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Photochemical Reactions of Aromatic Compounds. XXXIII.[1] Photoreactions of 1-Cyanonaphthalene with Indene in Various Solvents

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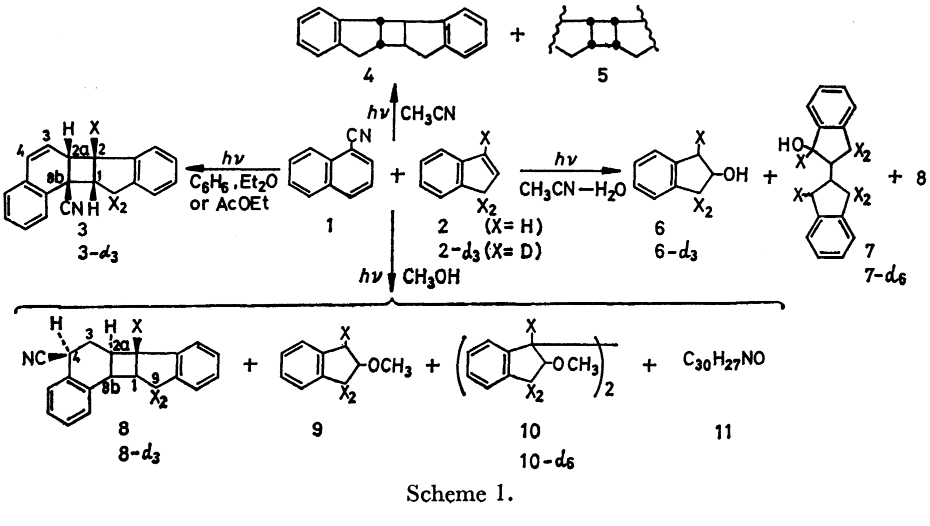
The stereospecific photocycloaddition of 1-cyanonaphthalene to indene occured in cyclohexane, benzene, diethyl ether, tetrahydrofuran, and ethyl acetate, giving the *endo* head-to-head cycloadduct as the sole 1 : 1-adduct. The mechanism was discussed in terms of the exciplex intermediacy. In methanol or in acetonitrile in the presence of water, the photoreaction gave the dihydrocycloadduct (**8**), accompanied by the formation of 2-methoxyindan and 2,2′-dimethoxy-1,1′-biindanyl or 2-indanol and 1-hydroxy-2,2′-biindanyl. In these solvents, the reactions were suggested to be initiated by photochemical electron transfer; the methoxylated or hydroxylated compounds are formed by the nucleophilic attack of methanol or water on the indene cation. Anionic species, including the 1-cyanonaphthalene anion, were suggested to play important roles in the formation of **8**.

Photocycloadditions of aromatic nitriles to furan and olefinic compounds have been extensively investigated with regard to the chemistry of exciplexes.[2,3] The photoreactions more or less depend on the solvent polarity[2a,b,e,f,i,3b,4] and, in a few cases, afford other products in polar solvents which arise from ion radicals.[2f,4] Solvent effects on the photophysics of typical exciplexes have been well documented,[5] and the dissociation into ion radicals has been confirmed to occur in polar solvents.[5,6] The irradiation of exciplex-formation systems in very polar solvents can thus provide a convenient method for the generation of ion radicals, and synthetic applications have been increasingly reported in recent years.[7-9] However, the formation of the final products must compass complex reaction pathways since there independently or concurrently participate such various reaction intermediates as exciplexes, ion-pairs, cation radicals, anion radicals, and free radicals. For example, the photochemical *anti*-Markownikoff addition of methanol to an aromatic olefin in the presence of an electron acceptor includes, at least, a photochemical electron transfer from the olefin to the electron acceptor, the nucleophilic attack of methanol on the cation radical of the olefin, and the reduction of the methoxylated radical by the anion radical of the electron acceptor.[9] Moreover, electron acceptors which are usually aromatic nitriles are more or less consumed by unreclaimed reactions, and the products have not been fully characterized. Thus, the features of the photoreactions of exciplex-formation systems in polar solvents would often vary from system to system. During the course of our investigation of the photoreactions of aromatic nitriles with furan and olefinic compounds, we have found that the photoreactions of 1-cyanonaphthalene (**1**) with indene (**2**) depends not only on the solvent polarity, but also on the nature of the solvent, as is shown in Scheme 1, and that a novel type of photocycloaddition occurs in polar protic media to give a reduced cycloadduct (**8**), which is formed *via* the anionic species of **1**.

