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Photochemistry of Epoxynaphthoquinones. 8. Endo-Stereoselective Photocycloaddition of 2,3-Epoxy-2,3-dihydro-2,3-dimethyl-1,4-naphthoquinone to Olefins Containing Amide Group

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Irradiation of a benzene solution of 2,3-epoxy-2,3-dihydro-2,3-dimethyl-1,4-naphthoquinone with olefins containing amide group, i.e., *N*-substituted acrylamides and *N*-allylcarboxamides predominantly gave the endo-cycloadducts. Upon further irradiation, the cycloadducts underwent photorearrangement to give spirophthalides and alkylidenephthalides.

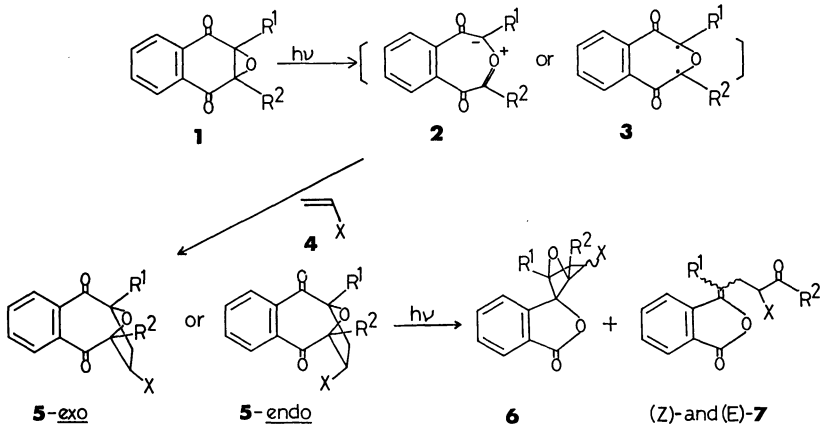
Recently, we reported the photochemical generation of the carbonyl ylide **2** or the 1,3-biradical **3** from several epoxynaphthoquinones **1**.[1] These intermediates were trapped by a variety of reagents including olefins,[2] ketones, aldehydes, singlet oxygen, and alcohol.[3] Reaction of **2** or **3** with olefin gave the tricyclic diketone **5**, which, upon further irradiation, underwent the secondary photorearrangement to produce the spirophthalide **6** and the alkylidenephthalides (*Z*)-**7** and (*E*)-**7**. (Scheme 1) The endo-exo stereoselectivity in the formation of the primary adduct **5** has been extensively studied in the photoreaction of 2,3-epoxy-2,3-dihydro-2,3-dimethyl-1,4-naphthoquinone (**1a**; R^1=R^2=Me) with a variety of functionalized olefins, whereby electron-releasing substituents show a endo-orientating tendency and electron-attracting substituents show a exo-orientating tendency.

Among these, cyano group has been found to be quite unique, since it shows remarkable high endo-orientating tendency in spite of its electron-attracting nature. In connection with these studies, we have studied the photoreaction of **1a** with olefins containing amide group, such as acrylamides and *N*-allylcarboxamides, so as to see the effect of nitrogen atom on the endo-exo stereoselectivity of the cycloaddition of **2** or **3**.

Results and Discussion

Photochemical Cycloaddition of 1a with *N*-Substituted Acrylamides. When a benzene solution of **1a** (0.04 M†) containing a high concentration (0.16 M) of *N*-phenylacrylamide (**4a**) was irradiated for 10 h, **1a** was mostly recovered and substantial amounts of polymeric materials derived from **4a** were formed. On the other hand, irradiation of a benzene solution of **1a** (0.04 M) containing a much less concentration (0.048 M) of **4a** for 10 h resulted in a smooth conversion of **1a**, giving the endo cyclodduct **5a**-*endo* (55%) along with the spirophthalide **6a** (25%) and the alkylidenephthalides (*Z*)-**7a** (6%) and (*E*)-**7a** (6%). In the latter photolysate, the amounts of polymeric materials derived from **4a** were greatly reduced.

