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Photochemical Reactions of 1,2-Dicyanonaphthalene with Alkenes and Dienes

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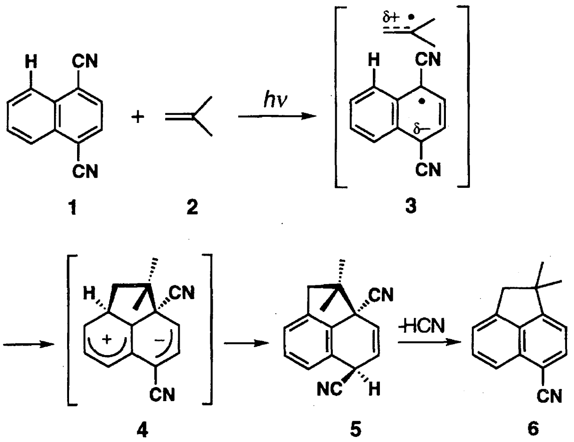
The photoreaction of 1,2-dicyanonaphthalene (**7**) with 2-methyl-1-propene (**2**) in acetonitrile gave a [3+2]adduct at the 1,8-position of the naphthalene ring of **7** with loss of hydrogen cyanide, a [2+2+2]adduct consisting of **7**, **2** and acetonitrile, and a cyclobutene-fused derivative, while that in benzene afforded a [3+2]adduct without loss of hydrogen cyanide and the cyclobutene-fused derivative. Yields of the products largely depended on the composition of the acetonitrile–benzene mixed solvent. The results suggested a polar nature of the [2+2+2]addition and a less polar nature of the formation of the cyclobutene-fused derivative. A maximal total yield (32%) of the [3+2]adducts was obtained in solvents containing 20—30 volume percent of acetonitrile. [3+2]Photocycloadditions at the 1,8-position of the naphthalene ring of **7** were found to be general in the reactions with cyclopentene, styrene, 1,3-butadiene, and isoprene. No photoreactions with 1-hexene were observed, possibly due to the poor electron-donating ability of 1-hexene. The generality of the [3+2]photocycloaddition was discussed in terms of the free energy change associated with single-electron transfer from alkenes or dienes to the singlet excited state of **7**.

There has been considerable interest in the photocycloadditions of arenes, such as benzene, naphthalene, anthracene, and phenanthrene derivatives, to alkenes and dienes from synthetic and mechanistic viewpoints.[1] Especially, [2+2]-,[2] [4+2]-,[3] and [4+4]photocycloadditions[4] of naphthalene derivatives to alkenes and dienes have been extensively investigated and have provided important clues to the mechanism of photocycloadditions. In contrast with the numerous investigations on [2+2]-, [4+2]-, and [4+4]photocycloadditions of arenes, a very limited number of [3+2]-cycloadditions, five-membered ring formation, has so far been known: these include meta-cycloadditions of benzene derivatives[5] and formal [3+2]cycloadditions by way of rearrangement of initially formed 1,4-biradicals to carbenes[6] and nitrenes.[7]

On the other hand, we have found a novel 1,8-photoaddition of naphthalene derivatives, such as 1,4-dicyanonaphthalene (**1**), to alkenes, a formal [3+2]cycloaddition, which proceeds from the singlet excited state of **1** possibly via formation of an exciplex **3** and almost synchronous two bond formation in **3** to give a zwitterion **4**, followed by proton transfer (Eq. 1).[8,9]



(1)

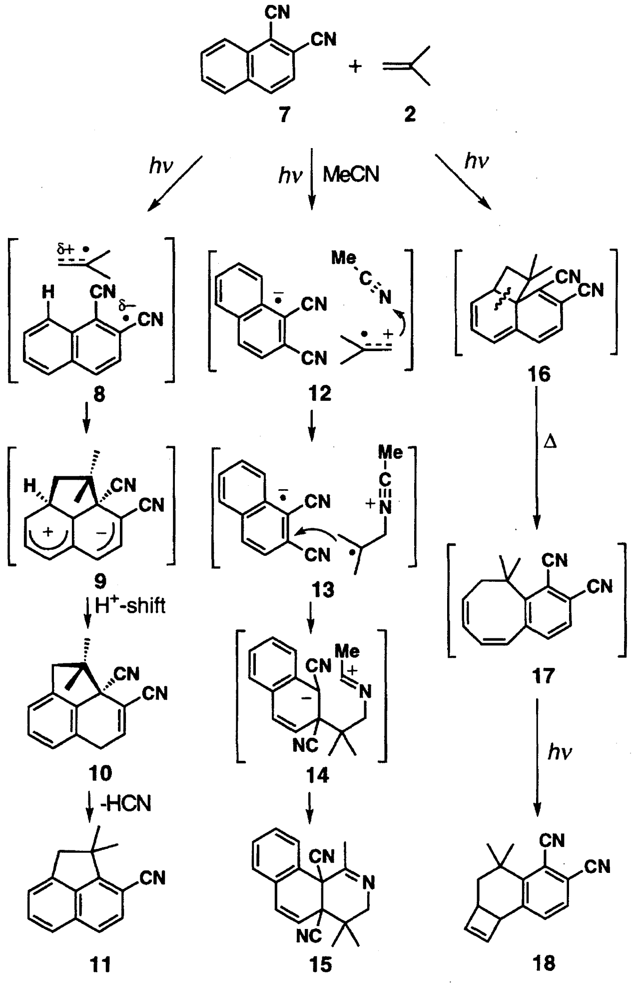
However, our studies on the [3+2]photocycloadditions have been restricted to the reactions of naphthalene derivatives having two electron-withdrawing substituents, such as cyano and methoxycarbonyl groups, at the 1,4-positions of the naphthalene ring. Our interest in the study of the effect of the positions of the substituents on the photoreactions prompted us to study the photoreactions of other position isomers of **1** with alkenes and dienes.[10]

We here report on photochemical reactions of 1,2-dicyanonaphthalene (**7**) with alkenes and dienes, in which [3+2]-cycloadditions at the 1,8-position of the naphthalene ring of **7** have been observed fairly generally. Other photoreactions, a [2+2+2]addition and a formation of a cyclobutene-fused derivative, are found to proceed in competition with the [3+2]cycloaddition in the reactions with 2-methyl-1-propene (**2**).