Results

Photoreaction in Less Polar Solvents. The irradiation of **1** and **2** in benzene through Pyrex with a high-pressure mercury arc at an ambient temperature gave **3** as the exclusive 1 : 1-adduct, accompanied by small amounts of indene dimers, though over-irradiation resulted in the formation of complex mixtures. Similar results were obtained in the photoreactions of cyclohexane, diethyl ether, tetrahydrofuran, and ethyl acetate solutions. Isomers of **3** could neither be detected



Scheme 1.

by the GLC of the photolysate nor by the NMR of a crude product which had been obtained by passing a photolysate through a short column of silica gel to remove indene dimers and polymeric materials.

The structure of **3** was indicated by its elemental composition and the spectral properties. The ^{1}H NMR spectrum consisted of two sets of double doublets for C_9-methylene protons, two sets of multiplets for H-1 and H-2a, a triplet for H-2, a doublet of doublets for H-3, a doublet for H-4, and multiplets for aromatic protons. Since the signal for H-2 appears as a triplet, **3** can be identified as a head-to-tail adduct. This assignment was further confirmed by the NMR spectrum of **3**-d_3; this compound was obtained by the photocycloaddition of **1** to indene-1,1,3-d_3 (**2**-d_3). It showed a broad singlet for H-1 and a broad doublet for H-2a at positions identical to those of the respective centers of the two sets of multiplets for **3**, while the olefinic and aromatic resonances were essentially identical to those for **3** in all respects.

The *endo*-configuration for **3** was suggested by the unusually high chemical shifts of the olefinic protons and an aromatic proton; the olefinic protons show upfield shifts of more than 0.34 and 0.27 ppm relative to the corresponding protons of similar compounds.[2b,h-j,3a,b,10] Similarly, the aromatic proton is considerably shielded (more than 0.2 ppm). The shielding effects on the protons can be reasonably understood by means of molecular models with the *endo*-configuration; the benzene ring of the indan moiety is located just over the olefinic protons and the aromatic proton of the indan moiety extends over the edge of the other benzene ring. On the other hand, the shielding effects can not be expected from the *exo*-configuration.

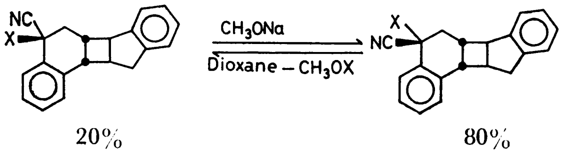
Photoreaction in Acetonitrile in the Presence of Water. The irradiation of an acetonitrile solution of **1** and **2** gave an *anti* head-to-head cyclobutane dimer, **4**, in a 50% yield, accompanied by only small amounts of **3** and the *syn* head-to-head cyclobutane dimer, **5**, whereas 70% of the **1** was recovered. Control experiments using 313 nm light, where **1** absorbed mostly the incident light, showed that **4** and **5** were formed in a 95: 5 ratio, while the head-to-tail dimers could not be detected.

The formation of the indene dimers was remarkably "quenched" by water. In the presence of 10 vol% of water we obtained 2-indanol, **6**, 1-hydroxy-2,2′-biindanyl, **7**, and a new cycloadduct, **8** in 58%, 23%, and 25% yields respectively, while the indene dimers were not formed. The structure of **6** was unambiguously determined by a direct comparison with an authentic sample prepared by the reduction of 2-indanone[11] with sodium borohydride.

The structure of **7** was deduced from the spectral properties. The NMR spectrum showed a broad triplet for H-1, a broad doublet for O–H, and complex signals for the other aliphatic protons and aromatic protons. On the addition of deuterium oxide, the broad doublet disappeared along with a collapse of the broad triplet into a sharp doublet. The NMR spectrum of **7**-d_6 showed a broad singlet for O–H at δ 1.7, a broad doublet for H-2 at δ 2.3, an asymmetrical broad triplet for H-2′ at δ 2.46, and two sets of doublets with small splittings for H-1′ at δ 2.86—3.24, clearly supporting the structure assigned. Probably, H-1′ is located in either a *cis* or *trans*-relationship with H-2′.

The mass spectrum of **8** which showed a very weak molecular ion peak at *m/e* 271 and strong fragment-ion peaks at *m/e* 116 and 155, indicates that **8** is a dihydro-adduct of **1** and **2**. The ^{1}H NMR spectrum consisted of signals for nine aliphatic protons and eight aromatic protons, but showed none for olefinic protons. Each signal for the aliphatic protons was resolved by means of extensive double-irradiation experiments, lanthanoid-induced shifts (LIS), and deuterium-labelling experiments. The data are listed in Table 1. For example, the doublet of doublets at δ 3.64 can easily be assigned to the signal for the proton (H-4) attached to cyanated carbon, since this signal showed the largest shift downfield on the addition of Eu(fod)$_3$ and since this signal was absent in the spectrum of **8**-*d*; this compound was obtained by refluxing a dioxane–methanol-*O*-*d* solution of **8** in the presence of sodium methoxide.

