydrogen donor,[12] or dideuterium selenide, a trapping agent.[13] In the presence of tributyltin hydride, however, no product other than those produced in the absence of these addenda was observed. In the presence of dideuterium selenide, neither was any deuterium incorporated into **5b**. These observations, in conjunction with the formation of **5b** even in benzene,[14] show that the isomerization of **8a** would occur either through a biradical in a solvent cage with a life-time too short to be trapped with such reagents or through an intramolecular concerted process which leads directly to **5b**. Such a process has been argued by

Lambert and Laarhoven in the photochemical di-π-methane rearrangement.[15]

As mentioned above, **6**, **15**, and **16** were found to rearrange in a concerted manner with inversion of the C-1 configuration in two directions, and a series of the rearrangement products following them has been established (Scheme 1).[3–5] Based on this knowledge, it is apparent that compounds **10b** and **11b** are formed *via* **4b** and compounds **9b** and **12b** *via* **2b**.[16] The process might proceed *via* an excited singlet state of **8a**, which will make bond reorganization follow either path a or path b to give **2b** and **4b**, respectively. It is possible that the rearrangement goes through a transient singlet biradical species such as **14a**.

Zimmerman introduced the K concept for predicting the multiplicity control of the di-π-methane rearrangement of 1,1,2,2-tetraphenyl-5,5-bis(methoxycarbonyl)-1,4-pentadiene and made a number of generalization to estimate the relative magnitude of K for different excited transition states or species.[17] A small K reaction is preferred by the singlet and the large K reaction is preferrd by the triplet species. In the generalization he proposed: "(1) Pericyclic reactions tend to have small *K*'s. (2) Biradical species with electron-withdrawing group on biradical centers have diminished *K*'s." According to his proposal, thus, transient biradical species such as **14** and **17** may possibly be in their singlet excited states if the transformation is not the concerted process. Sensitized irradiation *via* triplet states gave rise to different results.[6]

The schematic bird's eye-view of the movement of the exo-substituent on C-1 is shown in **18a** while that of the endo-substituent on C-1 in **18b**, where the ring carbons of **8** lie in a plane of the paper. The bonds to the substituents, H and CN, attached to C-1 are projected on the plane and are shown with a rod having a blackened circle at the end, which expresses a cyano group. The C-1 atom and the bonds from C-1 to the ring carbons are omitted. As the least-motion process should be energetically more favorable than the other,[18] the excited *endo*-isomer (**8b**) is expected to react toward both sides faster than the excited *exo*-isomer (**8a**). This trend is seen in all solvents, but especially in polar solvents. Thus, from Table 1, it is observed that the rates for the isomerization of **8a** and **8b** in several solvents stand in the decreasing order of: benzene, cyclohexane, acetonitrile, and *t*-butyl alcohol=methanol. This fact suggests that the transition state of this reaction would not be a polar one.

Similarities in the ratios (**A**) of the proportion of path a products (**9b**+**12b**) to that of path b products (**4b**+**10b**+**11b**+**5b**) in aprotic nonpolar solvents are observed on irradiation of **8a** and **8b** (in benzene, 0.50±0.01; in cyclohexane, 0.43±0.01). As compound **5b** is not formed from **8b**, **5b** must be formed from **8a** in compensation for the formations of **4b**, **10b**, and **11b**. The rates of the formation of **5b** are similar in every solvent, except in benzene. The values (**C**) of (**4b**+**10b**+ **11b**)/(**9b**+**12b**) for **8a** may be used as a criterium for how the path b is affected by solvents. The retardation (%) of the reaction through path b compared to that through path a in various solvents is obtained using cyclohexane as a standard: methanol (33%), acetonitrile (27%), *t*-butyl alcohol (12%), benzene (38%), and cyclohexane (0%). In accordance with these data, the molar fraction (**B**) of **5b** in path b products in methanol was found to be the highest (0.74±0.05), and in cyclohexane the lowest (0.52±0.04). The values for the other solvents were approximately the same (0.66±0.05). These facts may be explained as follows. The solvation of the cyano group in **8a** will not be specifically hindered. In the movement of the *exo*-substituent (**18a**), the molecule seems not to alter any solvation energy along path a, but the movement in path b resulted in the loss of the solvation energy by the interference of the substituent with a hydrogen on C-7. Thus the pathway b (**4b**+**5b**+**10b**+**11b**) will be more or less unfavorable compared to path a (**9b**+**12b**).[9] In **18b**, though one side facing the 6-membered ring is severly blocked to solvation, the degree of solvation is not much altered along both pathways a and b. The interaction of C_7-H with the solvated cyano group and the loss of solvation energy in **19** will raise the energy barrier for symmetry allowed excited Berson-Willcott rearrangement. The situation for solvation of **5b** would not differ from that of **8a**. Therefore, the molecular portion *via* the 1,2-hydrogen shift to **5b** will increase among the molecules following path b. The 1,2-hydrogen shift may also be the symmetry-allowed [$\sigma 2_a + \sigma 2_a$] in the excited state; the orbitals involved are shown in **20**.

