Tetrahedron Vol. 48, No. 44, pp. 9673-9686, 1992
Printed in Great Britain

0040-4020/92 \$5.00+.00

Photochemical Reactions of 1,4-Dicyanonaphthalene with Allylic Silanes: Control of Reaction Modes by Use of Solvent and Additive Effects

Kazuhiko Mizuno,*[1a] Toshinori Nishiyama,[1a] Kiyotaro Terasaka,[1a] Masahide Yasuda,[1b] Kensuke Shima,[1b] and Yoshio Otsuji*[1a]

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture,
Sakai, Osaka 593, Japan; Department of Industrial Chemistry, Faculty of Engineering,
Miyazaki University, Gakuen-Kibanadai, Miyazaki 889-21, Japan

(*Received in Japan* 13 *July* 1992)

Key Words: Photoinduced Electron Transfer, Allylic Silanes, 1,4-Dicyanonaphthalene, Solvent Effect, Salt Effect

Abstract: Solvent and additive effects on the photoreaction of 1,4-dicyanonaphthalene (1,4-DCN) with allylic silanes (**1a-c**) have been investigated. Irradiation of acetonitrile solutions containing 1,4-DCN and **1a-c** in the presence of NaOMe selectively afforded the substitution products 1-(2'-alkenyl)-4-cyanonaphthalenes (**2a-c**) in high yields. The photoreaction of 1,4-DCN with **1a-c** in the presence of pyrene in CH_3CN-MeOH (4:1) selectively afforded the addition products 1-(2'-alkenyl)-1,4-dicyano-1,2-dihydronaphthalenes (**3a-c, 3c'**) in high yields. The photoreaction of 1,4-DCN with **1a-c** in the presence of phenanthrene in CH_3CN-MeOH (4:1) afforded the tricyclic compounds 3,6-dicyano-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonenes (**4a-c, 4c'**) and **5b** (the regioisomer of **4b**), which were produced via an intramolecular ($2\pi+2\pi$) photocycloaddition of **3a-c** and **3c'**. The mechanistic features of these photoreaction are discussed.

Photoinduced electron transfer between donor and acceptor molecules is a convenient route for the generation of a pair of the radical cation of donor molecule and the radical anion of acceptor molecule. A variety of new types of photoreactions have been developed by utilizing characteristic reactivities of these radical ion species.[2] However, carbon-carbon bond forming reactions involving organosilicon compounds are so far not much developed.[3-6]

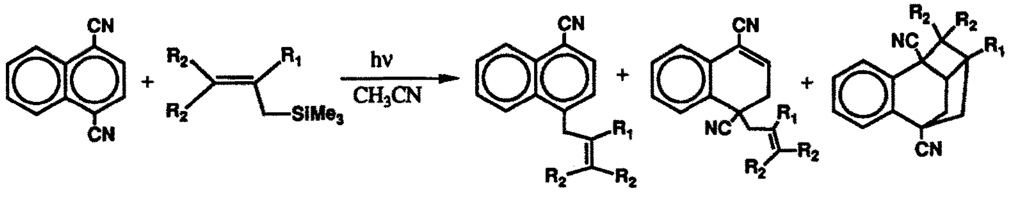
Mariano et al. reported the photoallylation and benzylation of iminium salts by allylic and benzylic silanes.[3] We reported the photoallylation and arylmethylation of electron-deficient aromatic compounds and alkenes by allylic and arylmethyl silanes.[4,7-9] These photoreactions proceed via photoinduced electron transfer from the organosilicon compounds to the electron deficient compounds and the carbon-silicon bond cleavage occurs from the radical cations of the former compounds, giving allylic and arylmethyl radicals and silyl cation species. The carbon radicals react then with radical anions of the electron-deficient compounds. We now report three types of photoreactions involving 1,4-

dicyanonaphthalene (1,4-DCN) and allylic silanes.[6] Emphasis is placed on the control of the modes of the photoreactions and we demonstrate that photosubstitution, photoaddition, and photocycloaddition products can be obtained in a highly selective fashion by utilizing solvent and additive effects.

