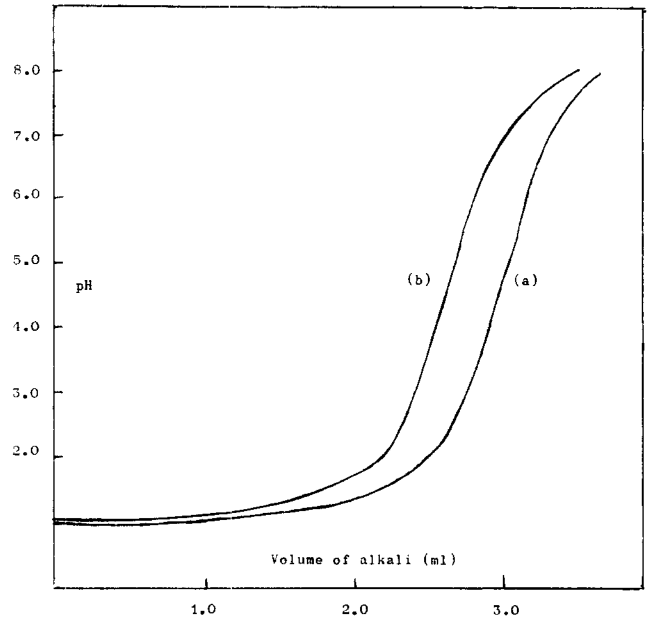

Figure 1. pH metric curves of $HClO_4$–Bu_4NOH systems in alcoholic medium when ionic strength (0.06 M) was maintained with $Bu_4N^+I^-$: (a) in the absence of chalcone, and (b) in the presence of chalcone (0.005 M).

Table II. Efficiency of Different Alkalies toward Cyclization of Chalcone (Medium of Work, E_{75}; Alkali:Chalcone, 1:1)

Molar concn of each reactant, M	Time of contact, h	% cyclization		
		KOH	NaOH	LiOH
0.1	2	72[a]	68[a]	Nil[b]
	5	82	80	Nil
	20	86	86	Nil
0.03	2	75	71	Li^+–$Chal^-$ + flavanone[c]
	5	87	88	92[d]
	20	90	90	Flavanone + Li^+–$Chal^-$
0.01	2	78	76	Flavanone Li^+–$Chal^-$
	5	88	88	94
	20	92	93	94[d,e]

[a] In the earlier stages of the reaction NaOH and KOH are even less efficient; for a contact period of 30 min, % cyclization with KOH (70) and NaOH (61) is as shown in parentheses. [b] Li^+–chalconate only was recovered. [c] Products are shown in the order of relative yield. [d] A few crystals of Li^+–chalconate were present. [e] Contamination by Li^+–chalconate shows that decyclization of the product also starts taking place due to an extended period of contact of the latter with LiOH.

MOH because the proton eliminated as MOH is polarized indirectly by M^+ which is a Lewis acid.

Cyclization of Chalcone. Very dilute (4×10^{-4} M) solutions of chalcone at pH 11 are cyclized by LiOH, NaOH, KOH, and Bu_4NOH in 54, 38, 23, and 18 min, respectively. This indicates that the anion of M^+–chalconate cyclizes rapidly as the charge density of M decreases and the strength of the M^+–phenoxide ion pair loosens. The results in Table II also indicate that at high concentration (0.1 M) cyclization is favored in the order LiOH, NaOH, and KOH and as the alkali/chalcone ratio is decreased. However, at intermediate concentrations (e.g., 0.03 M) efficiency of the alkalies is in the order KOH, NaOH, and LiOH. This can be attributed to M^+–π interaction as shown for E in Scheme I, an interaction which fails to contribute toward the stability of the M^+–chalconate at high dilution (4×10^{-4} M) and goes undetected at high concentrations (0.1 M) due to a dominating contribution of the M^+–phenoxide ion pair. The following observation confirms the activity of unsaturation of the aliphatic part in E.