In the NMR spectrum of **8**-d_3, the signal for H-8b appeared as a broad triplet, demonstrating that **8** is a head-to-tail adduct. The *cis*-relationship between H-2a and H-4 was deduced from the vicinal couplings with H-3A (one of the C-3 methylene protons); the coupling constants are very similar to those of the axial-axial couplings for cyclohexane compounds.[12] When a solution of **8** in dioxane–methanol was refluxed in the presence of sodium methoxide, an equilibrium mixture



20% **8** (X=H) **8**-*d* (X=D)

80% **12** (X=H) **12**-*d* (X=D)

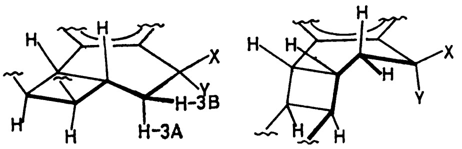
TABLE 1. ^{1}H NMR SPECTRAL DATA FOR **8** AND **12**[a)]

Compd	Chemical shifts (ppm in $CDCl_3$) (multiplicities)									Coupling constants/Hz
	H-1	H-2	H-2a	H-3A	H-3B	H-4	H-8b	H-9	H-9	
8	3.4—3.8	4.1	2.9—3.2	1.16	2.0	3.64	3.94	2.7	3.1	$J_{3A,2a}=J_{3A,3B}=J_{3A,4}=13.0$
	(m)	(t)	(m)	(q)	(d-d-d)	(d-d)	(t)	(d-d)	(d-d)	$J_{3B,2a}=7.0, J_{3B,4}=3.0$
LIS[b)]	3.6—4.0	4.3	3.3—3.6	1.82	2.68	4.82	4.22	2.95	3.2	$J_{1,8b}=J_{2a,8b}=9.0$
12	3.2—3.8	4.1	3.2—3.4	1.3—2.0		3.0	4.0	2.44	2.9	$J_{3A,4}=7.5, J_{3B,4}=5.0$
	(m)	(t)	(m)	(m)		(d-d)	(t)	(d-d)	(d-d)	$J_{3A2a}=5.0, J_{3B,2a}=6.5$

a) Aromatic signals (δ 6.9—7.5) are omitted. b) 0.4 equiv of Eu(fod)$_3$ added.

of **8** and **12** was obtained in a 1 : 4 ratio, clearly demonstrating that **8** is thermodynamically less stable than **12**.

For **8**, the half-chair conformation (A) would be much more favorable than the negative half-chair conformation (B) because of the steric repulsion between the cyano group and the cyclobutane ring. In fact, the vicinal coupling constants of H-3A and H-3B are very similar to those of the axial-axial and axial-equatorial couplings for cyclohexane compounds respectively. Similarly, the B conformer or, more probably, an equilibrium mixture of A and B would be favorable for **12**. With the *endo*-structure, however, B is extremely unstable because of the nonbonding interaction between H-4 and the benzene ring of the indan moiety, since the closest separation between them is only 1.8—2.0 Å, as is shown by the molecular models. If **8** and **12** had this structure, **8** could be expected to be more stable than **12**. Therefore, this structure can not be accepted. On the other hand, **12** can exist in either A or B with the *exo*-configuration; it is thus more stable than **8**. Therefore, the *exo*-configuration can be assigned to **8** and **12**.



A 8 (X=H; Y=CN)

B 12 (X=CN;Y=H)

Photoreaction in Methanol. The irradiation of a methanolic solution of **1** and **2** gave **8** in a 35% yield, along with several other products, including mainly 2-methoxyindan (**9**) and diastereoisomeric mixture of 2,2′-dimethoxy-1,1′-biindanyl (**10**). These compounds were confirmed to be the primary photoproducts, since their formation increased linearly with the irradiation time up to *ca.* a 10% conversion.

The structure of **9** was determined by a direct comparison of its spectral properties with those of an authentic sample which had been prepared by the methylation[13] of 2-indanol with diazomethane in the presence of boron trifluoride etherate.