These photoproducts were separated by column chromatography on silica gel, and their structures were determined on the basis of their spectroscopic properties (see Tables 5 and 6). The endo-



Scheme 1.

† 1 M=1 mol dm^{-3}.

stereochemistry of phenylcarbamoyl group in **5a**-*endo* was unambiguously determined by its independent synthesis from the tetracyclic adducts **8**, whose stereochemistry is apparently endo because of the hemiacetal structure.[2] Jones' oxidation of **8** afforded the corresponding carboxylic acid **5q**-*endo*, which, after treatment with oxalyl dichloride in dichloromethane, was reacted with aniline to give **5a**-*endo* in a 45% overall yield. In order to investigate the substituent effect of *N*-substituted acrylamides on the stereochemistry of the photocycloaddition of **1a**, we examined the photochemical reactions of **1a** with *N*-substituted acrylamides **4b—f**. The results are summarized in Table 1.

In the reaction with *N*-monosubstituted acrylamides **4a—d**, the stereochemistry of the primary adduct **5** is exclusively endo, regardless of the steric hindrance of *N*-substituents in olefins. Under identical conditions, isolated yields of **5c** and **5d** were lower than those of **5a** and **5b**, indicating that the secondary photorearrangements of **5c** and **5d** are faster than **5a** and **5b**. Since the secondary photorearrangement of **5** to **6** or **7** can be considered to proceed via a reversible α-cleavage (Eq. 1), more efficient secondary photoreaction of **5c**-*endo* and **5d**-*endo* may be ascribed to the buttressing effect of bulky substituents st the nitrogen, which may suppress the recombination of biradical **10** to **5**.

In sharp contrast to **4a—d**, the photochemical reaction of **1a** with *N*,*N*-disubstituted acrylamides **4e** and **4f** gave substantial amounts of **5e**-*exo* and **5f**-*exo*, along with **5e**-*endo* and **5f**-*endo*, **6e** and **6f**, and **7e** and **7f**, respectively. Structure determinations of the primary cycloadducts **5e**-*endo* and **5f**-*endo* were based on the independent synthesis of these compounds from **8**. Similary, the isomeric adducts **5e**-*exo* and **5f**-*exo* were independently synthesized from the tricyclic compounds **9**, whose structure had previously been well-established.[2]

Next, we have investigated the photochemical

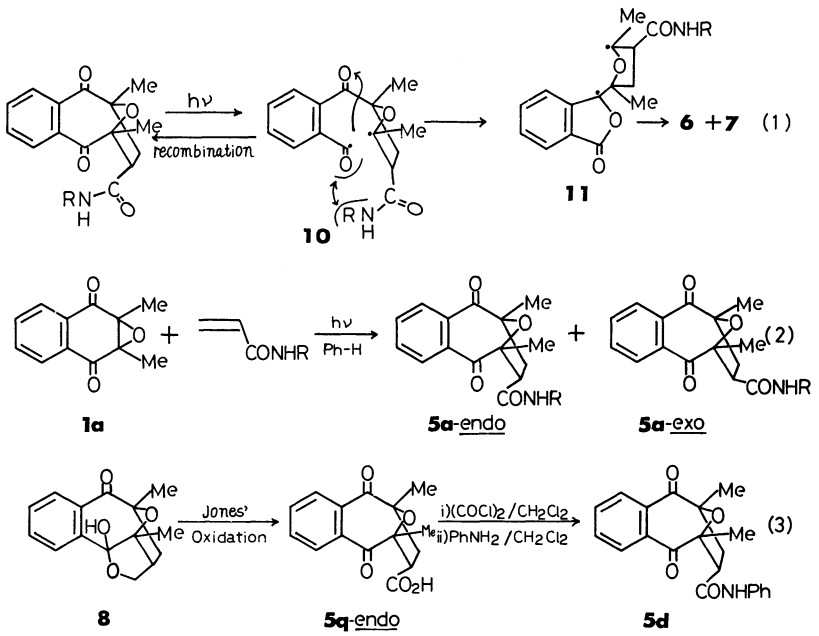


Table 1. Photoinduced Cycloaddition of Epoxynaphthoquinone **1a** to *N*-Substituted Acrylamides[a]

