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Photoreactions of *N*-Methyl-1,2-naphthalenedicarboximide with Dienes. Formation of Naphthazepinediones and Their Secondary Reactions

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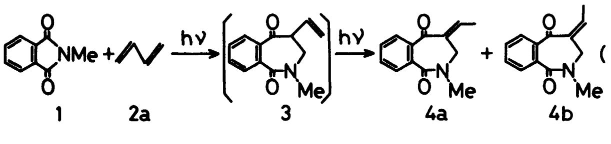
Synopsis. In the photolysis of a benzene solution of *N*-methyl-1,2-naphthalenedicarboximide (**5**) in the presence of dienes, i.e., 2,3-dimethyl-1,3-butadiene and 1,3-butadiene, insertion of one of the double bond in the dienes into a C(=O)-N bond of **5** was observed to give naphthazepinediones. These products were found to convert further into cyclobutanes and α,β-unsaturated ketones via photochemical intramolecular cycloaddition and via hydrogen migration, respectively.

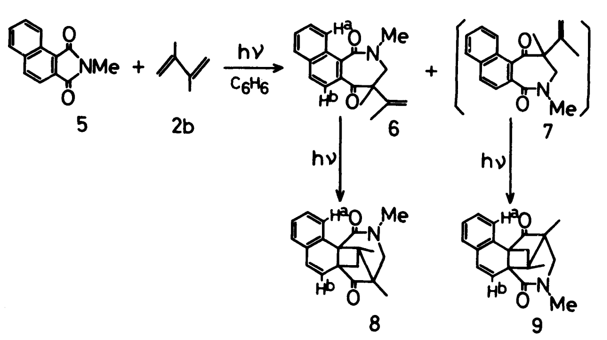
In recent years, the photochemistry of imides has been the subject of intensive investigations.[1] A characteristic photoreaction of arenedicarboximides in the presence of alkenes is the insertion of the alkene into a C(=O)-N bond of the imide moiety.[2] Concerning the reactions with dienes, Mazzocchi and his co-workers have reported that the photoreaction of *N*-methylphthalimide (**1**) with, for example, 1,3-butadiene (**2a**) gives **4a** and **4b** by insertion of one of the double bonds in **2a** into a C(=O)-N bond of **1** (**1**+**2a**→**3**) and successive photochemical hydrogen-migration (**3**→**4a**+**4b**) (Eq. 1).[2a,f] In the course of our systematic investigation of the photochemistry of arenedicarboximides with alkenes, we have established that the arene structure played a crucial role in determining the reaction pathways.[3] This paper describes the photoreactions of *N*-methyl-1,2-naphthalenedicarboximide (**5**) with dienes in benzene. The predominant reaction of **5** with dienes is found to be insertion of one of the double bonds in the dienes into a C(=O)-N bond of **5** (naphthazepinedione formation). New types of secondary reactions are observed at the same time.



(1)

Results and Discussion

Irradiation of a benzene solution of **5** (10 mM, 1 M=1 mol dm^{-3}) and 2,3-dimethyl-1,3-butadiene (**2b**) (100 mM) by a light of >320 nm (aq $CuSO_4$ filter) for a short time gave naphthazepinedione (**6**, 27%) and two regio-isomeric cyclobutanes (**8**, 17% and **9**, 38%) (Scheme 1). Prolonged irradiation of the same system gave only **8** (42%) and **9** (40%), and irradiation of **6** alone in benzene afforded **8** quantitatively. These results clearly show that **8** is a secondary photoproduct of **6**. Although **7** could not be isolated, product **9** seems to be formed similarly from the corresponding precursor **7** which is more reactive than **6** under the photochemical conditions used.