The repeated chromatography of mixtures of **10** on silica gel gave three isomers (**10a**, **10b**, and **10c**) contaminated by small amounts of the others and a fourth isomer (**10d**) in a mixture with an equal amount of **10b**. In the mass spectra, only **10c** showed the molecular ion peak at *m/e* 296, whereas the main fragment-ion peaks at *m/e* 262 and 198 were commonly observed for **10a**—**c**. The NMR spectra of **10a**—**c** commonly consisted of the signals for aliphatic protons, methoxyl protons, and aromatic protons in the area ratio of *ca.* 4 : 3 : 4, showing that **10a**—**c** are dimeric compounds of **2** which possess two methoxyl groups.

Table 2. ^{1}H NMR spectral data for **10(a—d)**-d_6

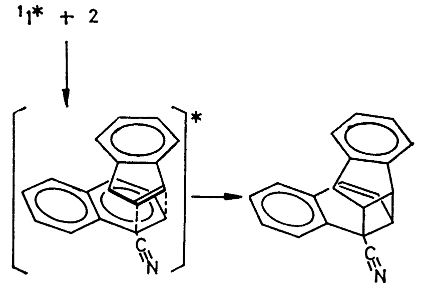
	H-2 and H-2′		OCH$_3$	
10a	3.65	3.98	2.80	3.15
10b	3.65	4.20	3.24	3.38
10c	3.60		2.96	
10d	3.88		3.25	

The signals of aliphatic protons are too complex to be assigned. Therefore, the d_6-compounds of **10** were prepared by a photoreaction using **2**-d_3; the NMR spectra were then taken (Table 2). The aliphatic resonances should be the signals for H-2 and H-2′. Since the chemical shifts are relatively low, two methoxyl groups can be said to attach themselves to C-2 and C-2′. For structural elucidation, it should be noted that H-2 and H-2′ or the two methoxyl groups are magnetically equivalent for **10c** and **10d**, but not for **10a** and **10b**. Therefore, **10a** or **10b** appears to be either isomer of the *cis*, *trans*-structure. The *trans*, *trans*- or *cis*, *cis*-structure should be reserved for **10c** and **10d**.

From complex mixtures of oligomeric and polymeric materials, a 1 : 2 : 1-adduct of **1**, **2**, and methanol (**11**) was isolated by repeated chromatography. However, the isolation was poorly reproducible because of the low yields as well as difficulties in the isolation. The structure could not be determined.

Discussion

An excited-singlet mechanism is responsible for the formation of **3**, since the fluorescence of **1** was quenched by **2** at a diffusion-controlled rate ($k_q = 1.2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} in benzene) and the triplet photosensitization using benzophenone or Michler's ketone did not give **3** at all. It is of mechanical interest to note that the *endo* cycloadduct (**3**) was exclusively formed. This stereoselectivity can be interpreted in terms of the intermediacy of the **1**—**2** exciplex possessing a sandwich-type configuration. The excited singlet **1** has been known to form exciplexes with a variety of alkenes,[14] and the ionization potential of **2** is low (8.14 eV)[15] enough for the formation of the **1**—**2** exciplex. Therefore, the exciplex mechanism is not unreasonable, though exciplex emission could not be detected. Moreover, it should be noted that the head-to-tail structure of **3** can not be expected from the most stable 1,4-biradical and 1,4-dipolar intermediates. This suggests that the photocycloaddition is stereospecific in nature, as has been reported in the photocycloaddition of **1** to *cis*- and *trans*-1-phenoxypropenes.[2h]



This photocycloaddition still occurs in such a moderately polar solvent as ethyl acetate, but it does not in acetonitrile and methanol; the exciplex formation is dominant in ethyl acetate and less polar solvents. In very polar solvents, however, a complete electron-transfer reaction predominantly occurs to give the anion radical of **1** ($\mathbf{1}^{\bar{\cdot}}$) and the cation radical of **2** ($\mathbf{2}^{\dagger}$), a conclusion supported by the free-energy change (ΔG) calculated using Eq. 1:[16]

$$\Delta G(\text{kcal/mol}) = 23.06[E_{1/2}(\mathbf{2}/\mathbf{2}^{+}) - E_{1/2}(\mathbf{1}/\mathbf{1}^{-}) - e_0{}^2/\varepsilon\alpha] - E_{0-0}(\mathbf{1}) \qquad (1)$$