RESULTS AND DISCUSSION

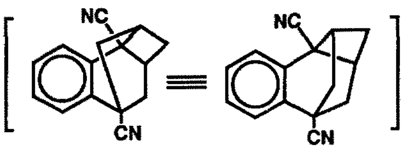
Products. Irradiation of an acetonitrile solution containing 1,4-DCN and excess allyltrimethylsilane (**1a**) with a high pressure Hg lamp through a Pyrex filter under argon atmosphere gave a mixture of 1-allyl-4-cyanonaphthalene (**2a**), 1-allyl-1,4-dicyano-1,2-dihydronaphthalene (**3a**), and 3,6-dicyano-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (**4a**) in 96% total yield (ϕ=0.1). The photoreaction of 1,4-DCN with allyltriethylgermane (**6**) and allyltrimethylstannane (**7**) also afforded a mixture of **2a**, **3a**, and **4a**. From 1,4-DCN and 2-methyl-2-propenyltrimethylsilane (**1b**), a mixture of **2b**, **3b**, **4b** and **5b** was obtained. The photoreaction of 1,4-DCN with 3-methyl-2-butenyltrimethylsilane (**1c**) gave a mixture of **2c**, **3c**, **3c'**, **4c** and **4c'**.

The products were isolated by column chromatography on silica gel. The structures of the products were determined by their spectral properties, elemental analyses, chemical transformations and X-ray crystalography.

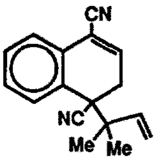


1,4-DCN 1a-c 2a-c 3a-c 4a-c

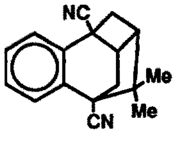
a ; R_1=R_2=H
b ; R_1=Me, R_2=H
c ; R_1=H, R_2=Me



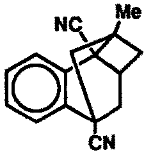
5a



3c'



4c'



5b

Treatment of **3a** with NaOMe in methanol gave **2a** in 92% yield. Irradiation of **3a** in acetonitrile through Pyrex gave **4a** in a quantitative yield. Similar irradiation of **3a** in the presence of NaOMe also gave **4a** in a high yield. In this case, **2a** was not obtained. These results indicate that **2a** and **3a** are primary products, and **4a** is produced from **3a** under the reaction conditions. The ^{1}H NMR (270 MHz) spectrum of **4a** showed nonequivalent eight aliphatic proton signals. The ^{13}C NMR spectrum exhibited nonequivalent seven aliphatic carbon signals. These spectral data exclude structure **5a** for **4a**; since **5a** has a symmetry plane bisecting the benzene ring, it should show four kinds of aliphatic proton signals and