A considerable rate acceleration and anomalies for the photoreaction of **8a** and **8b** were observed in benzene compared with the data in the other solvents studied. Similar phenomena had been observed for the photoreaction of **4b**.[9] The reason for the accleration in benzene is still unclear.

Orbital Symmetry Considerations. In order to obtain knowledge about the polarity signs of the lobes for the frontier orbitals during the Berson-Willcott rearrangement, we calculated some phases of the electronic states during the rearrangement of **1** (R=H) to 1,1a-dihydro-1*H*-cyclopropa[*a*]naphthalene (**21**; R=H) making use of the extended Hückel M. O. calculations.[19] The molecular geometry of norcaradiene was taken from the X-ray crystallographic analysis data of 2,5-dimethyl-7,7-dicyanobicyclo[4.1.0]hepta-2,4-diene[20] with some modifications of the double bond to that of a benzene ring (1.43 Å). In line with the Woodward-Hoffmann rule, the C-1 orbital-lobe of the HOMO at the half way of the rearrangement in 120° mechanism[4] comes near the C-7a orbital-lobe of the same mathematical sign (bonding; allowed), while that of the LUMO comes near the opposite sign of C-7a orbital-lobe (*anti*-bonding; forbidden). On the other hand, the C-1

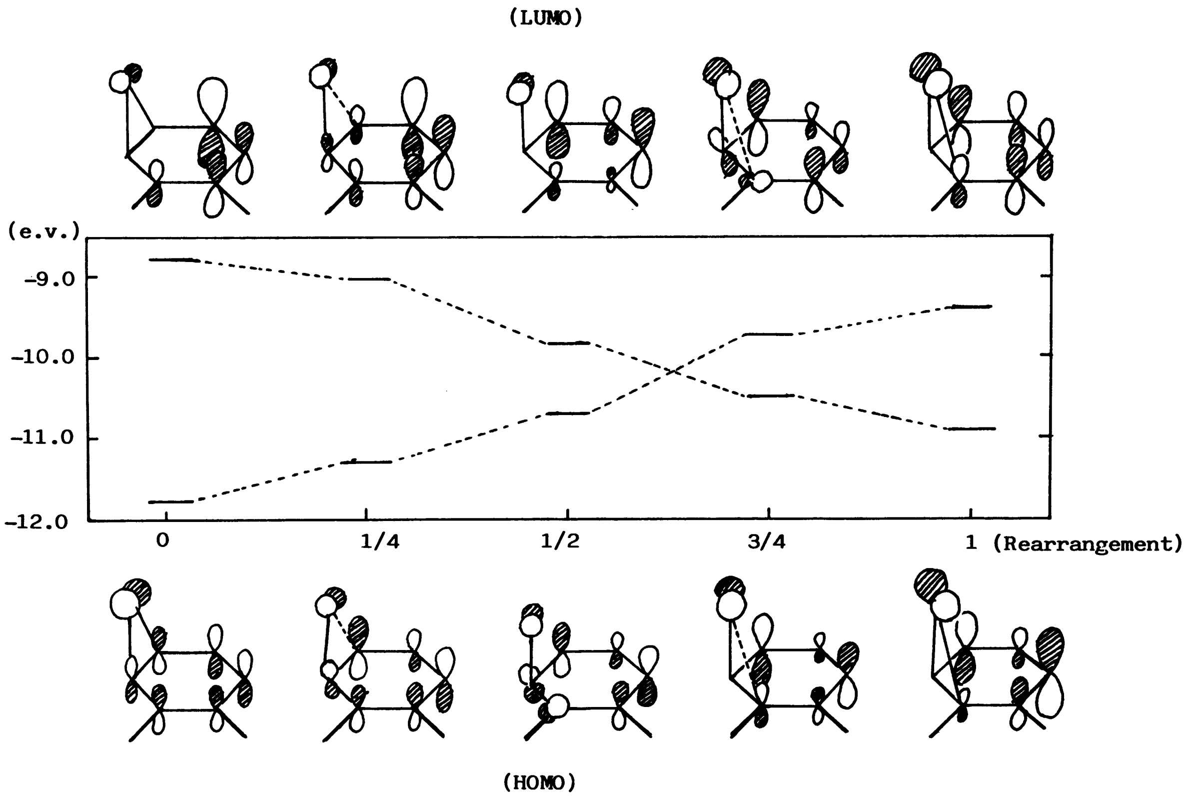


Fig. 1. The schematic orbital-lobes with their polarity signs and the corresponding orbital energy levels of the HOMO and the LUMO during rearrangement of 1 in the 60° mechanism.

orbital-lobe of the LUMO at the half way in 60° mechanism[4] comes near the C-7a orbital-lobe of the same sign (bonding; allowed). The schematic orbital-lobes with their polality signs and the corresponding orbital energy levels of the HOMO and the LUMO during rearrangement in 60° mechanism, calculated at the stages of the start, 1/4, 1/2, 3/4, and the complete rearrangements, are shown in Fig. 1. It is interesting to see that the LUMO (or HOMO) of the starting material is linked continuously with the HOMO (or LUMO) of **21** (R=H) in the polarity sings and their rough sizes of orbitals. The difference in the energy levels between the HOMO and the LUMO becomes smallest near the half way of the rerrangement. Though the calculations are classical, the rearrangement in the 60° mechanism would be photochemically allowed in the excited states, therefore, may proceed in a concerted manner.