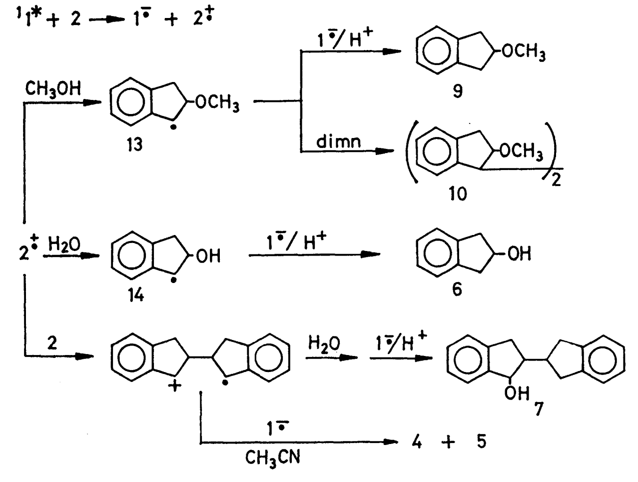
where $E_{1/2}(\mathbf{2}/\mathbf{2}^{+}) = 1.24$ V *vs.* Ag/Ag^{+} in acetonitrile, $E_{1/2}(\mathbf{1}/\mathbf{1}^{-}) = -2.33$ V *vs.* Ag/Ag^{+} in acetonitrile, and $E_{0-0}(\mathbf{1}) = 89.1$ kcal/mol.[17] If the Coulombic term ($e_0{}^2/\varepsilon\alpha$) is estimated to be small (*ca.* 1.5 kcal/mol), the value of ΔG can be calculated to be *ca.* −5 kcal/mol, indicating that the electron-transfer process is substantially exothermic, probably occuring at a diffusion-controlled rate.[16]

TABLE 3. ISOMER RATIOS OF INDENE CYCLOBUTANE DIMERS

Reaction type	Head-to-head		Head-to-tail	
	syn	*anti*	*syn*	*anti*
This work	5±2	95±2	0.0	0.0
Cation radical mechanism[a)]	3	97	0.0	0.0
Direct irradiation[b),c)]	14—18	69—72	5	7—9
Benzophenone-sensitization[c)]	3	84	5	8

a) Ref. 18. b) In the presence of 1,3-cyclohexadiene. c) W. Metzner and D. Wendisch, *Ann.*, **730**, 111 (1969).

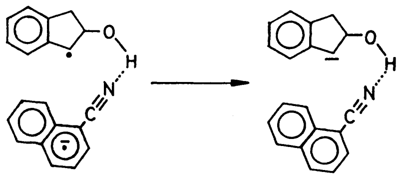
In fact, the photoreaction in acetonitrile gave the *syn* and *anti* indene dimers in a ratio very similar to that observed in the dimerization *via* $\mathbf{2}^{\dagger}$,[18] as is shown in Table 3. This cation radical mechanism is further supported by the remarkable "quenching" of dimer formation on the addition of only a few vol% of methanol or water. This "quenching" appears to be caused by the nucleophilic attack of methanol or water on $\mathbf{2}^{\dagger}$, which ultimately results in the formation of **9** and **10** or **6**, as is shown in Scheme 2.



Scheme 2.

Table 4 lists the product distribution of the photoreactions in methanol and in acetonitrile in the presence of methanol and water. The most notable points are (1) the slow formation of the products in methanol, (2) the poor yields of **9** and the formation of considerable amounts of **10** in either methanol or acetonitrile–methanol, and (3) the relatively good yield of **6** and the lack of any formation of a compound corresponding to **10** (*i.e.* 2,2′-dihydroxy-1,1′-biindanyl) in acetonitrile–water.

Apparently, the **13** radical can undergo the dimerization reaction competitively with the reduction by $\mathbf{1}^{\bar{\cdot}}$, while the reduction of the **14** radical by $\mathbf{1}^{\bar{\cdot}}$ is much faster than the dimerization reaction. The reduction potential of **13** is not significantly different from that of **14**, as is to be expected from their similar π-electronic structures. Therefore, the efficient reduction of **14** must be caused by factors other than the reduction potential. For example, a hydrogen-bonding between $\mathbf{1}^{\bar{\cdot}}$ and **14** would necessitate their approaching within an effective distance for the reduction and/or would facilitate the electron flow from $\mathbf{1}^{\bar{\cdot}}$ to **14**. On the other hand, such a hydrogen-bonding can not occur with **13**.