When $HClO_4$ is titrated in the pH range 2 to 8 (where the chalcone does not ionize) in the presence and absence of chalcone employing NaOH and Bu_4NOH as alkalies, chalcone is found to decrease the concentration of $HClO_4$ but only in the case of Bu_4NOH (see Figure 1). This shows that a neutral molecule of chalcone deprotonates $HClO_4$ to become itself protonated in the cavity through M^+–π bonds as with M^+ in E. The "encapsulated" proton can be replaced by the small-sized Na^+ during titration but not by the bulky Bu_4N^+ which competes unfavorably on steric as well as charge-density grounds. If protonation should have taken place outside the cavity, say at the carbonyl group, then both the alkalies could deprotonate the H^+–chalcone complex successfully.

Mechanism of Cyclization. The mechanism of the cyclization is also described in Scheme I. The M^+–π interaction in E enhances the carbonium character at the β carbon and also loosens the $-O^-M^+$ ion pair. The phenoxy anion so destabilized attacks the β carbon to produce the closed-ring labile carbanion salt (F). The latter hydrolyzes easily to produce the flavanone.

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Registry No.—HAP, 582-24-1; BLD, 100-52-7; chalcone, 94-41-7; flavanone, 487-26-3.

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Photochemical Reactions of Aromatic Compounds. 27.[1] Stereospecific Photocycloaddition of *cis*- and *trans*-1-Methoxypropenes to 2-Naphthonitrile

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The photocycloadditions of olefinic compounds and furan to aromatic nitriles usually occur in a stereoselective manner[2-4] and have been discussed in terms of exciplexes. In a previous paper,[2a] we reported that irradiation of 2-naphthonitrile (**1**) and alkyl vinyl ethers at 313 nm exclusively gives endo [2 + 2] cycloadduct **5a**, whereas that at >280 nm for a longer time results in formation of a cyclobutene compound **3** as a main product. In this note, we report the stereospecific photocycloadditions of *cis*- and *trans*-1-methoxypropenes (**4c** and **4t**) to 2-naphthonitrile (**1**).

Table I. ^1H NMR Spectra of 5 and 6[a]

Registry no.	Compd	δ (multiplicity) H-1	H-4	H-5	H-7	H-8	CH_3	OCH_3	Coupling constant, Hz $J_{1,8}$	$J_{7,8}$	J_{8,CH_3}
62930-47-6	**5c**	3.79	6.50	5.68	4.38	2.88	0.81	3.42	9.5	8.0	7.5
		(d)	(AB quartet)		(d)	(m)	(d)	(s)			
62961-30-2	**5t**	2.87	6.59	5.63	3.90	2.52	1.14	3.44	9.5	8.5	6.5
		(d)	(AB quartet)		(d)	(m)	(d)	(s)			
62961-31-3	**6c**	3.48	6.50	5.70	3.81	2.66	1.14	3.53	8.5	6.5	7.0
		(d)	(AB quartet)		(d)	(m)	(d)	(s)			
62961-32-4	**6t**[b]	*c*	6.34	5.76	3.90	3.20	0.87	3.37	*c*	*c*	7.0
			(AB quartet)		*c*	(m)	(d)	(s)			

[a] In CCl_4 using tetramethylsilane as internal standard. Aromatic resonances [δ 7.9–8.5 (m, 4 H)] are omitted. [b] The spectrum was obtained by subtracting the signals of **5t** from the spectrum of a mixture of **5t** and **6t**. [c] Not determined.

Table II. Rate Constants (k_q) for Quenching of 2-Naphthonitrile Fluorescence by Enol Ethers[a]

Registry no.	Enol ether	Adiabatic IP, eV	$k_q\tau$, M^{-1}	k_q, $M^{-1}s^{-1}$	log k_q
109-92-2	**2**[b]	8.49[h]	0.46	4.17×10^7	7.62
116-11-0	**7**[c]		1.43	1.29×10^8	8.11
110-87-2	**8**[d]	8.34[i]	2.46	2.22×10^8	8.35
4696-26-8	**9t**[e]		12.2	1.10×10^9	9.04
4696-25-7	**9c**[f]	8.04[h]	25.3	2.28×10^9	9.36
17574-84-4	**10**[g]	7.65[h]	93.9	8.46×10^9	9.93