Run	Olefin		Irrad. time/h	Conversion %	Isolated yield[b]/%			
					5		6	7
					endo	exo		(Z)- (E)-
1	CH_2=CH·CONHPh	**4a**	3	61	55	0	25	12
2	CH_2=CH·CONHEt	**4b**	3	60	45	0	20	22
3	CH_2=CH·CONH·*t*-Bu	**4c**	3	90	7	0	32	48
4	CH_2=CH·CONHC_8H_{17}	**4d**	3	70	9	0	67	18
5	CH_2=CH·CONMe_2	**4e**	3	78	1	20	42	31
6	CH_2=CH·CONMe(Ph)	**4f**	2	72	0.8	18	29	41

a) A benzene solution of **1a** (0.04 M) and acrylamides (0.048 M) were used. b) Isolated yield based on the consumed amounts of **1a**.

cycloaddition reactions of **1a** with *N*-allylcarboxamides **4g—k**, which can be regarded as electron-rich olefin. Photoreaction of **1a** with **4g—k** proceeded well similarly with **4a—f**, giving **5g—k**-*endo*, **5g—j**-*exo*, **6g—k**, and **7g—k** in moderate to good yields. Isolated yields and physical properties of these photoproducts are listed in Tables 2, 5, and 6.

Photoinduced cycloaddition of **1a** to olefin consists primarily of two processes, namely photochemical oxirane ring opening leading to the formation of **2a** or **3a** and subsequent (presumably thermal) 1,3-dipolar cycloaddition of olefin to **2a** or **3a**. The first step has been well-shown to occur from the lowest triplet state of **1a**. In the previous studies on the photoreaction of **1a** with olefins, there has been also shown to exist a deactivating process for ^{3}(**1a**)* by charge transfer interactions with olefin.

Quantum yields for the disappearance of **1a** (0.04 M) in benzene containing various concentrations of olefins were determined at 313 nm by using valerophenone as the chemical actinometer[4] (Table 3). Quantum yields for the disappearance of **1a** in the reaction with acrylamide **4a**, **4d**, *N*-allylpropion-

Table 3. Quantum Yields for Disappearance of **1a**, Acrylamides, and *N*-Allylcarboxamides[a,b]

Olefin	Concd/M[c]	Φ_d^{1a} [d]	Φ_d^{o} [e]
CH_2=CH·CONHPh (**4a**)	0.04	0.027	0.040
	0.08	$<10^{-3}$	0.112
	0.16	$<10^{-3}$	0.141
CH_2=CH·CONHEt (**4b**)	0.04	0.032	0.037
	0.08	0.012	0.056
	0.20	$<10^{-3}$	0.087
CH_2=CH·CH_2NHCOEt (**4h**)	0.04	0.038	0.044
	0.08	0.008	0.042
	0.32	$<10^{-3}$	0.101
CH_2=CH·CH_2NHCOPh (**4j**)	0.04	0.041	0.053
	0.08	$<10^{-3}$	0.124
	0.16	$<10^{-3}$	0.190

a) Benzene solution of **1a** (0.04 M) were used. b) The conversions of **1a**, acrylamides, and *N*-allylcarboxamides were determined by HPLC. c) Concentration of olefin. d) Quantum yield for disappearance of **1a**. e) Quantum yield for disappearance of olefin.