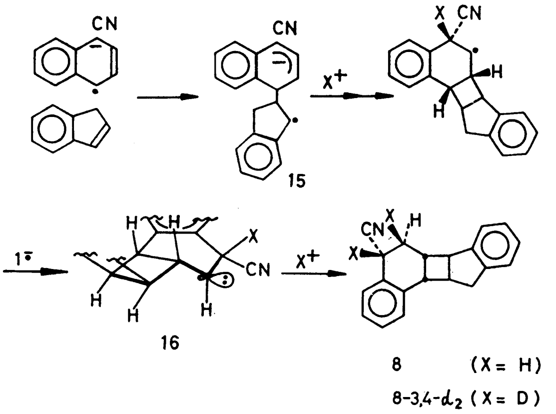


Compound **8** was confirmed to be formed *via* anionic species including $\mathbf{1}^{\bar{\cdot}}$, since the photoreaction in methanol-*O*-*d* gave **8**-3,4-d_2. In the NMR spectrum, the signals of H-4 and H-3B were completely absent, whereas that of H-3A at δ 1.16 appeared as a broad doublet ($J \simeq 13$ Hz). The NMR data demonstrate the stereospecific incorporation of the two deuterium atoms in the *cis*-relationship at C-3 and C-4. Scheme 3 delineates the possible mechanistic pathways which can interpret the stereochemistry in the formation of **8** and **8**-3,4-d_2. The anion radical of **1** would undergo a radical type of addition to **2**, giving the addend anion radical (**15**). The protonation of **15** probably occurs on the less hindered side at cyanated carbon, thus assuring the *cis*-relationship between the cyano group and the cyclobutane ring in **8**. Similarly, the deuterium incorporation at C-3 would stereospecifically occur on

TABLE 4. PRODUCT DISTRIBUTION OF THE PHOTOREACTIONS OF **1** WITH **2** IN PROTIC MEDIA[a)]

Solvent	Irradn time / h	Conversion/%		Product (yield/%)[b)]	
		1	**2**		
CH_3CN-H_2O (9: 1)	15	42	≈100	**6** (55)	**7** (25)
CH_3CN-CH_3OH (9: 1)	19	42	≈100	**9** (37)	**10** (53)
CH_3OH	22	56	63	**9** (23)	**10** (23)

a) [**1**]=[**2**]=0.1 mol dm^{-3}; irradiation at 313 nm using a merry-go-round apparatus. The yields of **8** were not determined. b) GLC yields based on the **2** consumed.



Scheme 3.

the *quasi*-equatorial position of the half-chair conformation A of the anion (**16**). On the other hand, the selective formation of **8** can not be reasonably interpreted by an alternative mechanism that includes the initial protonation at cyanated carbon of $\mathbf{1}^{\overline{\cdot}}$, followed by the addition of the protonated radical to **2**. According to this mechanism, the sterically favorable approach of **2** to the protonated radical seems to occur in the *trans*-relationship with the cyano group rather than in the *cis*-relationship, leading to the formation of **12**. Finally, it should be pointed out that this type of reductive photocycloaddition *via* the anion radical has not been reported previously, though photochemical cross-cycloadditions *via* cation radicals are known.[19]

Experimental

The following instruments were used for the spectral measurements: ^{1}H NMR, Hitachi R-24 (60 MHz) and JEOL JNM PS-100 (100 MHz); IR, Shimadzu IR-400; UV, Hitachi 124; MS, Hitachi RMU-6E; fluorescence spectra, Hitachi MPF-2A. The GLC was carried out on a Shimadzu GC-3BF apparatus using a column of SE-30 (5% on Celite 545, 0.75 m) at 195 °C for **3**, **7**, **8**, and **10** and at 180 °C for **4** and **5**, and a column of Ucon Oil LB-550X (5% on Celite 545, 0.75 m) at 170 °C for **6** and **9**. Irradiation was carried out in a Pyrex vessel with an Eikosha PIH-300 high-pressure mercury arc under cooling with water. All the solutions were bubbled with an N_2 stream for 30 min before irradiation. The melting points are uncorrected.

Materials. Commercial thiophene-free benzene was washed with sulfuric acid until no further coloration of the acid layer took place, and then washed with water and distilled from P_2O_5. Spectrograde cyclohexane (Nakarai Chemicals) was used without further purification. The dioxane was refluxed over sodium and then distilled. The tetrahydrofuran and diethyl ether were distilled from $LiAlH_4$. The acetonitrile was distilled three times from P_2O_5 and then from CaH_2. The methanol was refluxed over CaH_2 and then distilled. The indene was distilled from sodium under reduced pressure prior to use. The 1-cyanonaphthalene (Tokyo Kasei) was chromatographed on silica gel and then distilled *in vacuo*.