[a] Concentration of **1**, 1.5×10^{-4} M in air-saturated cyclohexane. [b] Ethyl vinyl ether. [c] 2-Methoxypropene. [d] Dihydropyran. [e] *trans*-1-Ethoxypropene. [f] *cis*-1-Ethoxypropene. [g] 1-Methoxy-2-methylpropene. [h] N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **97**, 2482 (1975). [i] K. Watanabe, T. Nakayama, and J. R. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

Results and Discussion

Irradiation of a benzene solution containing **1** and **4c** through Pyrex with a high-pressure mercury arc gave **5c** and **6c** in ca. 7:3 ratio in quantitative yield. Similarly, irradiation of **1** and **4t** gave **5t** and **6t** in ca. 4:1 ratio. VPC and NMR analyses of the photolysates showed that any other 1:1 adducts were not formed. Irradiation for a longer time resulted only in the slight change of the **5** to **6** ratio.

From NMR and mass spectra, all the products were confirmed to have an identical skeletal arrangement. By means of VPC–mass analyses, they were found to reveal essentially identical mass spectra, the weak parent peak at *m/e* 225 and the strong fragment peaks at *m/e* 153 and 72. The UV spectra of **5c** and **5t** were characteristic of the 1,2-dihydronaphthalene chromophore.[5]

The NMR spectra of the four adducts were very similar. They consisted of an AB quartet of olefinic protons, a sharp singlet of methoxy protons, a sharp doublet of methyl protons, and two sets of doublets and a multiplet of three methine protons. The couplings of the methine protons were readily analyzed by the first-order analyses and double irradiation experiments. In the case of **5c**, for example, the doublets at δ 0.31, 3.79, and 4.38 were collapsed into singlets by irradiation at δ 2.88 (m), respectively, thus confirming the vicinal couplings of the proton (H-8) attaching to methyl-substituted carbon with the other methine protons (H-1 and H-7). The NMR data are listed in Table I. The configurations of the cyclobutane ring were determined by comparing the chemical shifts of H-7, H-8, and methyl protons of the four cycloadducts; molecular models show that the protons located in the endo direction must be shielded by the anisotropic effects of the benzene ring and/or the double bond, unlike the corresponding protons located in the exo direction.

When **5c** and **6c** were heated at 300 ± 10 °C, **4c** and **4t** were obtained in 9:1 ratio. Similarly, the thermolysis of **5t** gave **4c** and **4t** in 1:4 ratio. Moreover, the direct photolysis of **5c** or **5t** in the presence of a triplet quencher[6] gave **4c** or **4t** each in >95% specificity. The thermal decomposition of cyclobutane compounds usually favors stereochemical retention in formation of olefins[7] and the Woodward–Hoffmann rule predicts that the concerted $[2_s + 2_s]$ cycloreversion is allowed in the electronically excited state.[8] Therefore, these results provide further support for the structures assigned.