Table 2. Photoinduced Cycloaddition of Epoxynaphthoquinone **1a** to *N*-allylcaboxamides[a]

Run	Olefin		Irrad. time/h	Conversion %	Isolated yield[b]/%			
					5		**6**	**7**
					endo	exo		(Z)- (E)-
1	CH_2=CH·CH_2NHCOMe	**4g**	3	58	52	6	15	24
2	CH_2=CH·CH_2NHCOEt	**4h**	3	60	60	3	12	21
3	CH_2=CH·CH_2NHCOC_7H_{15}	**4i**	3.5	90	46	4	12	31
4	CH_2=CH·CH_2NHCOPh	**4j**	3.5	85	23	0	25	48
5	CH_2=CH·CH_2N(Me)COMe	**4k**	2.5	88	1	17	15	57

a) A benzene solution of **1a** (0.04 M) and *N*-allylcarboxamides (0.048 M) were used. b) Isolated yields based on the consumed amounts of **1a**.

Table 4. The endo/exo Ratio of the Primary Adducts at an Early Stage[a] of Photochemical Reaction of **1a** with Acrylamides and *N*-Allylcarboxamides

Runs	Olefin		The *endo*/*exo* ratio of the Primary Adducts[b]		
			Ph-H	Ph-H/*t*-BuOH[c]	Ph-H/DMF[c]
1	CH_2=CH·CONHPh	**4a**	99	99	99
2	CH_2=CH·CONHEt	**4b**	99	99	99
3	CH_2=CH·CONH·*t*-Bu	**4c**	99	99	99
4	CH_2=CH·CON(Me)$_2$	**4e**	0.3	0.1	0.1
5	CH_2=CH·CON(Me)Ph	**4f**	0.1	0.06	0.1
6	CH_2=CH·CH_2NHCOEt	**4h**	4	2	3
7	CH_2=CH·CH_2NHCOPh	**4j**	99	99	99
8	CH_2=CH·CH_2N(Me)COMe	**4k**	0.3	0.2	0.2
9	CH_2=CH-CH_2-OH		18	5	3

a) The conversion of **1a** was less than 5%. b) The endo/exo of the primary adducts were determined by use of HPLC in the case of acrylamides and *N*-allylcaboxamides and by use of GC in the case of allyl alcohol. c) The ratio of Ph-H/*t*-BuOH and Ph-H/DMF was 50/50 by the volume.

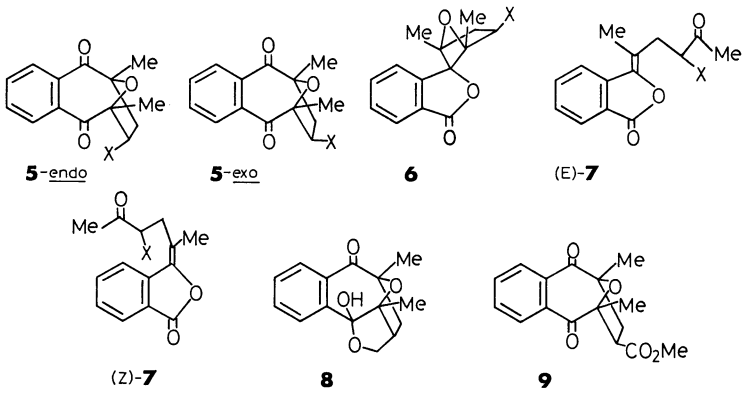


Fig. 1. Photoproducts of **1a** with acrylamides and *N*-allylcarboxamides.
a; X=CONHPh, b; X=CONHEt, c: X=CONH-*t*-Bu, d; X=CONH-*n*-C_8H_{17}, e; X=$CON(Me)_2$, f; X=CON(Me)Ph, g; X=$CH_2NHCOMe$, h; X=$CH_2NHCOEt$, i; X=CH_2NHCO-*n*-C_7H_{15}, j; X=$CH_2NHCOPh$, k; X=$CH_2N(Me)COMe$, q; X=CO_2H.