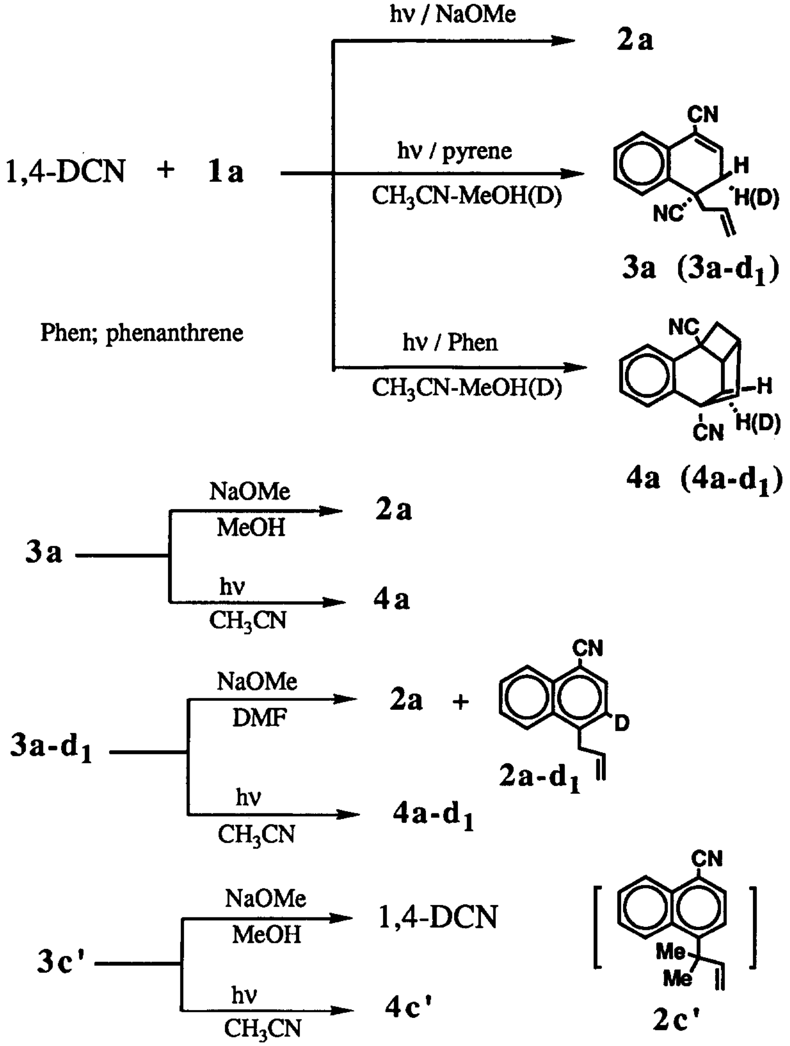


Table I. Photoallylation of 1,4-Dicyanonaphthalene by Allylic Silanes[a]

Allylic Silane	Solvent[b]	Additive[c]	Irradn time /h	Product(s) (yield/%)
1a	CH_3CN	——	2.5	**2a** (48), **3a** (20), **4a** (28)
1a	CH_3CN	NaOMe	2	**2a** (98)
1a	CH_3CN	NaOH	2	**2a** (84)
1b	CH_3CN	NaOMe	2	**2b** (67)
1c	CH_3CN	NaOMe	2	**2c** (61)
1a	CH_3CN-MeOH	Pyrene	1.5	**2a** (tr), **3a** (78)
1b	CH_3CN-MeOH	Pyrene	1.5	**2a** (tr), **3b** (45)
1c	CH_3CN-MeOH	Pyrene	1.5	**3c** (35), **3c'** (23)
1a	CH_3CN-MeOH	Phen	2	**2a** (19), **4a** (72)
1b	CH_3CN-MeOH	Phen	2	**4b** (32), **5b** (32)
1c	CH_3CN-MeOH	Phen	2	**4c** (50), **4c'** (33)
6	CH_3CN	——	1	**2a** (56), **3a** (22), **4a** (11)
7	CH_3CN	——	1	**2a** (10), **3a** (54), **4a** (5)

[a] [1,4-DCN] = 1.1 x 10^{-2} mol/dm^3, [1a-c] = 0.1 mol/dm^3. [b] CH_3CN : MeOH = 4 : 1.
[c] [NaOMe] = [NaOH] = 0.05 mol/dm^3, [Pyrene] = 1.6 x 10^{-3} mol/dm^3,
[Phen] = 1.1 x 10^{-2} mol/dm^3

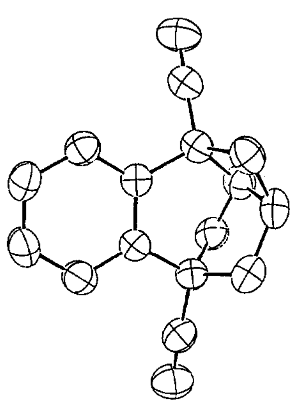


Fig 1. ORTEP drawing of **4a**.

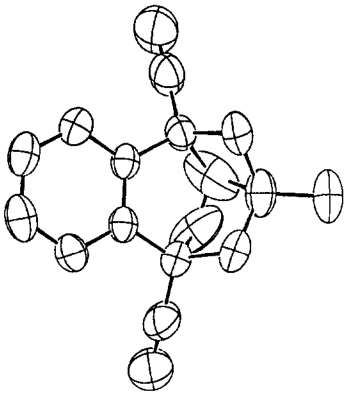


Fig 2. ORTEP drawing of **4b**.

five kinds of aliphatic carbon signals in the ^{1}H NMR and ^{13}C NMR spectra, but this was not the case. Treatment of **3b** and **3c** with NaOMe afforded **2b** and **2c**, respectively. However, the reaction of **3c'** with NaOMe gave 1,4-DCN, but did not give **2c'**. Irradiation of **3b** in acetonitrile afforded **4b** and **5b** in a 1:1 ratio. Similar irradiation of **3c** and **3c'** gave **4c** and **4c'**, respectively. The structures of **4a** and **4b** were finally confirmed by X-ray diffraction studies (Figs. 1 and 2).