Results and Discussion

Photoreactions with 2-Methyl-1-propene. Irradiation of an acetonitrile solution of **7** (4.0×10^{-3} mol dm^{-3}) and **2** (1.0 mol dm^{-3}) with a high-pressure Hg lamp through a uranium filter (> 320 nm) under a nitrogen atmosphere at ambient temperature gave, as the major products, a [3+2]-adduct **11** at the 1,8-position of the naphthalene ring of **7** with loss of hydrogen cyanide, together with a [2+2+2]adduct **15** consisting of **7**, **2** and acetonitrile, and a cyclobutene-fused derivative **18**, which may have occurred from a [2+2]photocycloaddition of **7** to **2** at the 8,8a-position of the naphthalene ring of **7** to give a cyclobutane **16** followed by a thermal ring opening to **17** and a photochemical electrocyclic reaction of **17** (Scheme 1). Formation of a similar cyclobutene-fused derivative has been reported in the photoreaction of 2-cyanonaphthalene with ethyl vinyl ether.[11] On the other hand, when the photoreaction was carried out in benzene, a [3+2]-adduct **10** without loss of hydrogen cyanide, instead of **11**, and **18** were obtained as the major products.

These products were separated by repeated column chromatography on silica-gel. However, **10** could not be obtained in pure form due to the partial loss of hydrogen cyanide in the purification process. Ready conversion of **10** into **11** in acetonitrile at ambient temperature in an almost quantitative yield confirmed that **10** is the precursor of **11** in the photoreaction in acetonitrile. The elimination of hydrogen cyanide from **10** may have a polar nature and may be promoted in polar solvents, such as acetonitrile. Although a number of inseparable minor products were observed in the photoreaction mixtures obtained in acetonitrile and in benzene, there was no evidence for the formation of other isomers of the adducts **10**, **11**, **15**, and **18**, such as [3+2]adducts at the 4,5-position of the naphthalene ring of **7** and regioisomers of **15** and **18**.



Scheme 1.

The structures of **10** and **11** were assigned mainly on their ^{1}H NMR spectra, while IR and mass spectral properties together with elemental analysis strongly supported the structure of **11**. Thus, the ^{1}H NMR spectrum of **10** shows the presence of the one vinyl proton ($\delta = 7.18$, $J = 2.6$ and 5.5 Hz, CH_2–C*H*=C–CN) adjacent to the methylene group ($\delta = 3.58$ and 3.83) and the presence of the three consecutive aromatic protons ($\delta = 7.09$, 7.20, and 7.31). The presence of the long range coupling ($J = 0.8$ Hz) between one of the methylene protons ($\delta = 3.32$) attached to the newly formed five-membered ring and one of the aromatic protons ($\delta = 7.09$) supports the assigned structure of **10**, and thus the regiochemistry of the addition of **2**.

The structure of **15** was assigned on the basis of the spectral properties. The mass spectrum of **15** showed the M^+ peak at m/z 275 ($C_{18}H_{17}N_3$), which firmly supported the incorporation of acetonitrile in **15**. The IR (1667 cm^{-1}) and ^{13}C NMR ($\delta = 156.32$) spectra clearly demonstrated the presence of the C=N structure in **15**. The ^{1}H NMR spectrum shows the presence of the long range coupling ($J = 1.4$ and 2.4 Hz) between the methyl protons ($\delta = 1.83$) which result from acetonitrile and the methylene protons ($\delta = 3.50$ and 3.72) which result from **2**. Furthermore, the structure of **15**, thus the regiochemistry of addition of **2** and acetonitrile, was confirmed by the observed nuclear Overhauser effect (NOE): irradiation of one ($\delta = 1.32$) of the gem-dimethyl group led to enhancement (9.0%) of one ($\delta = 5.86$) of the vinyl protons and irradiation of the vinyl proton ($\delta = 5.86$) also led to enhancement (2.3%) of the methyl protons ($\delta = 1.32$). Irradiation of the protons of other methyl groups ($\delta = 1.32$ and 1.55) did not result in enhancement of the vinyl protons. Similar NOE has been reported for other acetonitrile-incorporated [2+2+2]adducts.[12,13]

The structure of **18** was also assigned on the basis of the spectral properties. The presence of the long range coupling ($J = 1.0$ Hz) between one of the methine protons attached to the cyclobutene ring ($\delta = 4.02$) and one of the aromatic protons ($\delta = 7.51$) in the ^{1}H NMR spectrum supports the assigned structure, thus the regiochemistry of the addition of **2**. The regiochemistry of the addition of **2** corresponded well to the regiochemistry of addition observed in the photoreaction of 2-cyanonaphthalene with ethyl vinyl ether.[11]

Yields of the products **10**, **11**, **15**, and **18**, based on the consumed **7**, during the course of the photoreactions of **7** with **2** in benzene and in acetonitrile were determined by ^{1}H NMR analyses; the results are summarized in Table 1. Table 1 shows that the yields of the products remain almost constant in the range of about 30—90% conversion. The results confirmed the stability of the products under the photoreaction conditions. Table 1 also shows that the photoreaction in acetonitrile is approximately five to six times faster than that in benzene.

