Site-Selective Photochemical Ene Reaction of 2-Methylene-1,2-dihydronaphthalene

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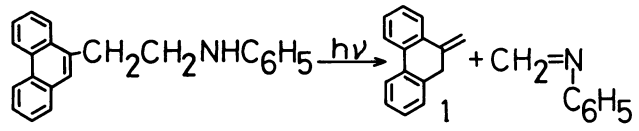
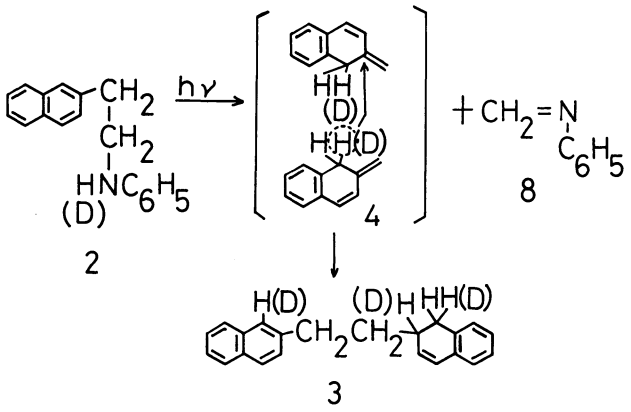
Synopsis. The title compound, formed by the photolysis of 2-(2-anilinoethyl)naphthalene, reacted with olefins having a conjugated double bond to give an ene reaction product under irradiation conditions.

In the course of our studies on the intramolecular photochemical reactions of aromatic compounds with the anilino group, we came across the photolytical formation of *exo*-methylene compounds such as 9-methylene-9,10-dihydrophenanthrene (**1**).[1] A



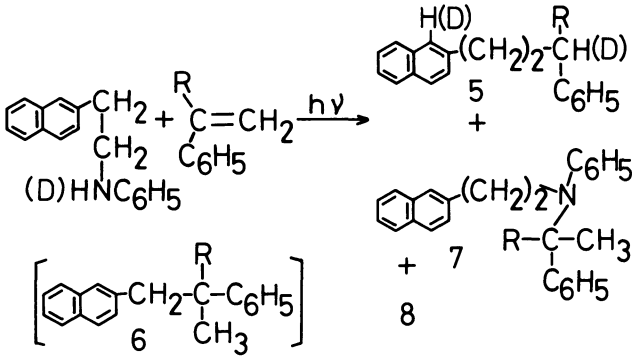
similar result was obserbed in the case of 1-(2-anilinoethyl)naphthalene.[2] Upon irradiation, 2-(2-anilinoethyl)naphthalene (**2**) afforded 2-[2-(2-naphthyl)ethyl]-1,2-dihydronaphthalene (**3**) seemed to be formed by the ene reaction of 2-methylene-1,2-dihydronaphthalene (**4**) (Scheme 1.).[2,3] We now give evidence for the transient existence of **4** and its ene reaction with various olefins.

Upon irradiation of a solution of **2** (1.6×10^{-2} mol dm^{-3}) in degassed benzene with a high-pressure mercury lamp, **3** was obtained as the main product.[4a] The identification of the structure of **3** was based on spectral data and the conversion of **3** to 1,2-di-2-naphthylethane.[5] The mass spectrum of **3**, isolated from the irradiated mixture in D_2O-saturated benzene, showed an M^+ ion peak at m/z=286.[4b] This indicated an incorporation of two deuterium atoms in **3** (vide infra).



Scheme 1.

On the other hand, the irradiation of **2** in the presence of a large excess of styrene (30 times) gave 2-(3-phenylpropyl)naphthalene (**5**), but not **6** (Scheme 2, R=H). When the same irradiation was carried out in D_2O-saturated benzene, monodeuterated **5** (confirmed by mass spectrum) was obtained. The formations of **3** and **5** may be reasonably interpreted in terms of the ene reaction of **4**, as illustrated in Schemes 1 and 2. The deuteration examination demonstrated that an ene reaction occurred between **4** and an enophile molecule (**4** or styrene). In the formation of **3**, almost all of **4** formed was consumed and no other photoreactions occurred because the yield of **3** was comparable to that of imine (**8**).



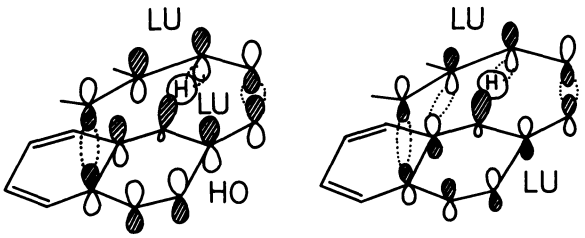
Scheme 2.