Table 5. Physical Properties of Primary Adducts **5**

Compound	Mp (θ_m/°C)	Formula	Found(%)	Calcd(%)	ν_{max}/cm^{-1} (KBr)
5a-*endo*	128—130	$C_{21}H_{19}O_4N$	C, 71.90	C, 72.19	2970, 1680, 1645
			H, 5.34	H, 5.48	1600, 1275, 1140
			N, 4.04	N, 4.01	
5b-*endo*	137—139	$C_{17}H_{19}O_4N$	C, 67.71	C, 67.76	2980, 1680, 1650
			H, 6.39	H, 6.35	1270, 1140, 980
			N, 4.81	N, 4.65	
5c-*endo*	199—201	$C_{19}H_{23}O_4N$	C, 69.50	C, 69.28	2980, 1670, 1640
			H, 7.13	H, 7.04	1250, 1145, 975
			N, 4.20	N, 4.25	
5d-*endo*	116—118	$C_{23}H_{31}O_4N$	C, 71.82	C, 71.66	2990, 1670, 1640
			H, 8.18	H, 8.10	1265, 1125, 975
			N, 3.60	N, 3.63	
5e-*exo*	127—129	$C_{17}H_{19}O_4N$	C, 67.60	C, 67.76	2980, 1685, 1640
			H, 6.39	H, 6.35	1270, 1145
			N, 4.80	N, 4.65	
5f-*exo*	134—136	$C_{22}H_{21}O_4N$	C, 72.80	C, 72.71	2980, 1680, 1640
			H, 5.88	H, 5.82	1600, 1275
			N, 3.90	N, 3.85	
5g-*endo*	145—147	$C_{17}H_{19}O_4N$	C, 67.71	C, 67.76	2975, 1680, 1650
			H, 6.25	H, 6.35	1280, 1150
			N, 4.67	N, 4.65	
5h-*endo*	137—139	$C_{18}H_{21}O_4N$	C, 68.45	C, 68.55	2990, 1670, 1640
			H, 6.75	H, 6.71	1280, 1150
			N, 4.52	N, 4.44	
5i-*endo*	149—151	$C_{23}H_{31}O_4N$	C, 71.53	C, 71.66	2950, 1690, 1640
			H, 8.23	H, 8.10	1240, 1170
			N, 3.72	N, 3.63	
5j-*endo*	137—139	$C_{22}H_{21}O_4N$	C, 72.50	C, 72.71	2960, 1680, 1645
			H, 5.79	H, 5.82	1600, 1245
			N, 3.90	N, 3.85	
5k-*exo*	132—134	$C_{18}H_{21}O_4N$	C, 68.33	C, 68.55	2960, 1695, 1645
			H, 6.84	H, 6.71	1275, 1160
			N, 4.49	N, 4.44	

amide (**4h**), *N*-allylbenzamide (**4j**) were one or two orders of magnitude lower compared with other functionalized olefins. Upon increasing the concentration of olefins, quantum yields for the formation of primary cycloadduct **5** decreased, whereas those for the disappearance of the olefin increased. Typically, irradiation of **1a** in the presence of high concentration of **4b** or **4j** (<ca. 0.2 M) merely resulted in the polymerization of the olefin, leaving **1a** almost intact in the reaction mixture. These facts clearly indicate the quenching of ^{3}(**1a**)* by olefins, presumably through the chrarge-transfer interactions.[5]