To clarify the effect of the solvent polarity on product yields, the photoreactions of **7** with **2** were carried out in various acetonitrile–benzene mixed solvents; the results are summarized in Table 2. Table 2 clearly shows a remarkable difference of dependency of the three types of the photore-

Table 1. Photoreactions of 1,2-Dicyanonaphthalene (**7**) with 2-Methyl-1-propene (**2**)[a)]

Solvent	Irradiation time/h	Conversion/%	Yield[b)]/%			
			10	**11**	**15**	**18**
C_6H_6	12	34	11	—	—	21
	24	76	10	—	—	20
	36	81	12	—	—	23
MeCN	2	31	—	17	16	4
	4	53	—	17	18	4
	6	71	—	16	17	4
	8	88	—	17	16	4

a) Irradiation conditions are as follows; $h\nu > 320$ nm, under N_2, at ambient temperature, [**7**] = 4.0×10^{-3} mol dm^{-3}, [**2**] = 1.0 mol dm^{-3}. b) Yield, based on consumed **7**, determined by ^{1}H NMR analysis.

actions on the solvent composition. Thus, as decrease of the volume percentage of acetonitrile in the solvent, the total yield of **10** and **11** increased up to 32% in the range of 20—30 volume percent of acetonitrile and then sharply decreased finally to 11% in pure benzene; the yield of **15** decreased markedly in the range of 50—30 volume percent of acetonitrile; on the contrary, the yield of **18** gradually increased as decrease of the volume percentage of acetonitrile. The results suggest a polar nature of both the [3+2]cycloaddition and the [2+2+2]addition, and a less polar nature of the formation of the cyclobutene-fused derivative. The mechanisms for the [3+2]cycloaddition, involving polar intermediates such as an exciplex **8** and a zwitterion **9**, and that for the formation of the cyclobutene-fused derivative, involving less-polar intermediates such as **16** and **17**, may reasonably explain the dependency of the reactions on the solvent polarity. It may be interesting that the total yield of the [3+2]adducts **10** and **11** can be considerably improved by using a suitable mixed solvent, compared with those in pure solvent systems.

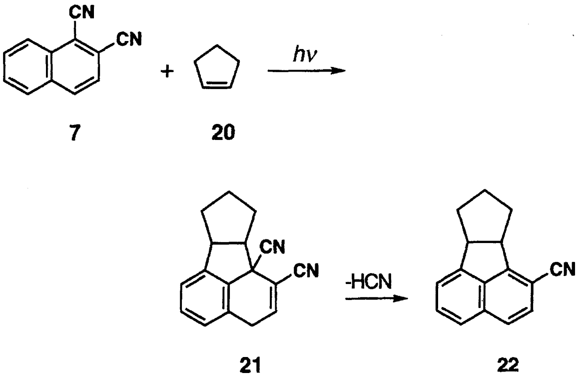
Photoreactions with Other Alkenes. The photoreactions of **7** (4.0×10^{-3} mol dm^{-3}) with 1-hexene (**19**, 1.0 mol dm^{-3}) in acetonitrile and in benzene resulted only in almost quantitative recoveries of the starting material **7**. The relatively large positive free energy change ΔG_{et} associated with the single-electron transfer from **19** to the singlet excited states of **7** and a negligibly small fluorescence quenching by **19** in both solvents (vide infra) can account for the low photoreactivity of **7** toward **19**.

Table 2. Photoreactions of 1,2-Dicyanonaphthalene (**7**) with 2-Methyl-1-propene (**2**) in Acetonitrile–Benzene Mixed Solvents[a)]

Vol% of MeCN	Yield[b)]/%				
	10	**11**	**10+11**	**15**	**18**
100	0	17	17	16	4
80	0	17	17	17	4
60	0	19	19	15	6
50	0	23	23	13	7
40	15	14	29	8	8
30	25	7	32	0	11
20	26	6	32	0	13
10	21	3	24	0	15
0	11	0	11	0	21

a) Irradiation conditions are as follows; $h\nu > 320$ nm, under N_2, at ambient temperature, [**7**] = 4.0×10^{-3} mol dm^{-3}, [**2**] = 1.0 mol dm^{-3}. b) Yield, based on consumed **7**, determined by ^{1}H NMR analysis (conversion 70—90%).

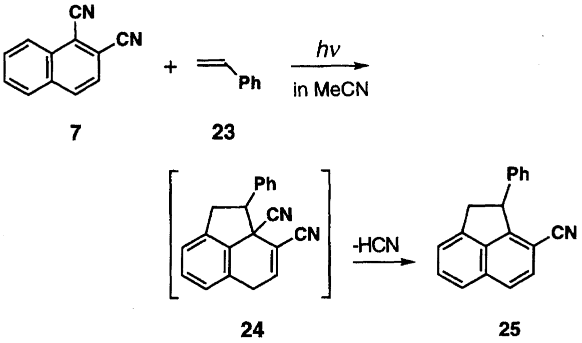
The photoreaction of **7** (4.0×10^{-3} mol dm^{-3}) with cyclopentene (**20**, 8.0×10^{-1} mol dm^{-3}) in benzene gave a [3+2]adduct **22** with loss of hydrogen cyanide in 40% yield, together with a trace amount of a [3+2]adduct **21**, which could not be isolated in pure form due to the instability as in the case of **10** (Eq. 2). The result indicates that the loss of hydrogen cyanide in **21** proceeds easier than that in **10**, the [3+2]adduct of **7** to **2**. The photoreaction in acetonitrile only gave a mixture of a number of inseparable minor products.



(2)

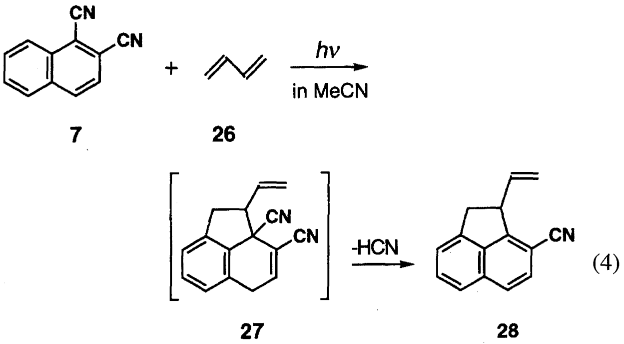
The photoreactions of **7** (4.0×10^{-1} mol dm^{-3}) with 2-methyl-2-butene (1.0×10^{-1} mol dm^{-3}) in acetonitrile and in benzene and those with 2,3-dimethyl-2-butene (1.0×10^{-1} mol dm^{-3}) in the two solvents only gave respective complex mixtures of a number of inseparable minor products. In these cases,there was no evidence for the formation of [3+2]adducts despite the careful examinations of the reaction mixtures.