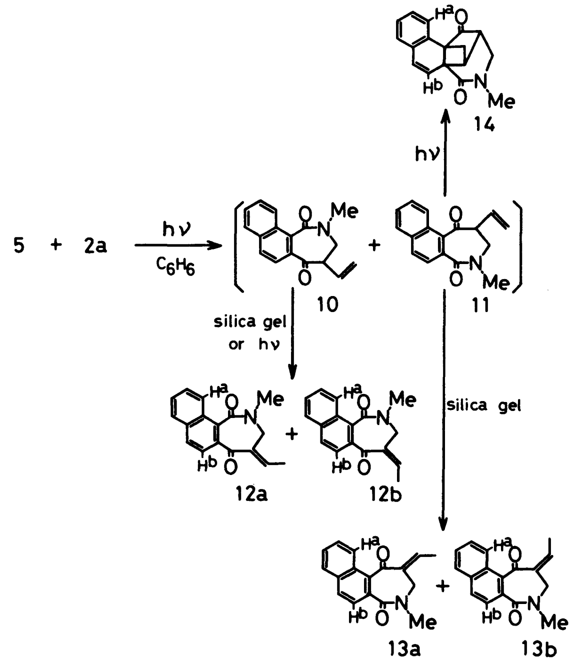


Scheme 1.

The structure of **6** was supported by the spectral resemblance to the analogous naphthazepinediones obtained by the photoreactions of **5** with alkenes.[3b] The regiochemistry was deduced mainly from the chemical shift of H^b, which generally appeared at a lower field region than that of H^a in such a regio-isomer.[3b] The structures of **8** and **9** were assigned on the basis of IR and ^{1}H NMR spectra. The IR spectra of **8** and **9** show characteristic five-membered carbonyl absorption bands at 1758 and 1762 cm^{-1}, respectively. The H^a signal of **8** shifted considerably to a lower field (δ=7.95) than that of **9**, probably due to the deshielding effect of the lactam carbonyl group. Molecular model examination shows that the five-membered carbonyl groups in **8** and **9** are fixed in configurations where no anisotropic effects of the carbonyl groups exerts on H^a and H^b.

After irradiation of a benzene solution of **5** (10 mM) and **2a** (100 mM) for a short time, chromatography of the resultant mixtures on silica-gel column gave a mixture of **12a** and **12b** (45%, isomer-ratio=2.9:1) and a mixture of **13a** and **13b** (40%, isomer-ratio=2.6:1), respectively (Scheme 2). These products were only weakly observed in the ^{1}H NMR spectrum of the original mixture before chromatography. Judged from the ^{1}H NMR spectra of the original mixtures, the main products seem to be **10** and **11** (not isolated) because of their spectral resemblance to the naphthazepinediones obtained by the reactions of **5** with alkenes.[3b] These results may indicate that the initially formed **10** and **11** were converted by silica-gel treatment to a mixture of **12a** and **12b**, and a mixture of **13a** and **13b**, respectively.

On the other hand, prolonged irradiation of **5** and **2a** gave a mixture of **12a** and **12b** (38%, isomer-



Scheme 2.

ratio=2.0:1), and **14** (33%) together with a trace amount of a mixture of **13a** and **13b**. In this case, the ^1H NMR spectrum of the irradiation mixture was a simple combination of those of the isolated products, indicating that the unchanged products were isolated by chromatography.

The structures of **12a,b** and **13a,b** were supported by the spectral resemblance to the benzo analogues.[2a,f] The regiochemistry was deduced from the chemical shifts of H^a and H^b as in the case of the regiochemistry-determination of the naphthazepinediones obtained by the reactions of **5** with alkenes.[3b] The structure of **14** was supported by the spectral resemblance to **9**.

The photoreaction of **5** and 2,5-dimethyl-2,4-hexadiene (**2c**) was slow and only gave a mixture of unidentified minor products.

The results obtained here indicate that the insertion of one of the double bonds in dienes into a C(=O)–N bond of **5** is a predominant reaction in the photoreaction of **5** with dienes. The predominance of the insertion is a characteristic nature of the excited state of **5**, since no significant predominance was observed in the reactions of *N*-methyl-1,8- and -2,3-naphthalenedicarboximides with dienes.[3c] In the present system a new type of secondary photoreaction is found, i.e., intramolecular cycloaddition, which was not observed in the reaction of the benzo analogue. The hydrogen-migration (**10**→**12a,b**) is found to occur by the action of silica gel as well as by already known photochemical process. The photochemical pathways from **10** and **11** were strongly structure-dependent, i.e., *β*-naphthyl ketone (**10**) or *α*-naphthyl ketone (**11**) structure determines whether hydrogen-migration (**10**→**12a,b**) or cycloaddition (**11**→**14**) is favored.