Since the primary cycloadducts **5** underwent the secondary photoreaction with different efficiencies depending upon their structures, the endo/exo ratios were determined at low conversions (<5%)(Table 4[5]). Results with allyl alcohol were included in Table 4 for the purpose of comparison. The cycloaddition with *N*-monosubstituted acrylamide **4a**, **4b**, and **4c** proceeds exclusively with endo stereoselectivity, while *exo*-cycloaddition was favored in the reaction with *N*,*N*-disubstituted acrylamide. The reaction with *N*-allylpropinamide (**4h**) and *N*-allylbenzamide (**4j**) proceeded also with endo-stereoselectivity, but the selectivity of **4h** was much less than in the reaction with *N*-monosubstituted acrylamide and **4j**. However, as in the reaction with acrylamides, endo-stereoselectivity was inverted from endo to exo in the reaction with *N*-allyl-*N*-methylacetamide (**4k**); the endo/exo=0.3. Remarkably high endo-stereoselectivity observed with **4a**—**c**, **4i**, and **4j** and inversed exo-stereoselectivity with **4e**, **f**, and **k** suggest the favorable

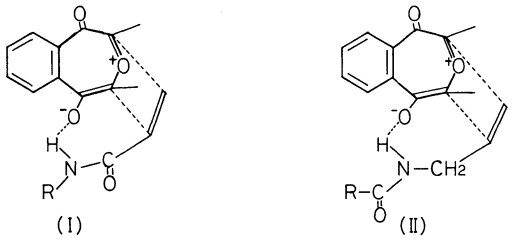


Fig. 2. Photochemical cycloaddition of **1a** with acrylamides and *N*-allylcarboxamides.

Table 6. ^{1}H NMR ($CDCl_3$, δ) of Primary Adducts **5**

Compound	Me^1, Me^2	H_{arom}	H_{others}
5a-*endo*	1.62	7.3—7.6(m, 5H)	2.39(dd, J=8 and 14Hz, 1H), 2.84(dd, J=8 and 13Hz,
	1.66	7.7—7.9(m, 2H)	1H), 3.30(dd, J=7 and 12Hz, 1H), 6.02(br, 1H)
		7.9—8.2(m, 2H)	
5b-*endo*	1.50	7.5—7.8(m, 2H)	1.18(t, 3H), 2.50(dd, J=8 and 14Hz, 1H), 2.85(dd,
	1.62	7.8—8.1(m, 2H)	J=8 and 15Hz, 1H), 3.35(t, 1H), 5.74(br, 1H)
5c-*endo*	1.67	7.7—7.9(m, 2H)	1.31(s, 9H), 2.23(dd, J=8 and 13Hz, 1H), 2.68(dd,
	1.77	7.9—8.2(m, 2H)	J=6 and 12Hz, 1H), 3.21(dd, J=8 and 12Hz), 6.30 (br, 1H)
5d-*endo*	1.54	7.6—7.8(m, 2H)	0.90(t, 3H), 1.32(br, 12H), 2.34(dd, J=6 and 12Hz, 1H),
	1.68	7.9—8.2(m, 2H)	2.52(dd, J=7 and 13Hz, 1H), 3.35(m, 2H), 5.75(br, 1H)
5e-*exo*	1.48	7.6—7.8(m, 2H)	2.40(dd, J=7 and 12Hz, 1H), 3.04(s, 3H), 2.80(dd,
	1.72	7.9—8.0(m, 2H)	J=8 and 13Hz, 1H), 3.12 (s, 3H), 3.60 (dd, J=6 and 8Hz, 1H)
5f-*exo*	1.40	7.2—7.6(m, 4H)	2.24(dd, J=8 and 13Hz, 1H), 2.85(dd, J=8 and 13Hz,
	1.55	7.7—8.1(m, 4H)	1H), 3.08(s, 3H), 3.38(t, 1H)
5g-*endo*	1.56	7.5—7.7(m, 2H)	1.96(s, 3H), 2.34(dd, J=8 and 12Hz, 1H), 2.64(dd,
	1.60	7.7—7.9(m, 2H)	J=6 and 8Hz, 1H), 2.90(dd, J=6 and 8Hz, 1H), 3.58—3.88(m, 2H), 6.04(br, 1H)
5h-*endo*	1.58	7.7—7.9(m, 2H)	1.16(t, 3H), 2.24(q, 2H), 2.62(dd, J=6 and 11Hz, 1H),
	1.62	7.9—8.1(m, 2H)	3.48(dd, J=6 and 10Hz, 1H), 3.72(dd, J=6 and 8Hz, 1H)
5i-*endo*	1.60	7.6—7.8(m, 2H)	0.91(t, 3H), 1.28(br, 8H), 1.66(br, 2H), 2.22(t, 2H),
	1.62	7.9—8.2(m, 2H)	2.64(dd, J=6 and 8Hz, 1H), 2.91(dd, J=6 and 8Hz, 1H), 3.60(dd, J=6 and 8Hz, 1H), 3.73(dd, J=6 and 8Hz, 1H), 6.54(br, 1H)
5j-*endo*	1.53	7.2—7.5(m, 4H)	2.14(dd, J=8 and 11Hz, 1H), 2.68(dd, J=8 and 13Hz,
	1.55	7.6—7.9(m, 4H)	1H), 3.60(dd, J=6 and 8Hz, 1H), 3.70—3.96(m, 2H), 6.05(br, 1H)
5k-*exo*	1.62	7.5—7.7(m, 2H)	2.10(s, 3H), 2.48(dd, J=8 and 13Hz, 1H), 2.67(dd,
	1.74	7.8—8.1(m, 2H)	J=8 and 12Hz, 1H), 2.93(d, 2H), 3.42(dd, J=8 and 12Hz, 1H), 3.92(t, 2H)