The photoreaction of **7** (4.0×10^{-3} mol dm^{-3}) with styrene (**23**, 8.8×10^{-2} mol dm^{-3}) in acetonitrile gave a complex mixture of minor products, from which a [3+2]adduct **25** with loss of hydrogen cyanide was obtained in only 5% yield (Eq. 3). The photoreaction in benzene only gave a mixture of a number of inseparable minor products.



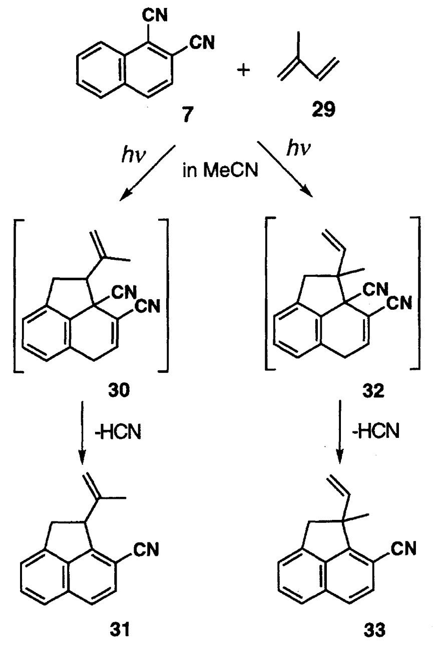
(3)

Photoreactions with Dienes. The [3+2]photocycloadditions of **7** also proceeded to dienes. Thus, the photoreaction of **7** (4.0×10^{-3} mol dm^{-3}) with 1,3-butadiene (**26**, 1.0 mol dm^{-3}) in acetonitrile gave a [3+2]adduct **28** at the 1, 8-position of the naphthalene ring of **7** in 80% yield (Eq. 4). There was no evidence for the formation of [3+2]adducts at the 4,5-positions of the naphthalene ring of **7**, despite the careful examinations of the reaction mixture. The photoreaction in benzene only gave a mixture of a number of inseparable minor products.



(4)

The photoreaction of **7** (4.0×10^{-3} mol dm^{-3}) with isoprene (**29**, 8.0×10^{-1} mol dm^{-3}) in acetonitrile gave two isomers of [3+2]adducts **31** and **33** at the 1,8-position of the naphthalene ring of **7** in 20 and 20% yield, respectively (Scheme 2). From the viewpoint of the product yields, the selectivity of the [3+2]photocycloaddition to the two kinds of the double bonds in **29** was rather low. The photoreaction in benzene only gave a mixture of a number of inseparable minor products.



Scheme 2.

Fluorescence Quenching and Calculations of the Free Energy Change ΔG_{et} Associated with the Photochemical Electron Transfer. There was no evidence from the UV spectra for a preformed ground-state complexes between **7** and 2-ethyl-1-butene, a liquid model compound for **2**, or between **7** and **20**. On the other hand, **7** showed clear fluorescence in air-saturated benzene and acetonitrile with lifetimes, τ, of 7.4 and 7.9 ns, respectively. The fluorescence of **7** was inefficiently but significantly quenched by 2-ethyl-1-butene and **20** without changing the shape and wavelength of the maximum emission, although the fluorescence quenching by **19** was found to be negligibly small. Stern–Volmer plots of the fluorescence quenching by 2-ethyl-1-butene and **20** in air-saturated benzene and acetonitrile gave straight lines against concentration of the alkenes. Fluorescence quenching rate constants k_q calculated from the Stern–Volmer slopes $k_q\tau$ and the τ values, assuming that the quenching processes are irreversible, are shown in Table 3. The results imply that the 72% of the singlet excited state of **7** is quenched by **2** in acetonitrile under the reaction conditions ([**2**] = 1.0 mol dm^{-3}), based on the $k_q\tau$ value of 1.59 mol^{-1} dm^{3} for the model compound.

The free energy changes ΔG_{et} associated with the single-electron transfer from the alkenes and diene to the singlet excited state of **7** can be calculated by using[14]

$$\Delta G_{et} = 96.4[E^{ox} - E^{red}] - E_S - C. \qquad (5)$$

In this equation, E^{ox} is the one-electron oxidation potential for the alkenes and diene, E^{red} is the one-electron reduction potential for **7** (−1.36 V), E_S is the energy of the singlet excited state of **7** (336.5 kJ mol^{-1} estimated from the absorption and fluorescence spectra), and C is the "Coulombic attraction term," 5.4 kJ mol^{-1} in acetonitrile.[14] The E^{ox} values determined by cyclic voltammetry as a peak potential at the scan-

Table 3. Quenching of the Fluorescence of 1,2-Dicyanonaphthalene (**7**) by Alkene[a)]

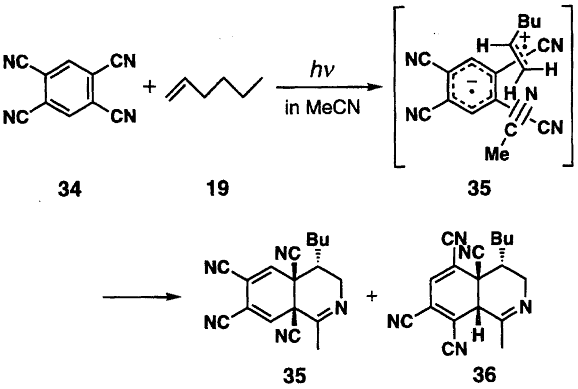
Alkene	Solvent	$k_q\tau$[b)]/mol^{-1} dm^3	τ/ns	k_q/mol^{-1} dm^3 s^{-1}
1-Hexene (**19**)	C_6H_6	0[c)]	7.4	0
	MeCN	0[c)]	7.9	0
2-Ethyl-1-butene[d)]	C_6H_6	0.563	7.4	1.4×10^{7}
	MeCN	1.59	7.9	2.0×10^{8}
Cyclopentene (**20**)	C_6H_6	1.04	7.4	1.4×10^{8}
	MeCN	31.6	7.9	4.0×10^{9}

a) Experimental conditions are as follows; [**7**] = 1.0×10^{-4} mol dm^{-3}, at 25 °C, in air-saturated solvent. b) Stern–Volmer slope for the fluorescence quenching. c) Negligibly small fluorescence quenching was observed. d) As a liquid model compound for 2-methyl-1-propene (**2**).