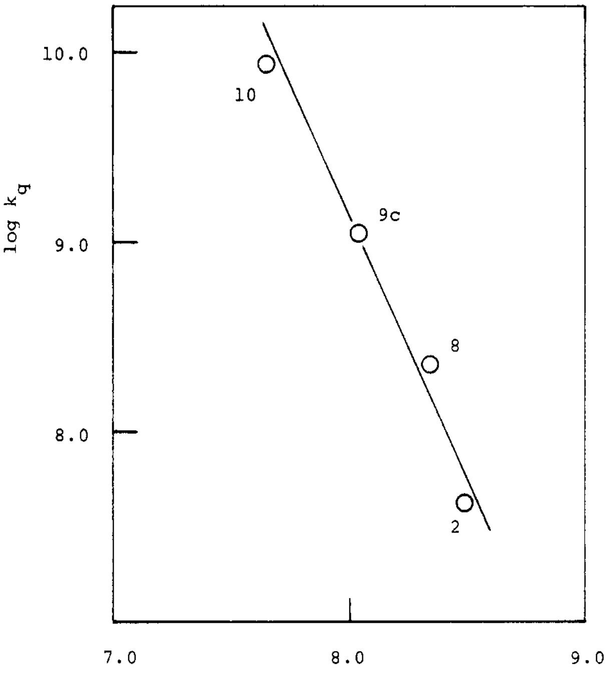
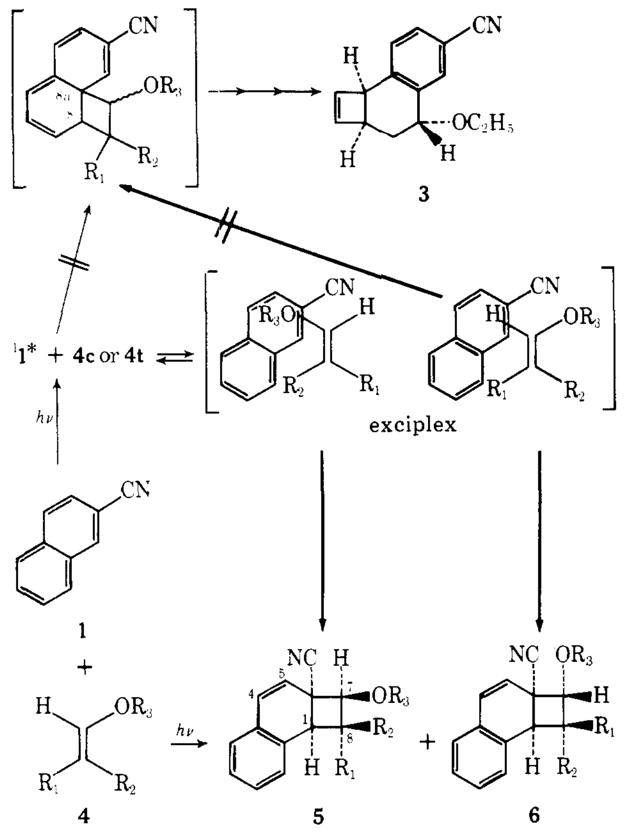


Figure 1. Correlation of log k_q vs. adiabatic ionization potential of enol ethers (abstracted from Table II).

The fluorescence of **1** was quenched by various enol ethers and the quenching rates increase with the decrease of the ionization potentials of enol ethers (Table II and Figure 1). The values of k_q were obtained from the Stern–Volmer slopes ($k_q\tau$) and the lifetime of excited singlet **1** (τ = 11 ns).[9] The

Scheme I



	R_1	R_2	R_3
2, 5a:	H	H	C_2H_5
4c, 5c, 6c:	H	CH_3	CH_3
4t, 5t, 6t:	CH_3	H	CH_3

linear correlation of log k_q vs. ionization potentials suggests a charge transfer mechanism for the fluorescence quenching. Fluorescence quenching by 1-methoxy-2-methylpropene was accompanied by the appearance of an exciplex emission (λ_{max} 435 ± 5 nm) with an isoemissive point at 418 nm. Moreover, the photocycloadditions of **4c** and **4t** were quenched by pyridine, but not at all by piperylene. This result provides evidence for the exciplex intermediacy, since pyridine is a good quencher for exciplexes involving **1**, but does not quench **1** fluorescence.[1] Therefore, the $_\pi2_s + _\pi2_s$ photocycloaddition of **4c** and **4t** proceeds in a concerted manner via singlet exciplexes.

It is noteworthy that **5c** and **5t** possessing the *endo*-methoxy group predominate over **6c** and **6t**, respectively. This endoselective orientation of the methoxy group reflects favorable configuration of the exciplexes.

In contrast to the photocycloaddition of **2** to **1**, that of **4c,t** gave the "exo" adduct **6c,t** even to minor extents, but not such adducts as **3**; steric effects of the methyl group of **4c,t** allow the approach of **4c,t** in the exo orientation of the methoxy group and inhibit the addition to the C(8)–C(8a) bond of **1** (Scheme I).