hydrogen-bonding interaction by amide N–H bond in the transition state of the cycloaddition such as I and II in Fig. 2. Similar interaction may explain a relatively high endo-selectivity of allyl alcohol.

Thus, we examined the effects of hydrogen-bond donating or accepting solvent upon the endo-exo stereoselectivity in the formation of **5** (Table 4). Exclusive endo-selective stereochemistry observed with **4a—c** and **4j** was not affected by addition of *t*-BuOH or *N,N*-dimethylformamide (DMF). However, the endo/exo ratio in the reaction with **4h** decreased by addition of *t*-BuOH and DMF (Run 6, in Table 4). Much more prominent solvent effects are observed in the reaction of **1a** with allyl alcohol (Run 9, in Table 4), indicating that the hydrogen-bonding interaction plays an important role in determination of 1,3-dipolar cycloaddition stereochemistry.

High endo-selective stereoselectivity in the reaction of **1a** with **4a—c** and **4j** may be accounted for in terms of the interplay of the strong hydrogen bond and the secondary orbital overlap between the carbonyl ylide and the amide nitrogen lone pair in the olefins. Although we have not succeeded in a quantitative assessment of these interactions, it may be considered that amide N–H bond at an appropriate position can control the stereochemistry of cycloaddition of epoxynaphthoquinone (**1a**).

Experimental

Apparatus. Melting points were measured on Yanagimoto micro-melting points apparatus and are uncorrected. Infrared spectra were taken on a JASCO-IR-1A spectrometer. ^{1}H NMR spectra were recorded on a JEOL GX-400 (400 MHz) and a JEOL FX-90Q (90 MHz) spectrometer with use of tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. UV spectra were taken by using a Shimadzu UV-200 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Mass spectra were recorded on a JEOL JNM DX-300 spectrometer. High pressure liquid chromatography (HPLC) analyses were performed on a Yanaco LC-2000 equipped with an UV detector (Yanaco M-315). The separations were made on a 250×4 mm stainless-steel column packed with Shodex ODS pack F-411 with a mixture of methanol and water (80/20) as the eluent. GC analyses were performed on a Hitachi Model 163, using a 3 mm i.d., ×2 M stainless-steel column packed with 10% SE-30 on celite 545 AM. Preparative separations were performed by column chromatography over silica gel (Wakogel C-200). UV irradiations were carried out in a Pyrex vessel (Fuji glass) under a nitrogen atmosphere with a Fuji glass 300-W high-pressure mercury lamp.