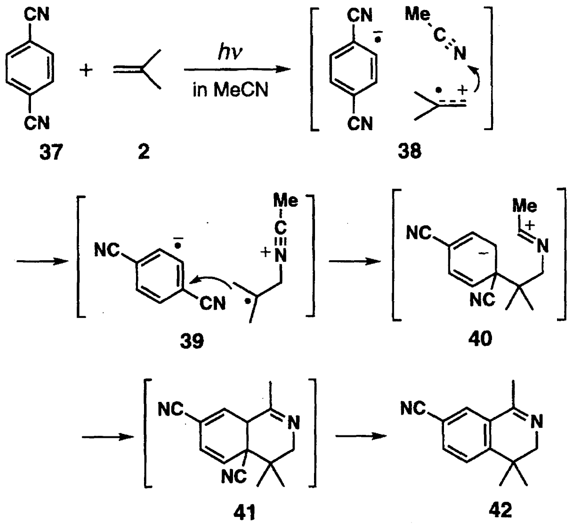
ning rate of 100 mV s^{-1} and the calculated ΔG_{et} values are summarized in Table 4, in which the ΔG_{et} values to the singlet excited states of **1** ($E^{\mathrm{red}} = -1.31$ V, $E_{\mathrm{S}} = 344.9$ kJ mol^{-1}), 1,3-dicyanonaphthalene ($E^{\mathrm{red}} = -1.16$ V, $E_{\mathrm{S}} = 357.8$ kJ mol^{-1}), and 2,3-dicyanonaphthalene ($E^{\mathrm{red}} = -1.70$ V, $E_{\mathrm{S}} = 348.6$ kJ mol^{-1}), together with observed types of the photoadditions in the reaction systems of dicyanonaphthalene and alkene or diene, are also shown.

A small positive ΔG_{et} value of 5.1 kJ mol^{-1} for the system of **7** and **2** can account the inefficient fluorescence quenching by the model compound of **2**.

[2+2+2]Photoaddition. As for the [2+2+2]addition, only two examples corresponding to the present reaction have so far been known, to our knowledge; a formation of [2+2+2]adducts **35** (29%) and **36** (12%) in the photoreaction of 1,2,4,5-tetracyanobenzene (**34**) with **19** in acetonitrile (Eq. 6) reported by Vanossi, Mella, and Albini[12] and a formation of a [2+2+2]adduct **42** (70%) with loss of hydrogen cyanide in the photoreaction of 1,4-dicyanobenzene (**37**) with **2** in acetonitrile (Eq. 7) reported by Lijser and Arnold.[13] In the reactions of **34** with a variety of alkenes, the [2+2+2]addition has been observed only in the reaction with one particular alkene **19**. The ΔG_{et} value for the single-electron transfer from **19** to the singlet excited state of **34** was reported to be -0.3 eV and that from **2** to the singlet excited state of **37** to be close to zero. Vanossi, Mella, and Albini have proposed a concerted mechanism within an exciplex **35** with no discrete charged intermediate for the addition (Eq. 6). Lijser and Arnold have proposed a stepwise mechanism, in which after initial electron transfer from **2** to the singlet excited state of **37**, radical coupling of the radical anion of **37** and a radical cation formed from the reaction of the radical cation of **2** with acetonitrile affords a zwitterion **40** as the key intermediate (Eq. 7).



(6)



(7)

In the photoreactions of **7**, the [2+2+2]addition was observed only in the reaction with **2**. Furthermore, the corresponding [2+2+2]addition has not been observed in the photoreactions of other isomers of dicyanonaphthalenes, such as **1**, 1,3- and 2,3-dicyanonaphthalenes, with a variety of alkenes and dienes (Table 4). Thus, the [2+2+2]addition seems to be not so general in the photoreactions of dicyanonaphthalenes

Table 4. Calculated Free Energy Change (ΔG_{et}) Associated with Single-Electron Transfer from Alkene and Diene to the Singlet Excited States of 1,2-, 1,3-, 1,4-, and 2,3-Dicyanonaphthalenes and Observed Types of the Photoadditions in the Systems

Alkene	E^{ox} a)/V	ΔG_{et} b)/kJ mol^{-1} (Observed type of photoaddition)c)			
		Dicyanonaphthalene			
		1,2 (**7**)	1,3	1,4 (**1**)	2.3
1-Hexene (**19**)	2.49	29.2	−11.3	16.0	49.9
		(No Reaction)	(3+2, 2+2)	(3+2)	(No Reaction)
2-Methyl-1-propene (**2**)	2.24	5.1	−35.4	−8.1	25.8
		(3+2, 2+2+2, 2+2)	(3+2, 2+2)	(3+2, 2+2)	(No Reaction)
1,3-Butadiene (**26**)	2.12	−6.4	−47.0	−19.6	14.2
		(3+2)	—d)	(3+2)	(4+4)
Styrene (**23**)	2.04	−14.1	−54.7	−27.4	6.5
		(3+2)	—d)	(3+2)	(2+2, 3+2)

a) Experimental conditions for measurements are as follows; [alkene or diene] = 1.0×10^{-3} mol dm^{-3} in 0.1 mol dm^{-3} $\mathrm{Bu_4NClO_4}$/acetonitrile, at ambient temperature, with a carbon electrode, normalized as E^{ox} (ferrocene) = 0.428 V. b) Calculated by Eq. 5. c) 3+2; [3+2]Photocycloadditions to form five-membered ring structures: 2+2; [2+2]photocycloadditions (cyclobutane formation) and formation of cyclobutene-fused derivatives occurred from secondary reactions of cyclobutanes: 4+4; [4+4]photocycloaddition to form eight-membered ring structure: 2+2+2; a [2+2+2]photocycloaddition of **7**, **2**, and acetonitrile. d) Not examined.

with alkenes and dienes, but a unique reaction restricted in the reaction with **2**. The [2+2+2]addition could proceed only under rigorous requirements. The ΔG_{et} value of close to zero (5.1 kJ mol^{-1}) may be the one of the requirements. Although it appears to be difficult to interpret the mechanism, as well as the observed regiochemistry, of the present [2+2+2]addition from our limited results, the polar nature of the reaction, as inferred from the effect on the solvent polarity, may support the more polar stepwise mechanism as shown in Scheme 1.