This ene reaction process was further confirmed by the irradiation of **2** in the presence of various olefins as an enophile. In these irradiations, the relative ratio of **2** and enophile had a great influence on the distribution of the photoproducts. For example, in the presence of equimolar of styrene, **2** exclusively afforded **3**, while in the presence of a large amount of styrene (10 times of **2** or more) it led to the formation of **5** together with **7**, the addition product of **2** to styrene (Scheme 2).[6] Similar results were observed in the presence of 2-phenylpropene. Therefore, irradiation of **2** was carried out in the presence of a large amount of olefins (30 times moles). The results are summarized in Table 1. Among the olefins shown, styrene, 2-phenylpropene, and 1,3-pentadiene afforded the ene reaction products together with **4**. Other olefins, however, gave no ene reaction product except for **3**. All isolated ene reaction products had such structures that a 2-naphthylmethyl group was site-selective bonded to the terminal carbon of the starting olefins. Namely, only terminal carbons were reactive. Terminal carbons of olefins such as 1,7-octadiene, hexene, and isobutyl vinyl ether, however, were not reactive. From these observations, it was deduced that the terminal carbon of a conjugated diene, including styrene and 2-phenylpropene, undergo an ene reaction with **4**. Upon irradiation without

Table 1. Isolated Yield of **3** and Those of the Other Ene Reaction Products[a)]

Enophile[b)]	Yield/%		Recovered **2**/%
	3	Other products	
None	37	—	37
C_6H_5-CH=CH_2	0	Compd **5**(R=H) 31	15
C_6H_5-C(CH_3)=CH_2	0	Compd **5**(R=CH_3) 21	30
C_6H_5-CH=CH-CH_3	26[c)]	0	54[c)]
CH_2=CH-$(CH_2)_3$-CH_3	35	0	46
CH_2=CH-$(CH_2)_4$-CH=CH_2	38	0	54
CH_2=CHCH=CH-CH_3	trace	20[c)]	41
CH=CH-$(CH_2)_4$	39	0	46
CH_2=CH-O-$CH_2CH(CH_3)_2$	22	0	51

a) Irrdiated for 7.5 h. b) 30 times of moles of **2** was used. c) Estimated values from the intensities of ^{1}H NMR signals because of the contamination with 1-phenylpropene. d) Yield of 2-hexylnaphthalene.



(a) (b)

Fig. 1.

such olefins, **4**, which has terminal conjugated double bonds, reacted as an enophile.

The interactions of the HOMO of π-bond of **4** with the LUMO of the C-H bond of the 1-position of **4**, and the LUMO of the π-bond of enophile led to the formation of ene reaction products[7] (Fig. 1a). As the carbon atoms having the largest coefficients of the LUMO or HOMO interact with each other, an enophile reacted with terminal methylene carbon of **4** at the terminal carbon.[8] On the other hand, the secondary orbital interaction between the LUMO of an enophile (Fig. 1b) may facilitate the reaction of **4** with olefins having a conjugated double bond.

According to Murata et al.,[9] **4** was reported to be isolated and gradually changed to 2-methylnaphthalene. In the present investigation, neither **4** nor 2-methylnaphthalene was detected in the irradiated mixture of **2**, even under high-diluted conditions (3×10^{-4} mol dm^{-3}). These results suggested that the dimerization reaction of **4** occurred photochemically and a significant contribution of the LUMO of **4** to the ene reaction.[10]

Experimental

All melting points were uncorrected. The mass spectra were obtained on a Shimadzu-LKB 9000 Gas chromatograph-Mass spectrometer. Other spectrometers used here were described previously.[11]

All preparative irradiation was performed in a way similar to that described previously.[11]

2-(2-Anilinoethyl)naphthalene (2). 2-Naphthaleneacetic acid was converted to the corresponding anilide by a standard method via acid chloride, yield 81%: mp 155—156 °C; IR (KBr) 3280 (NH), 1660 cm^{-1} (CO). Found: C, 83.00; H, 5.78; N, 5.30%. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36%. This anilide was treated with $LiAlH_4$ in THF-ether (1:1, v/v) in the usual manner to afford **2** (yield 60%): mp 54—56 °C; IR (KBr) 3380 cm^{-1} (NH); λ_{max}(hexane) 276 nm (log ε 3.83); ^{1}H NMR ($CDCl_3$) δ=2.7—3.8 (5H, CH_2CH_2NH) and 6.3—7.8 (12H, m, aromatic); m/z=247 (M^+). Found: C, 87.40; H, 6.68; N, 5.60%. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66%.