Preparation of Indene-1,1,3-d_3. A solution containing indene-d_0 (23 g, 0.2 mol), 1,8-diazabicyclo[5.4.0.]undec-7-ene (3 g, 20 mmol), and deuterium oxide (40 g, 2.0 mol) in dry dioxane (100 ml) was refluxed under an N_2 atmosphere for 20 h and then about one half of dioxane was distilled off. The remaining solution was poured into 1000 ml of ice-water. The oil layer was separated, washed with 1 mol dm^{-3} hydrochloric acid, with an aqueous solution of $NaHCO_3$, and three times with water, and then dried ($MgSO_4$). After filtration, the filtrate was distilled *in vacuo* to give deuterated indene. The above procedure was repeated for this indene. Finally, 12 g of indene-1,1,3-d_3 (50% yield) were obtained. The isotopic purity was confirmed to be over 95% by a study of the NMR and mass spectra.

Photoreaction in Less Polar Solvents. As a typical run, the photoreaction in diethyl ether will be described. A solution of **1** (0.47 g, 3 mmol) and **2** (7.5 g, 67 mmol) in 200 ml of diethyl ether was irradiated for 20 h. After the removal of the diethyl ether, 6.5 g of **2** was recovered by the vacuum distillation of the remaining oil. The residue was chromatographed on silica gel, using mixtures of hexane and benzene as the eluents. After **4** and **5** (*ca.* 0.1 g) had been eluted with hexane, 0.32 g of **1** was eluted with 30% benzene in hexane. Further elution by a 1: 1-mixture of hexane–benzene gave 0.1 g of **3** (38% yield based on the unrecovered **1**), which was then recrystallized from ethanol–benzene; mp 146—147 °C; IR (Nujol): 2220 (C≡N) and 1640 cm^{-1} (C=C); UV (CH_3CN): λ(log ε)=302 (sh), 273 (3.89), and 265 nm (3.89); MS: 269 (M$^+$, vw), 153, and 116; NMR ($CDCl_3$): δ 2.8 and 3.2 (d-d each, 2H, $-CH_2-$), 3.9 (m, H-1), 4.1 (m, H-2a), 4.32 (t, J=8.0 Hz, H-2) 5.38 (d-d, J=4.5 and 10.0 Hz, H-3), 5.96 (d, J=10.0 Hz, H-4), 6.5 (d, 1×ArH), and 6.8—7.3 (m, 7×ArH); Found: C, 89.03; H, 5.58; N, 5.11%. Calcd for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20%.

Photoreaction in Acetonitrile. A solution of **1** (0.94 g, 6 mmol) and **2** (11 g, 100 mmol) in 250 ml of acetonitrile was irradiated for 100 h. After the removal of the acetonitrile, 9.3 g of **2** were recovered by vacuum distillation. The residue was chromatographed on silica gel; subsequent elution with hexane gave 0.85 g of the *anti* head-to-head indene dimer **4** (50% yield based on the unrecovered **2**), which was then recrystallized from ethanol; mp 109—110 °C (lit,[20] 110 °C). Further elution with 30% of benzene in hexane gave 0.7 g of **1**.

Photoreaction in Acetonitrile–Water. A solution of **1** (0.2 g, 1.3 mmol) and **2** (2.0 g, 18 mmol) in 55 ml of acetonitrile–water (10: 1) was irradiated for 50 h. GLC showed that the **1** had been completely consumed. The solids which had been precipitated during the irradiation were filtered out and then washed with 10 ml of cold methanol; 0.19 g of **7** was thus obtained. The filtrate was condensed, and then 10 ml of hot methanol were added. After cooling, the solids were again precipitated; filtration and washing with 10 ml of cold methanol gave another 0.18 g of **7**. The combined yield of **7** was 23%, based on the unrecovered **2**. The **7** was then recrystallized from ethanol; mp 182—183 °C; UV (CH_3CN): λ (log ε)=272 (3.32), 265 (3.31), and 259 nm (sh); MS: 250 (M$^+$, vw), 232 (M$-H_2O$), and 116; NMR ($CDCl_3$): δ 1.8 (d, O-H), 2.14—3.46 (m, 8H), 4.96 (t, OCH), and 7.0—7.5 (m, 8H); Found: C, 86.14; H, 7.11%. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25%.

To the filtrate, a 20-ml portion of chloroform was added, and then the mixture was dried ($MgSO_4$). After filtration, vacuum distillation gave 0.5 g of **2** and 1.0 g of 2-indanol **6** (mp 68—69 °C, 58% yield). The residue was chromatographed on silica gel; elution with 40% benzene in hexane gave 90 mg of **8** (25% yield based on the **1** used), which were then recrystallized from ethanol–benzene; mp 207—208 °C; IR (KBr): 2220 cm^{-1} (C≡N); MS: 271 (M$^+$, vw), 155, and 116; UV (cyclohexane): λ (log ε)=274 (3.11), 267 (3.11), and 262 nm (3.04); Found: C, 88.27; H, 6.28; N, 5.20%. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.32; N, 5.16%.