[3+2]Photocycloadditions. The present investigations clearly indicate that, in contrast with the [2+2+2]addition, the [3+2]photocycloadditions are fairly general in the photoreactions of **7** with a variety of alkenes and dienes as in the reactions of other position isomers of dicyanonaphthalenes (Table 4).

The [3+2]cycloadditions of **7** proceeded only at the 1,8-position of the naphthalene ring; no [3+2]cycloadditions at the 4,5-position of the naphthalene ring of **7** were observed even in the photoreaction systems, in which the [3+2]adducts were obtained in high yields. The regiochemistry of the [3+2]cycloadditions of **7** differs markedly from that of the [3+2]cycloadditions of 1,3-dicyanonaphthalene to alkenes, in which the [3+2]cycloadditions occur only at the 4,5-position of the naphthalene ring of the dicyanonaphthalene. The difference in regiochemistry of the [3+2]cycloadditions may be rationalized on the basis of the spin and charge densities of the radical anions of the dicyanonaphthalenes.[10)]

As for the effect of the alkene structure, the [3+2]photocycloadditions of **7** were quite general in the reactions with ethylenes substituted by two alkyl groups, such as **2** and **20**, and with ethylenes substituted by a vinyl or a phenyl group, such as **23**, **26**, and **29**. On the contrary, no photoreactions proceeded in the reactions with **19**, an ethylene substituted by one alkyl group, and only complex mixtures of minor products other than the [3+2]adducts were obtained in the photoreactions with 2-methyl-2-butene and with 2,3-dimethyl-2-butene, ethylenes substituted by three and four alkyl groups, respectively. Table 4 indicates that, in the photoreactions with **19**, no reactions are observed in the reactions of the 1,2-isomer (**7**) and 2,3-isomer of dicyanonaphthalenes, but the [3+2]cycloadditions readily proceed in the reactions of 1,3-isomer and 1,4-isomer (**1**). Furthermore, as for the photoreactions of the 2,3-isomer no reactions proceed even in the reactions with **2**, an ethylene substituted by two alkyl groups.

For a given arene-alkene pair, the ΔG_{et} associated with single-electron transfer from the alkene to the excited state of the arene has been recognized to be a good measure for prediction of the mode of addition when the interaction between the arenes and alkenes involves extensive charge transfer.[15)] As for the photoreactions of dicyanonaphthalenes with alkenes, Table 4 shows the relationship between the ΔG_{et} values for the systems and the observed types of the photoadditions. Table 4 clearly indicates that, in the region $\Delta G_{\mathrm{et}} > +25.8$ kJ mol^{-1}, no reactions are observed, as in the cases of the reaction of **7** with **19** and those of 2,3-dicyanonaphthalene with **19** and **2**. In the meantime, Table 4 shows that the [3+2]cycloadditions are characteristic reactions in the region $+16.0 > \Delta G_{\mathrm{et}} > -35.4$ kJ mol^{-1}. Thus, the occurrence of the [3+2]cycloadditions may be governed by the generation of reactive partners as exciplexes (or contact ion pairs) from the interaction between the singlet excited state of dicyanonaphthalenes with alkenes and dienes, involving less extensive charge transfer.

Experimental

Melting points were obtained on a Yanagimoto micro melting point apparatus and are uncorrected. NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) instrument. Chemical shifts are reported in ppm (δ) relative to internal $\mathrm{SiMe_4}$. IR spectra were determined by use of a JASCO FT/IR-350 spectrometer. Low-resolution (EI, 70 eV) and high-resolution (EI) mass spectra were recorded on a Hitachi M-80B mass spectrometer. Fluorescence spectra and fluorescence lifetimes were obtained on a Hitachi 850 spectrophotometer and on a Horiba NAES-1100 time-resolved spectrofluorometer, respectively. Combustion analyses were performed on a Yanagimoto CHN corder MT-5. Reduction potential was determined by use of a Yanaco cyclic polarography P-900.

Materials. 1,2-Dicyanonaphthalene (**7**) was available from Tokyo Kasei Inc. and was used after recrystallization from ethanol Unsaturated compounds **2**, **19**, **20**, **23**, **26**, and **29** were also commercially available and were purified by distillation if liquid. Solvents were purified by distillation after dehydration. Fluorescence-spectrograde solvents obtained from Nacalai Tesque Inc. were used as received for the fluorescence spectrum measurement and the lifetime determination.

Photochemical Procedures and Product Isolation. UV irradiation of **7** (4.0×10^{-3} mol dm^{-3}) and unsaturated compounds **2**, **19**, **20**, **23**, **26**, and **29** (concentrations are given in the text) in $\mathrm{N_2}$ purged solvent was carried out with an Eikosha EHB-W-300 high-pressure Hg-lamp through a uranium-filter ($\lambda > 320$ nm). The reaction was monitored by TLC (Merck, Kieselgel 60 F254) analyses and ^{1}H NMR measurements. After evaporation of the solvent, the residue was subjected to column chromatography (Wakogel C-200; eluent, benzene–ether). Yields of the products are given in the text or in Tables 1 and 2.

Data for Photoproducts. Irradiation of 7 with 2-Methyl-1-propene (2). Data for (2a*RS*)-2a,3-Dicyano-2,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene (10): Oil; ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 0.97$ (s, 3H), 1.75 (s, 3H), 2.67 (d, $J = 15.5$ Hz, 1H), 3.32 (dd, $J = 0.8$, 15.5 Hz, 2H), 3.58 (dd, $J = 5.5$, 22.6 Hz, 1H), 3.83 (dd, $J = 2.6$, 22.6 Hz, 1H), 7.09 (dd, $J = 0.8$, 7.6 Hz, 1H), 7.18 (dd, $J = 2.6$, 5.5 Hz, 1H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H).