Materials. 2,3-Epoxy-2,3-dihydro-2,3-dimethyl-1,4-naphthoquinone[2] (**1a**) was prepared by the epoxidation of 2,3-dimethyl-1,4-naphthoquinone with 10% aqueous sodium hypochlorite in pyridine. *N*-Substituted acrylamides **4a—f** were prepared by the condensation of acryloyl chloride with the corresponding amines at temperature below 5 °C.[6] *N*-Allyl-carboxamides **4g—k** were prepared by condensation of allyl amine with the corresponding acyl chlorides at temperature below 5 °C. *N,N*-Dimethylacrylamide **4e** and *N*-Allyl-*N*-methyl-acetamide **4k** were prepared by the alkylation of the corresponding amides with methyl iodide in dimethyl sulfoxide.

General Procedure for the Photochemical Reaction of 1a with Acrylamides and *N*-Allylcarboxamides. A degassed solution of **1a** (1 mmol) and acrylamides or *N*-allylcarboxamides (1.2 mmol) in 25 ml of benzene in a Pyrex tube, using a 300-w high-pressure mercury lamp from outside. The progress of the reaction was followed by thin-layer chromatography (TLC), HPLC or GC. After removal of solvent, the residual oil was separated by chromatography on silica gel with ethyl acetate / hexane as an eluent. Final purification was usually accomplished by preparative TLC and recrystallization. Physical properties of the photoproducts were summarized in Table 5 and 6.

Transformation of 9 into the Primary Adduct (5e-*exo*). A mixture of **9** (100 m), 10 ml of 5% aqueous NaOH, and 10 ml of isopropyl alcohol was heated at 50 °C under a nitrogen atmosphere for 4 h. Then the reaction mixture was acidified with 5% aqueous HCl. The resulting mixture was extracted twice with ether, and the combined extracts were washed with water and dried over Na_2SO_4. Removal of the solvent on a rotary evaporator afforded crude acid (**5q**-*exo*). This was treated with oxalyl dichloride in dry dichloromethane, giving the acid chloride. After dimethylamine hydrochloride was added to the acyl chloride under a nitrogen atmosphere, the reaction mixture was stirred at room temperature for 12 h. Removal of the solvent on a rotary evaporator afforded the crude amide, which was chromatographed on silica gel to yield the primary adduct (**5e**-*exo*) (47 mg, 45%) (mp 128—129 °C).

Measurement of Quantum Yields. Valerophenone actinometry was used for quantum yield determination. The 313-nm line was isolated with a filter solution containing 0.002 M K_2CrO_4 in a 1% aqueous solution of K_2CO_3. The degree of the reaction was determined by HPLC analyses relative to a known concentration of internal standard (naphthalene) in the case of acrylamides and *N*-allylcarboxamides. The standard naphthalene was added after the photoreaction. And in the case of allyl alcohol the degree of the reaction was determined by GC analysis relative to a known concentration of internal standard (dodecane).

References

1) S. Arakawa, *J. Org. Chem.*, **42**, 3800 (1978).

2) A. Osuka, H. Suzuki, and K. Maruyama, *J. Chem. Soc., Perkin. Trans. 1*, **1982**, 2671 and references cited therein.

3) A. Osuka, *J. Org. Chem.*, **48**, 1712 (1983) and references cited therein.

4) The energy (E_T) of the lowest triplet state of **1a** is determined to be 68 kcal mol^{-1} (1 cal=4.184 J) by its phosphorescence spectrum, although E_T of **4a**, **4d**, **4h**, and **4g** is not available.

5) For example, the relative reactivity of **5h**-*endo*/**5h**-*exo* was about 4.

6) R. E. Harm, B. L. Jensen, S. K. Gupta and J. D. Nelson, *J. Org. Chem.*, **35**, 825 (1970).