Experimental Section

The following instruments were used for spectral measurements: ^{1}H NMR, Hitachi R-24 (60 MHz) and JEOL JNM JS-100 (100 MHz); IR, Hitachi EPI-S2; UV, Hitachi 124; mass spectra, Hitachi RMU-6E; fluorescence spectra, Hitachi MPF-2A. VPC–mass analyses were carried out on a Hitachi RMS-4 machine. VPC was carried out on a Shimadzu GC-2C equipped with a flame ionization detector using a column of Ucon oil LB-550X (5% on Celite 545, 1.5 m) at 160 °C or PEG 20M (20% on Celite 545, 3 m) at 100 °C. 2-Naphthonitrile was obtained from tokyo Kasei and was purified by vacuum distillation and recrystallization from hexane. *cis*- and *trans*-1-Methoxypropenes were prepared according to the method cited in literature[10] and were separated by preparative VPC using a column of PEG 6000. The purities were over 95%. Methyl isobutenyl ether was prepared by the method of Böhme and Bentler.[11] All the enol ethers were distilled from anhydrous potassium carbonate before use.

Photoreaction with *cis*-1-Methoxypropene (4c). A solution of **1** (0.3 g, 2 mmol) and **4c** (3 mL) in 30 mL of benzene placed in a Pyrex glass tube was irradiated with an Eikosha PIH-300 high-pressure mercury arc for 10 h at ambient temperature. After removal of solvent and excess **4c**, the residual oil was chromatographed on silica gel using mixtures of benzene–hexane as eluent. After recovery of 50 mg of **1**, further elution gave 200 mg of **5c**: mp 65–66 °C; IR (CCl_4) 2240, 1150 cm^{-1}; UV (cyclohexane) λ_{max} 275 sh (ϵ 6300), 267 nm (6800); mass spectrum *m/e* 225 (M^+).

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.84; H, 6.65; N, 6.16.

Further elution gave 150 mg of a mixture of **5c** and **6c**, from which 30 mg of **5c** crystallized out. Repeated chromatography of the mixture gave ca. 50 mg of **6c**, including a small amount of **5c** which was an oil. On storage of this mixture in a refrigerator it did not solidify.

Photoreaction with *trans*-1-Methoxypropene (4t). In a similar way, a benzene solution (30 mL) of **1** (0.3 g, 2 mmol) and **4t** (3 mL) was irradiated for 10 h. Column chromatography of the photolysate on silica gel gave 60 mg of **1** and 230 mg of **5t**, which was recrystallized from methanol: mp 127.5–129 °C; IR (CCl_4) 2240, 1150 cm^{-1}; UV (cyclohexane) λ_{max} 277 sh (5300), 268 nm (5800); mass spectrum *m/e* 225 (M^+).

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.75; H, 6.71; N, 6.08.

Further elution gave ca. 100 mg of a mixture of **5t** and **6t**, from which 30 mg of **5t** crystallized out. Repeated chromatography of the mixture gave only a mixture enriched by **6t**, which did not solidify on storage in a refrigerator.

Photolysis of 5c and 5t. A solution of **5c** or **5t** (10 mg) and ferrocene (5 mg) in 1 mL of acetonitrile placed in a Pyrex tube was irradiated with a high-pressure mercury arc. During the course of the irradiation, the photolysate was analyzed by VPC at 5-min intervals for the initial 30 min; it was found that **1** and **4c** or **4t** increased linearly with the disappearance of **5c** or **5t**. Irradiation for 1 h resulted in the complete decomposition of **5c** or **5t**.

Quenching Experiments. Solutions of 0.05 M **1** and 0.5 M **4c** or **4t** in ethyl acetate and in pyridine were prepared. Another solution of 0.05 M **1**, 0.5 M **4c** or **4t**, and 0.05 M piperylene in ethyl acetate was also prepared. Irradiation was carried out for 2 mL of each solution through an aqueous potassium biphthalate solution (>300 nm) with a high-pressure mercury arc using a merry-go-round apparatus. The photolysates were analyzed by VPC; it was found that irradiation for 30 min resulted in ca. 20% conversion of **1** for ethyl acetate solutions, independently of the presence and absence of piperylene, while any products could not be detected for pyridine solutions.

Registry No.—**1**, 613-46-7; **4c**, 4188-68-5; **4t**, 4188-69-6.

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