Data for 3-Cyano-2,2-dimethyl-1,2-dihydroacenaphthylene (11): Mp 89—90 °C (ether–hexane); ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 1.65$ (s, 6H), 3.33 (s, 2H), 7.36—7.68 (m, 5H); ^{13}C NMR ($\mathrm{CDCl_3}$) $\delta =$ 28.01 (q), 45.41 (s), 48.35 (t), 101.35 (s), 118.24 (s), 121.19 (d), 122.82 (d), 124.14 (d), 129.32 (d), 131.17 (d), 132.93 (s), 136.58 (s), 144.03 (s), 160.20 (s); IR (KBr) 820, 1618, 2220, 2961 cm^{-1}; MS *m*/*z* (rel intensity) 207 (M^{+}; 29), 192 (100), 177 (18), 165 (24), 96 (13), 69 (14). Found: *m*/*z* 207.1077. Calcd for $\mathrm{C_{15}H_{13}N}$: M, 207.1048. Found: C, 87.13; H, 6.28; N, 6.69%. Calcd for $\mathrm{C_{15}H_{13}N}$: C, 86.92; H, 6.32; N, 6.76%.

Data for 4a,10b-Dicyano-1,4,4-trimethyl-3,4,4a,10b-tetrahydrobenz[*h*]isoquinoline (15): Oil; ^{1}H NMR ($\mathrm{CDCl_3}$) $\delta = 1.32$ (s, 3H), 1.55 (s, 3H), 1.83 (dd, $J = 1.4$, 2.4 Hz, 3H), 3.50 (dd, $J = 2.4$, 8.6 Hz, 1H), 3.72 (dd, $J = 1.4$, 8.6 Hz, 1H), 5.86 (d, $J = 9.8$ Hz, 1H), 6.71 (d, $J = 9.8$ Hz, 1H), 7.18 (m, 1H), 7.46 (m, 2H), 7.93 (m, 1H); ^{13}C NMR (CDCl$_3$) δ = 23.53, 24.19, 24.75, 29.29, 34.21, 45.56, 48.02, 58.59, 96.12, 116.28, 117.32, 121.49, 125.38, 127.05, 127.70, 128.33, 129.56, 130.32, 132.12, 156.32; IR (CHCl$_3$) 1375, 1522, 1667, 2239 3023 cm^{-1}; MS *m/z* (rel intensity) 275 (M$^+$; 3), 194 (17), 178 (46), 72 (18), 56 (100). Found: *m/z* 275.1458. Calcd for C$_{18}$H$_{17}$N$_3$: M, 275.1422.

Data for (2a*RS*,8b*SR*)-5,6-Dicyano-4,4-dimethyl-2a,3,4,8b-dihydrocyclobuta[*a*]naphthalene (18): Oil; ^{1}H NMR (CDCl$_3$) δ = 1.46 (s, 3H), 1.67 (dd, $J = 11.4$, 14.2 Hz, 1H), 1.70 (s, 3H), 1.93 (dd, $J = 6.8$, 14.2 Hz, 1H), 3.42 (m, $J = 4.4$, 6.8, 11.4 Hz, 1H), 4.02 (dd, $J = 1.0$, 4.4 Hz, 1H), 6.18 (d, $J = 2.7$ Hz, 1H), 6.35 (d, $J = 2.7$ Hz, 1H), 7.51 (dd, $J = 1.0$, 7.9 Hz, 1H), 7.59 (d, $J = 7.9$ Hz, 1H); IR (CHCl$_3$) 815, 1520, 2222, 2957 cm^{-1}; MS *m/z* (rel intensity) 234 (M$^+$; 19), 219 (88), 208 (33), 193 (100), 178 (65), 165 (36), 152 (25), 138 (27). Found: *m/z* 234.1180. Calcd for C$_{16}$H$_{14}$N$_2$: M, 234.1157.

Irradiation of 7 with Cyclopentene (20). **Data for (6b*SR*,9a*RS*,9b*SR*)-1,9b-Dicyano-6b,7,8,9,9a,9b-hexahydro-3*H*-cyclopent[*a*]acenaphthylene (21):** Oil; ^{1}H NMR (CDCl$_3$) δ = 1.0—2.1 (m, 6H), 3.41 (m, 1H), 3.58 (dd, $J = 5.9$, 23.3 Hz, 1H), 3.76 (d, $J = 23.3$ Hz, 1H), 4.11 (m, 1H), 7.11 (dd, $J = 0.8$, 7.2 Hz, 1H), 7.17 (d, $J = 5.5$ Hz, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.31 (t, $J = 7.2$ Hz, 1H).

Data for (6b*SR*,9a*RS*)-1-Cyano-6b,8,9,9a-tetrahydro-7*H*-cyclopent[*a*]acenaphthylene (22): Oil; ^{1}H NMR (CDCl$_3$) δ = 1.52—2.31 (m, 6H), 4.15 (m, 1H), 4.26 (m, 1H), 7.38 (m, $J = 1.2$, 3.2 Hz, 1H), 7.55 (d, $J = 8.6$ Hz, 1H), 7.65 (dd, $J = 0.7$, 8.6 Hz, 1H), 7.61 (m, 1H), 7.65 (m, 1H); IR (CHCl$_3$) 823, 1620, 2232, 2960 cm^{-1}; MS *m/z* (rel intensity) 219 (M$^+$; 100), 177 (65), 151 (27). Found: *m/z* 219.1052. Calcd for C$_{16}$H$_{13}$N: M, 219.1048.