Photolysis of 2. A solution of **2** (79 mg, 0.32 mmol) in benzene (20 cm^3) was irradiated. The residue after solvent evaporation was chromatographed (Silica gel with benzene) to yield **3** (17 mg, 37%) and was found to be contaminated by a trace of hydrocarbon which was isolated by repeated chromatography with benzene-hexane (1:3. v/v). A solvent evaporation of the second fraction of the latter chromatography gave pure **3** (13 mg): mp 81—85 °C; λ_{max}(hexane) 266 nm (log ε 4.14); ^{1}H NMR ($CDCl_3$) δ=1.6—2.1 (2H, m, CH_2), 2.3—3.0 (5H, m, CH and CH_2), 5.86 (1H, dd, J=10 and 3 Hz, CH=), 6.36 (1H, d, J=10 Hz, CH=), and 6.9—7.8 (11H, m, aromatic); m/z=284 (M^+). Found: C, 93.01; H, 7.26%. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09%. This compound changed to an unidentified hydrocarbon upon irradiation of a solution for 7.5 h (25 mg from 64 mg of **3**, and 36 mg of **3** was recovered); mp 115—117 °C. Found: C, 92.63; H, 7.10%.

Photoreaction Products in the Presence of Additives (30 times mole to 2). Styrene: The first eluent of the chromatography on silica gel with benzene-hexane (1:3, v/v) yielded **5** (31%); viscous oil; ^{1}H NMR ($CDCl_3$) δ=1.8—3.0 (6H, m, $CH_2CH_2CH_2$) and 6.8—7.9 (12H, m, aromatic); m/z=246 (M^+). Found: C, 92.51; H, 7.45%. Calcd for $C_{19}H_{18}$: C, 92.64; H, 7.36%. The second eluent yielded *N*-[2-(2-naphthyl)ethyl]-*N*-(1-phenylethyl)aniline **7** (12%); viscous oil; ^{1}H NMR ($CDCl_3$) δ=1.4—1.8 (3H, m, CH_3), 2.7—4.0 (5H, m, CH and CH_2), and 6.5—7.9 (17H, m, aromatic); m/z=351 (M^+). Found: 88.63; H, 7.53; N, 3.89%. Calcd for $C_{26}H_{25}N$: C, 88.85; H, 7.17; N, 3.98%. The third eluent gave the starting amine **2** (15%).

2-Phenylpropene: The first eluent of the chromatography with benzene-hexane (1:3, v/v) yielded 2-(3-phenylbutyl)naphthalene (21%); viscous oil; ^{1}H NMR ($CDCl_3$) δ=1.28 (3H, d, CH_3), 1.8—2.9 (5H, m, CH_2CH_2CH), and 7.0—8.0 (12H, m, aromatic); m/z=260 (M^+). Found: C, 92.24; H, 7.90%. Calcd for $C_{22}H_{20}$: C, 92.26; H, 7.74%. The

second eluent yielded *N*-[2-(2-naphthyl)ethyl]-*N*-(1-methyl-1-phenylethyl)aniline (14%); viscous oil; ^{1}H NMR ($CDCl_3$) δ=1.30 (6H, s, CH_3), 2.4—3.4 (4H, m, CH_2), and 7.0—8.0 (17H, m, aromatic); *m/z*=365 (M^+). Found: C, 88.93, H, 7.58; N, 3.80%. Calcd for $C_{27}H_{27}N$: C, 88.72; H, 7.45; N, 3.83%. The third eluent gave **2** (30%).

1,3-Pentadiene: The first eluent of the chromatography with benzene–hexane (1:3, v/v) afforded a product mixture of *cis*-and *trans*-2-(4-hexenyl)naphthalene [suggested by ^{1}H NMR spectrum and GC–MS signals at *m/z*=210 (M^+)]. This mixture was hydrogenated over Pd/C (5%, 40 mg) in benzene (15 cm^3) to give 2-hexylnaphthalene (27 mg, 20% from **2**, 158 mg) which was purified by TLC; viscous oil; ^{1}H NMR ($CDCl_3$) δ=0.7—2.1 (11H, m, $CH_3(CH_2)_4$), 2.75 (2H, t, CH_2Ar), and 7.0—7.9 (7H, m, aromatic); *m/z*=212 (M^+). Found: C, 90.41; H, 9.78%. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49%. The ^{1}H NMR spectral pattern of this compound at the region of δ=0.7—3.0 was almost identical to that of hexylbenzene.[12] The second eluent gave **2** (41%).

1,2-Di-2-naphthylethane: A solution of **3** (35 mg, 124 mmol) and DDQ (104 mg, 373 mmol) in benzene (100 cm^3) was refluxed for 6.5 h. After evaporating the solvent, the residue was chromatographed on alumina with benzene, and then purified by TLC to give 1,2-di-2-naphthylethane (79%); mp 183.5—185 °C (lit,[5] 185—186 °C).

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4) a) Small amounts of an unidentified hydrocarbon ($C_{22}H_{20}$) was isolated from the first elution of chromatography. This compound was formed from **3** on irradiation. Therefore, unless otherwise noted, the yield of this hydrocarbon was included in the yield of **3**. b) Calcd for $C_{22}H_{18}D_2$: M^+=286.

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