Effects of Solvents and Additives. The photoallylation did not occur in less polar solvents such as benzene, ether and ethyl acetate. The product distribution in the photoreaction of **1a** with 1,4-DCN in acetonitrile strongly depended on reaction conditions and also on added materials to the reaction system. The results are summarized in Table I.

The addition of protic solvents such as methanol and water into the reaction system suppressed the formation of **2a** and accelerated the formation of **3a** and **4a**. Prolonged irradiation under these conditions resulted in a predominant formation of **4a**. The addition of NaOMe and NaOH suppressed the formation of **3a** and **4a** and accelerated the formation of **2a**. When the photoreaction was carried out in the presence of pyrene, **3a** was obtained as a predominant product. However, irradiation in the presence of phenanthrene (Phen) accelerated the formation of **3a** and **4a**, and prolonged irradiation under these conditions gave **4a** as a major product.

By applying these additive effects, we achieved a regioselective photosubstitution. Irradiation of 1,4-DCN and allylic silanes **1a-c** in the presence of powdered NaOH or NaOMe in acetonitrile gave **2a-c** as major products along with only small amounts of **3a-c** and **4a-c** (<10%). In the case of **1c**, sterically more hindered **2c'** was not detected. We could also achieve a regioselective photoaddition. Irradiation of acetonitrile-methanol (4:1) solutions containing 1,4-DCN and allylic silanes **1a-b** in the presence of pyrene with >320 nm light gave **3a-b** in a highly regioselective manner. In the case of **1c**, two regioisomers **3c** and **3c'** were obtained in high yields. When the photoreaction of 1,4-DCN with **1a** was carried out in acetonitrile-methanol-O-d_1 (4:1), the deuterium-incorporated **3a-d$_1$** was obtained. Tricyclic compounds were also obtained in highly selective manner. Irradiation of acetonitrile-methanol (4:1) solution containing 1,4-DCN and **1a** in the presence of Phen through Pyrex filter afforded **4a** in an excellent yield. Similarly, **4b** and **5b** were obtained from **1b** in a 1:1 ratio. In the case of **1c**, **4c** and **4c'** were obtained in a 3:2 ratio.

Fluorescence Quenching and Redox Properties. Fluorescence of 1,4-DCN in acetonitrile was efficiently quenched by allylic silanes in nearly diffusion controlled rates. However, the emission from exciplexes between 1,4-DCN and allylic silanes was not observed in this solvent. Free energy changes (ΔG) estimated by the Rehm-Weller equation for a one-electron transfer process from allylic silanes to ^{1}DCN* were negative.[10] These results are summarized in Table II.

Mechanism. We propose the mechanism shown in Scheme 1 for the above photoreactions. The first step is a photoinduced electron transfer from an allylic silane to ^{1}DCN* to produce the radical ion pair [DCN$^{-\bullet}\cdots$D$^{+\bullet}$] (RIP) in which D$^{+\bullet}$ represents the radical cation of allylic silane. The second step is the cleavage of the C-Si bonds of D$^{+\bullet}$ to give an allylic radical. This process may be assisted by a nucleophilic attack on D$^{+\bullet}$ by a solvent such as acetonitrile, methanol or water. Indeed, Dinnocenzo et

Table II. Oxidation Potentials, Free Energy Changes of Allylic Silanes, and Rate Constants for the Fluorescence Quenching of 1,4-DCN