Irradiation of 7 with Styrene (23). **Data for (2*RS*)-3-Cyano-2-phenyl-1,2-dihydroacenaphthylene (25):** Mp 106—107 °C (ether–hexane); ^{1}H NMR (CDCl$_3$) δ = 3.46 (dd, $J = 2.9$, 17.9 Hz, 1H), 4.04 (dd, $J = 8.3$, 17.9 Hz, 1H), 5.02 (dd, $J = 2.9$, 8.3 Hz, 1H), 7.14 (m, 2H), 7.29 (m, 3H), 7.46 (m, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.69 (m, 3H); ^{13}C NMR (CDCl$_3$) δ = 42.06 (t), 49.69 (d), 117.38 (s), 121.25 (d), 122.98 (d), 124.42 (d), 124.65 (d), 127.12 (d), 127.73 (d), 128.79 (d), 131.26 (d), 132.84 (s), 136.52 (s), 138.04 (s), 143.03 (s), 145.38 (s), 155.27 (s); IR (KBr) 705, 829, 1492, 2225, 2928 cm^{-1}; MS *m/z* (rel intensity) 255 (M$^+$; 100), 226 (13), 177 (61), 151 (19), 77 (19). Found: *m/z* 255.1072. Calcd for C$_{19}$H$_{13}$N: M, 255.1048. Found: C, 89.32; H, 5.17; N, 5.41%. Calcd for C$_{19}$H$_{13}$N: C, 89.38; H, 5.13; N, 5.49%.

Irradiation of 7 with 1,3-Butadiene (26). **Data for (2*RS*)-3-Cyano-2-vinyl-1,2-dihydroacenaphthylene (28):** Oil; ^{1}H NMR (CDCl$_3$) δ = 3.25 (dd, $J = 2.5$, 18.1 Hz, 1H), 3.73 (dddd, $J = 0.5$, 1.5, 7.9, 18.1 Hz, 1H), 4.46 (ddddd, $J = 0.7$, 1.5, 1.7, 7.9, 8.4 Hz, 1H), 5.25 (ddd, $J = 1.1$, 1.5, 10.3 Hz, 1H), 5.34 (ddd, $J = 1.1$, 1.7, 17.0 Hz, 1H), 5.89 (ddd, $J = 8.4$, 10.3, 17.0 Hz, 1H), 7.39 (ddd, $J = 1.5$, 3.0, 6.2 Hz, 1H), 7.53 (d, $J = 8.6$ Hz, 1H), 7.61 (dd, $J = 6.2$, 7.3 Hz, 1H), 7.65 (ddd, $J = 0.5$, 3.0, 7.3 Hz, 1H), 7.66 (dd, $J = 0.7$, 8.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ = 37.97 (t), 47.63 (s), 103.38 (s), 116.67 (t), 117.29 (s), 120.95 (d), 122.57 (d), 124.13 (d), 128.59 (d), 130.90 (d), 132.57 (s), 136.77 (d), 137.77 (s), 144.72 (s), 153.00 (s); IR (CHCl$_3$) 826, 1622, 2228, 2950 cm^{-1}; MS *m/z* (rel intensity) 205 (M$^+$; 55), 190 (100), 177 (38), 151 (20), 138 (14). Found: *m/z* 205.0925. Calcd for C$_{15}$H$_{11}$N: M, 205.0891.

Irradiation of 7 with Isoprene (29). **Data for (2*RS*)-3-Cyano-2-isopropenyl-1,2-dihydroacenaphthylene (31):** Oil; ^{1}H NMR (CDCl$_3$) δ = 1.58 (d, $J = 1.5$ Hdz, 3H), 3.28 (dd, $J = 2.9$, 18.1 Hz, 1H), 3.74 (dd, $J = 8.3$, 18.1 Hz, 1H), 4.56 (dd, $J = 2.9$, 8.3 Hz, 1H), 4.96 (s, 1H), 5.00 (q, $J = 1.5$ Hz, 1H), 7.41 (m, 1H), 7.58 (d, $J = 8.3$ Hz, 1H), 7.60—7.70 (m, 2H), 7.71 (d, $J = 8.3$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ = 19.05 (q), 37.90 (t), 51.53 (d), 103.78 (s), 113.91 (t), 117.40 (s), 121.05 (d), 122.82 (d), 124.37 (d), 128.98 (d), 131.11 (d), 132.80 (s), 138.47 (s), 143.74 (s), 145.35 (s), 153.36 (s); IR (CHCl$_3$) 824, 1620, 2228, 2950 cm^{-1}; MS *m/z* (rel intensity) 219 (M$^+$; 80), 204 (100), 190 (95), 177 (53), 151 (22), 138 (28). Found: *m/z* 219.1064. Calcd for C$_{16}$H$_{13}$N: M, 219.1048.

Data for (2*RS*)-3-Cyano-2-methyl-2-vinyl-1,2-dihydroacenaphthylene (33): Oil; ^{1}H HMR (CDCl$_3$) δ = 1.75 (s, 3H), 3.35 (d, $J = 17.8$ Hz, 1H), 3.56 (d, $J = 17.8$ Hz, 1H), 5.16 (d, $J = 17.1$ Hz, 1H), 5.21 (d, $J = 10.5$ Hz, 1H), 6.15 (dd, $J = 10.5$, 17.1 Hz, 1H), 7.40 (m, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.61—7.70 (m, 2H), 7.71 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl$_3$) δ = 24.82 (q), 47.31 (t), 51.09 (s), 102.73 (s), 113.37 (t), 117.71 (s), 121.28 (d), 122.98 (d), 124.49 (d), 129.46 (d), 131.24 (d), 132.98 (s), 133.02 (s), 142.10 (d), 143.71 (s), 157.06 (s); IR (CHCl$_3$) 826, 1620, 2230, 2958 cm^{-1}; MS *m/z* (rel intensity) 219 (M$^+$; 28), 204 (100), 190 (55), 177 (21), 149 (14), 88 (14), 69 (17). Found: *m/z* 219.1077. Calcd for C$_{16}$H$_{13}$N: M, 219.1048.

Fluorescence Quenching and Fluorescence Lifetime Measurement. For each quenching experiment five samples were prepared in 1.0×10^{-2} dm^3 volumetric flasks, each containing 1.0×10^{-4} mol dm^{-3} of **7** and appropriate concentrations of alkene in solvent. Fluorescence intensity at 380 and 381 nm was measured for each sample at excitation wavelengths of 350 and 315 nm in benzene and acetonitrile, respectively. No apparent exciplex emission was observed in the cases of the fluorescence quenching. Stern–Volmer plots were linear; the slopes are shown in Table 3. Fluorescence lifetimes were measured on air-saturated solutions containing 1.0×10^{-4} mol dm^{-3} of **7**.

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