Experimental

General Procedure. IR and ^{1}H-NMR were recorded according to the method given in the previous paper.[6,9] A Shimadzu Gas Chromatograph GC-4BM was used for the analytical purposes (Hydrogen ion flame detector). The column used was ϕ3.5 mm×1.0 m column charged with 3% Silicone OV-17 on Chromosorb WAW. For preparative column chromatography under medium pressure, a silica gel column (Merck Kiesegel 60, 230—400 mesh; ϕ8.2×500 mm) equipped with a F.M.I. pump (type RP-SY-1CSC) was used. For irradiation on a preparative scale, a solution charged in a vessel fitted with a Pyrex cooling jacket was purged with dry nitrogen for five min and internally irradiated with an Ushio High Pressure mercury lamp (HPL) (UM-452). The characterization of compounds, **4b**, **8a**, **8b**, **9b**, **10b**, **11b**, and **12b** had been reported previously.[1,2,8,9] In this experiment, the IR and NMR spectra, and the GLC retention times were compared with those of authentic specimens.

Irradiation of Racemic **8b**. Racemic **8b** (54.8 mg; 0.33 mmol) dissolved in anhydrous benzene (40 mL) was irradiated internally with a HPL (UM-102) under ice-water cooling for 30 min. After evaporation of the solvent, the residue taken in benzene was filtered through a short column of silica gel (10 g) and the product chromatographed on 23 g of silica gel using 10% ether-hexane as solvent under medium pressure (1.2 atm). The products were **8a** (1.1 mg; 2%), **8b** (19.1 mg; 35%), **10b** (8.4 mg; 15%), **11b** (9.7 mg; 18%), **9b** (6.1 mg; 11%), and **12b** (4.3 mg; 8%). The ^{1}H NMR spectra of **10b** and **11b** were identical with those of the reported ones[9] and those of **9b** and **12b** were identical with the ones obtained by the photolysis of **13b**.[1,2] **9b**: NMR ($CDCl_3$) δ=0.43 (1H, d,d, J=4.4, 6.4 Hz), 2.12 (1H, d,d, J=9.7, 4.4 Hz), 3.9 (1H, bd, 6.4, 9.7 Hz), 6.19 and 6.39 (2H, AB type, J=9.8 Hz), 7.1—7.4 ppm (Ar-H). **12b**: NMR ($CDCl_3$) δ=3.02—3.28 (2H, m), 4.37 (1H, b), 7.02 (1H, bs), 7.1—7.3 ppm (Ar-H). **5b**: NMR ($CDCl_3$) δ=4.13 (2H, s), 7.4—7.65 (4H, m), 7.8—7.95 (3H, m). The GLC retention times (min) for them were also coincident with those of authentic specimens: Column temperature, 150 °C; hydrogen flow rate, 30 mL min^{-1}; retention times: **11b**, 4.3 min; **12b**, 4.6 min; **10b**, 5.8 min; **9b**, 6.2 min; **8**, 9.4 min.