Allylic silane	$E^{ox}_{p/2}$ / V [a]	ΔG / kJ mol^{-1} [b]	kqτ / mol^{-1} dm^3 [c]	kq / mol^{-1} dm^3 s^{-1} [c]
1a	1.58	-32.5	82.9	0.83×10^{10}
1b	1.28	-61.4	88.2	0.88×10^{10}
1c	0.92	-96.2	107.5	1.08×10^{10}

[a] Oxidation potentials vs. Ag/Ag^+ in CH_3CN. [b] ΔG values were estimated by use of Rehm-Weller equation[10]; $E^{red}_{1/2}$ (DCN) = -1.59 V, E^s(1,4-DCN) = 3.45 V. [c] Fluorescence quenching of 1,4-DCN by allylic silanes in CH_3CN; τ(1,4-DCN) = 10 ns; Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.*, **1976**, *98*, 5931.

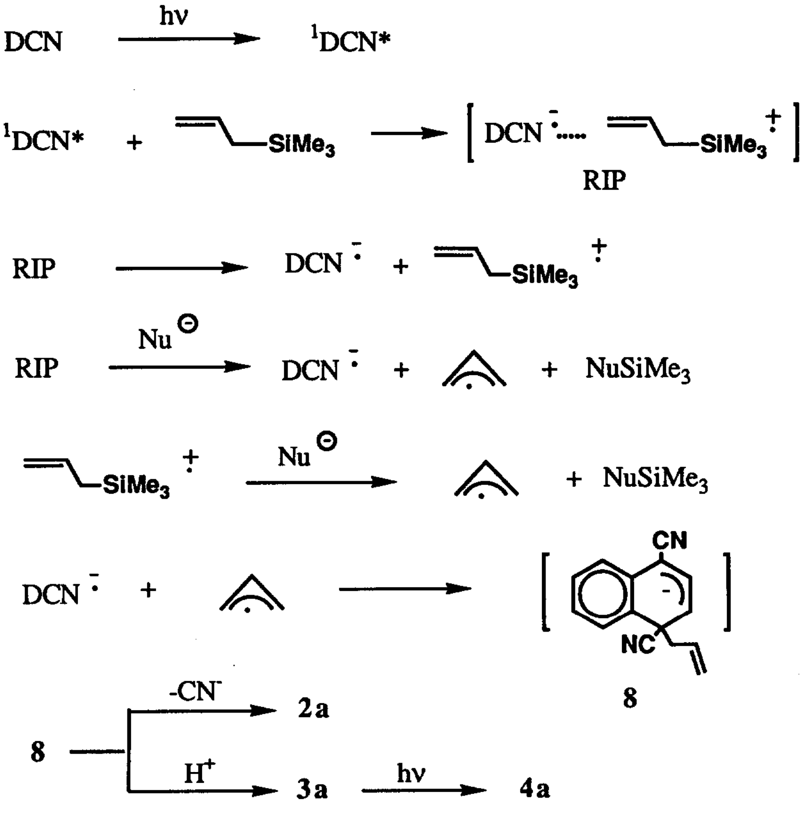
al. have recently reported the alcohol-assisted C-Si bond cleavage of benzylic silanes under photoinduced electron transfer reaction conditions.[11] Nakadaira et al. have also reported the nucleophilic attack of alcohols on the radical cations of polysilanes, thereby the cleavage of the Si-Si bond is induced.[12] The third step is the addition of the allylic radical on $DCN^{-\bullet}$. The anionic intermediate **8** thus produced is a key intermediate for the formation of **2** and **3**.

The photosubstitution products were produced effectively in the presence of NaOMe or NaOH. The formation of **2** occurs by the loss of cyanide ion from **8**. The other experiment showed that no deuterium incorporation into **2a** occurred when the photoreaction of 1,4-DCN with **1a** was carried out in the presence of MeOD. This result also indicates that **2a** is not obtained from **3a** under the reaction conditions. Indeed, treatment of the deuterated **3a** with NaOMe in DMF gave the deuterium-incorporated **2a** in 50% yield. The role of the base in the selective formation of **2** is, therefore, presumed to be the suppression of protonation on the anion intermediate **8**.