Experimental

The mps were measured by a Yanagimoto micromelting point apparatus, and are uncorrected. ^1H NMR spectra were determined on a JEOL JNM-MH-100 (100 MHz) in $CDCl_3$ solution. IR spectra were obtained with a Hitachi 260-50 spectrophotometer. Mass spectra were measured on a JEOL JMS-DX-300 apparatus. Microanalyses were performed on a Yanagimoto CHN corder MT-2.

Materials. *N*-Methyl-1,2-naphthalenedicarboximide (**5**) was prepared and purified as previously described.[3b] Dienes (**2a**—c) were commercially available and **2b,c** were purified by distillation.

General Procedure for Irradiation and Product Isolation. UV irradiation of 25 cm^3 of N_2 purged benzene solutions containing 10 mM of **5** and 100 mM of dienes (**2a**—c) was carried out with an Eikosha EHB-W-300 high-pressure Hg-lamp through aq $CuSO_4$ filter about 1 cm in thickness (>320 nm) at ambient temperature. The reaction was monitored by ^1H NMR measurements. After evaporation of the solvent, the residue was subjected to column chromatography (Wakogel C-200). Dichloromethane-ether was used as the eluant for the separation of the products.

Irradiation of 5 and 2,3-Dimethyl-1,3-butadiene (2b). 4-Isopropenyl-2,4-dimethyl-3,4-dihydro-1*H*-naphth[1,2-*c*]-azepine-1,5(2*H*)-dione (**6**): Mp 145—148 °C; ^1H NMR δ=1.55 (s, 3H, CMe), 1.87 (s, 3H, =CMe), 3.28 (s, 3H, NMe), 3.27 and 4.38 (ABq, *J*=14 Hz, 2H, CH_2), 4.84 and 5.08 (br s, 2H, =CH_2), 7.4—7.7 (m, 2H, Arom H), 7.7—8.1 (m, 3H, Arom H), 8.12 (d, 1H, H^b); IR (KBr) 1698 (ketone), 1643 (lactam), 1482, 1406, 1384, 1080 cm^{-1}. Found: C, 77.93; H, 6.74; N, 4.82%; M^+, 293. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77%; M, 293.

12,14,15-Trimethyl-12-azapentacyclo[12.2.1.$0^{1,10}$.$0^{4,9}$.$0^{10,15}$]-heptadecane-2,4,6,8-tetraene-11,17-dione (**8**): Mp 242—245 °C; ^1H NMR δ=1.21 (s, 6H, CMe), 1.77 and 3.08 (ABq, *J*=8 Hz, 2H, cyclobutane CH_2), 2.82 (s, 3H, NMe), 3.32 (s, 2H, NCH_2), 5.95 and 6.93 (ABq, *J*=10 Hz, 2H, CH=CH^b), 7.1—7.4 (m, 3H, Arom H), 7.95 (dd, 1H, H^a); IR (KBr) 1758 (ketone), 1648 (lactam), 1496, 1332, 796 cm^{-1}. Found: C, 77.92; H, 6.67; N, 4.86%; M^+, 293. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77%; M, 293.

12,14,15-Trimethyl-12-azapentacyclo[12.2.1.$0^{1,10}$.$0^{2,7}$.$0^{10,15}$]-heptadecane-2,4,6,8-tetraene-11,17-dione (**9**): Mp 235—238 °C; ^1H NMR δ=1.20 (s, 3H, CMe), 1.38 (s, 3H, CMe), 1.72 and 2.66 (ABq, *J*=8 Hz, 2H, cyclobutane CH_2), 2.87 (s, 3H, NMe), 3.32 and 3.51 (ABq, *J*=12 Hz, 2H, NCH_2), 6.19 and 6.68 (ABq, *J*=10 Hz, 2H, CH=CH^b), 7.2—7.6 (m, 4H, Arom H); IR (KBr) 1762 (ketone), 1658 (lactam), 1386, 1338, 1239, 801 cm^{-1}. Found: C, 78.04; H, 6.79; N, 4.63%; M^+, 293. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77%; M, 293.