Photoreaction in Methanol. A solution of **1** (1.0 g, 6.5 mmol) and **2** (6.0 g, 54 mmol) in 200 ml of methanol was irradiated for 25 h. After the removal of the methanol, vacuum distillation gave 3.5 g of **2** and 0.4 g of 2-methoxyindan **9** (12.5% yield, based on the unrecovered **2**). The residue was chromatographed on silica gel; after a mixture of **4** and **5** (*ca.* 0.1 g, 4% yield) had been eluted with hexane, elution with 40% benzene in hexane gave a viscous oil, to which 10 ml of hot methanol were then added. Cooling while the solution was scratched gave white solids, which were then filtered and washed with 5 ml of cold methanol; 0.31 g of **8** (35% yield based on the unrecovered **1**) was thus obtained. The subsequent vacuum distillation of the filtrate gave 0.5 g of **1**. Further elution with benzene and acetone gave mixtures of **10** and polymeric materials. Vacuum distillation gave 0.6 g of **10** (160—163 °C/0.1 mmHg, 19% yield), which was chromatographed on silica gel, using benzene and 2—10% ethyl acetate in benzene as the eluents. Each fraction was further chromatographed. This procedure was repeated three times for each fraction to give 30—50 mg of **10a**, **10b**, a mixture of **10b** and **10d**, and **10c**. **10a**: mp 97—98 °C (from methanol); MS: 262 ($M-CH_3OH$) and 147 ($M/2$); NMR (CCl_4): δ 2.7—3.15 (m, 4H), 2.83 (s, OCH_3), 3.16 (s, OCH_3), 3.6—4.0 (m, 4H), and 7.0—7.4 (m, 8H); Found: C, 81.37; H, 7.44%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%. **10b**: mp 170—172 °C (from methanol); MS: 262 ($M-CH_3OH$) and 147 ($M/2$); NMR ($CDCl_3$): δ 2.7—3.1 (m, 4H), 3.24 (s, OCH_3), 3.38 (s, OCH_3), 3.55—3.75 (m, 2H), 4.13—4.35 (m, 2H), and 7.0—7.3 (m, 8H); Found: C, 81.41; H, 7.39%. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%. **10c**: mp 70—73 °C (from methanol); MS: 294 (M^+, w), 262 ($M-CH_3OH$), and 147 ($M/2$); NMR (CCl_4): δ 2.7—3.1 (m, 4H), 2.96 (s, $2\times OCH_3$), 3.3—3.7 (m, 4H), and 6.9—7.3 (m, 8H).

In another run, a fraction which had been eluted with benzene was further chromatographed on silica gel. Subsequent elution with 30% hexane in benzene gave solids, which were then recrystallized from ethanol to give 50 mg of **11**; mp 229—231 °C; MS: 417 (M^+, vw), 301 ($M-C_9H_8$, w), 271 ($M-C_{10}H_{10}O$, w), 155, 154, 147 (100%), and 116 (24 %); NMR ($CDCl_3$): δ 1.5 (t, 1H), 2.27 (d-d, 1H), 3.02 (d-d, 1H), 3.38 (s, 3H, OCH_3), 3.3—3.8 (m, 3H), 4.0—4.4 (m, 3H), 5.68 (d, 1H), 6.7—7.6 (m, 13H); Found: C, 85.94; H, 6.44; N, 3.33%. Calcd for $C_{30}H_{27}NO$: C, 86.30; H, 6.52; N, 3.36%.

*Sodium Methoxide-catalyzed Isomerization of **8**.* A solution of **8** (100 mg, 0.6 mmol) and sodium methoxide (11 mg, 2 mmol) in dry dioxane–methanol (15 ml) was bubbled with an N_2 stream and then refluxed for 5 h. GLC showed that the solution contained an equilibrium mixture of **8** and **12** in a 1:4 ratio. After the evaporation of the solvent under reduced pressure, 50 ml of chloroform were added; the solution was washed three times with water and then dried ($MgSO_4$). Filtration and evaporation left a glassy material, to which 10 ml of hot methanol were added; the mixture was then allowed to stand overnight at room temperature. After the filtration of the **8** (10 mg) thus precipitated, the filtrate was condensed to *ca.* one half its original volume and allowed to stand overnight in a refrigerator; 60 mg of **12** were thus obtained; mp 79—80 °C; MS: 271 (M^+, vw), 155, and 116; IR (CCl_4): 2220 cm^{-1} ($C\equiv N$); Found: C, 88.35; H, 6.26; N, 5.22%. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.32; N, 5.16%.

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