The photoaddition products were effectively produced by the addition of MeOH or water in the presence of Phen. These products are obtained by the protonation on **8**. The rate of the addition of allylic radicals to $DCN^{-\bullet}$ is much faster than the protonation on $DCN^{-\bullet}$ by MeOH and H_2O. A noteworthy observation in this connection was that the photoreaction of 1,4-DCN with aromatic hydrocarbons such as Phen and biphenyl in the presence of MeOH but in the absence of allylic silanes did not give any of reduction products of 1,4-DCN such as 1,4-dicyano-1,2-dihydronaphthalenes, which would be obtained by the protonation of $DCN^{-\bullet}$. The role of Phen in the photoreaction is to suppress the back-electron transfer from $DCN^{-\bullet}$ to the radical cations of allylic silanes and to promote the effective formation of the radical cations of the allylic silanes through a secondary electron transfer from allylic silanes to the radical cation of Phen.[13]

In the presence of pyrene, the rate of the formation of **3a** decreased to two thirds compared to the rate of that in the absence of pyrene, but the selectivity of the formation of **3a** was highly enhanced. The

Scheme 1.



DCN ; 1,4-DCN RIP; Radical ion pair $Nu^{\ominus}$; Nucleophile

major role of pyrene in the photoreaction is that it probably acts as an internal filter for the intramolecular ($2\pi+2\pi$) photocycloaddition of **3a**. The intramolecular photocycloaddition of **3a** quantitatively afforded **4a**. In the case of **3b**, two cycloadducts **4b** and **4b'** were produced due to the steric effect of methyl group at 2-position of the allyl group.

EXPERIMENTAL

Materials. Acetonitrile was distilled three times over P_2O_5 and then once over anhydrous CaH_2 before use. Spectrograde benzene and ethyl acetate were distilled before use. Allylic silanes and 1,4-dicyanonaphthalene were prepared by the methods described in the literatures.[14,15] Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were also purchased and used without further purification.

General. Melting points were taken on a hot stage and are uncorrected. ^{1}H NMR spectra were recorded on JEOL JNM-PMX60SI (60 MHz) spectrometer and JEOL JNM-GX270 (270 MHz) spectrometer for solutions in $CDCl_3$ containing tetramethylsilane as an internal standard. Deuterium content was determined by 270 MHz ^{1}H NMR. ^{13}C NMR were recorded on a JEOL JNM-GX270 spectrometer for solutions in $CDCl_3$ with chloroform (δ=77.05) as an internal standard. Infrared spectra were obtained on a JASCO FT/IR-5000 spectrometer, mass spectra on a Hitachi RMU-6E spectrometer, and fluorescence spectra on a JASCO FP-500 spectrofluorometer. Elemental analyses were carried out on a YANACO MT-3 elemental analyzer. Gas liquid chromatographic analyses (GLC) were performed with a Hitachi 164 instrument, using 1 m x 3 mm glass colums packed with 10% SE30 on Shimalite W. Oxidation and reduction potentials were measured in argon-saturated acetonitrile solutions by cyclic voltammetry, using a Nichia NP-G 2550 potentiostat and an $Ag/AgClO_4$ reference electrode. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte.

Quantum yields were determined by the procedure of Murov using a potassium ferrioxalate actinometer.[16] The light source was a 500 W high-presssure mercury arc, Wacom BMO-500OD and 313 nm Hg line was isolated through a CrO_3 filter solution and Toshiba filter UV-29. The light intensity was determined twice before and once after actual photoreactions. No changes in light intensity were observed during experiments. For the quantum yield determination, photoreactions were carried out up to <10% conversion of 1,4-DCN, and the reaction mixtures were analyzed by GLC.

General Procedure for the Photoreaction with Allylic Silanes. A solution of 1,4-dicyanonaphthalene (1,4-DCN) and an excess of allylic silane in an appropriate solvent in the absence or presence of an additive was irradiated at ambient temperature (ca. 30 °C) with a 300 W high-pressure mercury lamp through Pyrex filter under argon atmosphere. The progress of the photoreaction was followed by measuring the amount of 1,4-DCN with GLC. After consumption (>90%) of 1,4-DCN, the solvent was removed under reduced pressure, and the residue was analyzed by ^{1}H NMR, from which the product ratio was determined by integration of the signals. The products were isolated by column chromatography on silica gel. The results were summarized in Table I.