Irradiation of Optically Active **8a**. Optically active **8a** ([α]$_D$ +103°; 54.7 mg, 0.33 mmol) dissolved in anhydrous benzene (40 mL) was irradiated as described above. The products were **8a** (26.2 mg; 48%), **8b** (3.0 mg; 6%), **9b** (7.4 mg; 14%), and **5b**[11] (10.5 mg; 19%). The recovered **8a** and **8b** were further purified by column chromatography under medium pressure (10% ether-hexane as an eluent): **8a** ($[\alpha]_D^{30}$ +94.2° (c=0.12 (CH_3OH)); **8b** ($[\alpha]_D^{31.5}$ +259° (c=0.15 (CH_3OH)).

*Irradiation of **8a** in the Presence of Tributyltin Hydride.* **8a** (116 mg; 0.69 mmol) and hexadecane (24 mg; 0.11 mmol) were dissolved in anhydrous benzene and made up to 100 mL solution. This solution was divided into three portions; 40 mL, 30 mL, and 30 mL. To these solutions, tributyltin hydride (53% in tributyltin chloride) was added in the amounts of 1.51 g (10 mol-equivalent to **8a**), 619 mg (5.5 mol-equivalent), 227 mg (2 mol-equivalent), respectively. They were irradiated independently with a HPL (UM-102) for 30 min. The peak areas of the products analyzed by GLC were as follows: for 10 mol-equivalent of the hydride; **8**:**9b**:**5b**= 58:9:15.5; for 5.5 mol-equivalent; **8**:**9b**:**5b**=61:8.8: 13.0; for 2.0 mol-equivalent; **8**:**9b**:**5b**=59:9:15.3. (The data were obtained by taking the initial amount of **8a** as 100 and normalizing with the peak of hexadecane as constant).

*Irradiation of **8a** in the Presence of Dideuterium Selenide.* To **8a** (56 mg; 0.33 mmol) dissolved in anhydrous benzene (15 mL) was added a solution of dideuterium selenide[21] in anhydrous benzene (1.75 mmol/25 mL) and the mixture was irradiated internally as above for 30 min. After irradiation (no precipitation of selenium was observed), the benzene solution was washed successively with 1 M aq sodium hydroxide (2 mL×2), water, saturated brine, and dried. Separation of the products by column chromatography gave **8b** (7 mg) and a mixture (41 mg) of **8a**, **9b**, and **5b**. Careful examination of ^1H NMR spectrum of the latter on the peak areas at 4.13 and 7.8—7.95 ppm for benzylic and α-protons of **5b**, respectively, shows that the resultant **5b** was not contaminated by more than 5% of the deuterated **5b**.

*Comparison of the Photoreaction of **8a** and **8b**.* The solvents used for photolysis were purified as reported earlier.[9] Methanol, *t*-butyl alcohol, acetonitrile, benzene, and cyclohexane were used as solvents. Each 1.0 mmol dm^{-3} solution of **8a** or **8b** was prepared in an appropriate solvent containing 0.10 mmol dm^{-3} of hexadecane as an internal standard. The photochemical reactions were carried out with the same technique (merry-go-round apparatus) described before.[9] Five tubes containing the same solution (5 mL) to be examined and two containing the benzene solution (5 mL) were photolyzed at the same time with a high pressure mercury lamp (UM-452) through a Pyrex filter under cooling (ice-water). During the irradiation, the test tube was taken out every one hour and each of 10 μL of the solution was examined by GLC with temperature programing (100 °C to 150 °C; 5 °C min^{-1}). The retention times of the products were as follows: Hexadecane, 9.1 min; **11b**, 12.3 min; **12b**, 13.1 min; **4b**, 13.9 min; **10b**, 14.3 min; **9b**, 14.7 min; **8**, 19.0 min; **5b**, 21 min. Each relative area of each peak was normalized to the area of the hexadecane and the data for each solvent were adjusted to the data obtained in benzene. The data in all solvents studied are listed in Table 1. No calibrations were made for each product because the use of a temperature programing technique might make the margin of error significant large. However, it may be said that the margin of error will be within 20% among different compounds and within 5% among the same compounds.

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