Irradiation of 5 and 1,3-Butadiene (2a). A mixture of (*E*)- and (*Z*)-4-ethylidene-2-methyl-3,4-dihydro-1*H*-naphth[1,2-*c*]azepine-1,5(2*H*)-dione (**12a**+**12b**, the isomer ratio=3:4): Mp 132—136 °C; ^1H NMR of **12a**, δ=2.05 (d, *J*=7 Hz, 3H, =CMe), 3.23 (s, 3H, NMe), 4.27 (br s, 2H, NCH_2), 7.19 (q, 1H, =CH), 7.4—8.1 (m, 6H, Arom H); ^1H NMR of **12b**, δ=2.39 (d, *J*=7 Hz, 3H, =CMe), 3.29 (s, 3H, NMe), 4.13 (br s, 2H, NCH_2), 6.23 (q, 1H, =CH), 7.4—8.1 (m, 6H, Arom H); IR (KBr) 1675 (ketone), 1641 (lactam), 1475, 1395, 1245, 773 cm^{-1}. Found: C, 77.16; H, 5.83; N, 5.31%; M^+, 265. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%; M, 265.

A mixture of (*E*)- and (*Z*)-2-ethylidene-4-methyl-3,4-dihydro-1*H*-naphth[2,1-*c*]-azepine-1,5(2*H*)-dione (**13a**+**13b**, the isomer ratio=1:3): Mp 152—158 °C; ^1H NMR of **13a**, δ=2.04 (d, *J*=7 Hz, 3H, =CMe), 3.27 (s, 3H, NMe), 4.08 and 4.43 (ABq, *J*=16 Hz, 2H, NCH_2), 7.32 (q, 1H, =CH), 7.5—7.8 (m, 2H, Arom H), 7.77 (d, *J*=8 Hz, 1H, Arom H), 7.9—8.0

(m, 1H, Arom H), 8.05 (d, 1H, J=8 Hz, 1H, H^b), 8.51 (dd, 1H, H^a); ^{1}H NMR of **13b**, δ=2.34 (d, J=7 Hz, 3H, =CMe), 3.27 (s, 3H, NMe), 3.44 and 4.58 (br ABq, 2H, NCH$_2$), 6.36 (q, 1H, =CH), 7.5—7.8 (m, 3H, Arom H), 7.9—8.0 (m, 1H, Arom H), 8.05 (d, 1H, J=8 Hz, 1H, H^b), 8.51 (dd, 1H, H^a); IR (KBr) 1672 (ketone), 1643 (lactam), 1476, 1386, 1248, 786 cm^{-1}. Found: C, 77.23; H, 5.95; N, 5.36%; M$^+$, 265. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28; M, 265.

12-Methyl-12-azapentacyclo[12.2.1.0^{1,10}.0^{2,7}.0^{10,15}]heptadecane-2,4,6,8-tetraene-11,17-dione (**14**): Mp 243—246 °C; ^{1}H NMR δ=1.61 (d, J=7 Hz, 1H, 1H of cyclobutane CH$_2$), 2.81 (s, 3H, NMe), 2.91 (dd, J=4, 7 Hz, 1H, 1H of cyclobutane CH$_2$), 2.9—3.1 (m, 1H, COCH), 3.2—3.3 (m, 1H, cyclobutane CH), 3.5—3.8 (m, 2H, NCH$_2$), 6.00 and 6.52 (ABq, J=10 Hz, 2H, CH=CH^b), 7.0—7.4 (m, 4H, Arom H); IR (KBr) 1768 (ketone), 1640 (lactam), 1342, 1244, 800 cm^{-1}. Found: C, 76.88; H, 5.95; N, 5.01%; M$^+$, 265. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28%; M, 265.

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