Photoreaction of 1,4-DCN with Allyltrimethylsilane (1a). An acetonitrile solution (25 mL) of 1,4-DCN (50 mg, 0.28 mmol) and **1a** (2.5 mmol) through Pyrex was irradiated for 2.5 h and then the solvent was removed. The residue was chromatographed on silica gel. Elution with hexane-benzene (7:3) gave 24.5 mg of **2a** (48%), that with hexane-benzene (6:4) a trace amount of 1,4-DCN, that with hexane-benzene (5:5) 11.3 mg of **3a** (20%), and that with hexane-benzene (3:7) 16.1 mg of **4a** (28%).

1-Allyl-4-cyanonaphthalene (2a): mp 59-60 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.87 (d, 2H, J=6 Hz), 5.06-5.20 (m, 2H), 6.00-6.15 (m,1H), 7.38 (d, 1H, J=7.4 Hz), 7.62 (t, 1H, J=7.4 Hz), 7.68

(t, 1H, J=7.4 Hz), 7.83 (d, 1H, J=7.4 Hz), 8.09 (d, 1H, J=7.4 Hz), 8.25 (d, 1H, J=7.4 Hz));^{13}C NMR δ 37.5, 109.0, 117.5, 118.1, 125.5, 126.0, 127.5, 128.2, 131.7, 132.5, 132.7, 135.5, 142.7;IR (KBr) 1650, 2200, 2880, 3020 cm^{-1}; MS m/z 165, 178, 193 (M$^+$, vw). Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.92; H 5.73; N 7.19.

1-Allyl-1,4-dicyano-1,2-dihydronaphthalene (3a):oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.45 (dd, 1H, J=7.9, 14.0 Hz), 2.54 (dd, 1H, J=6.7, 14.0 Hz), 2.91 (dd, 1H, J=5.5, 18.3 Hz), 2.99 (dd, 1H, J=3.7, 18.3 Hz), 5.14 (d, 1H, J=17.7 Hz), 5.25 (d, 1H, J=9.8 Hz), 5.69-5.84 (m, 1H), 6.75 (dd, 1H, J=3.7, 5.5 Hz), 7.41-7.59 (m, 4H); ^{13}C NMR δ 32.3, 40.2, 41.8, 114.6, 115.7, 121.1, 121.3, 125.8, 126.3, 126.8, 129.2, 130.2, 130.8, 131.8, 138.0; IR (neat) 1655, 2230, 2240, 2920, 3045 cm^{-1}; MS m/z 152, 168, 178, 179, 220 (M$^+$,vw); Exact mass calcd for $C_{15}H_{12}N_2$ 220.2754, found 220.0961

3,6-Dicyano-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4a):mp 152-153 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.72(d, 1H, J=11.6 Hz), 2.03 (d, 1H, J=12.2 Hz), 2.20 (d, 1H, J=14.0 Hz), 2.35 (dd, 1H, J=4.3,12.2 Hz), 2.54 (dd, 1H, J=9.7, 13.4 Hz), 2.97 (br q, 1H), 3.14 (dd, 1H, J=9.1, 11.0 Hz), 3.78 (dd, 1H, J=4.3,6.1 Hz), 7.37-7.76 (m, 4H); ^{13}C NMR δ 35.1, 37.0, 40.2, 41.4, 44.7, 45.4, 45.6, 120.9, 121.1, 125.2, 126.1,128.1, 129.2, 133.4, 137.3; IR (KBr) 2220, 2910, 2950 cm^{-1}; MS m/z 152, 178, 179, 220 (M$^+$,vw). Anal. Calcd for $C_{15}H_{12}N_2$:C, 81.79; H, 5.49; N, 12.72. Found: C, 81.56; H, 5.33; N, 12.67.

A Typical Procedure for Photosubstitution of 1,4-DCN in the Presence of Base. A dry acetonitrile solution (25 mL) of 1,4-DCN (50 mg, 0.28 mmol) and allyltrimethylsilane (**1a**, 2.5 mmol) in the presence of powdered NaOH (50 mg) or NaOMe (68 mg) was irradiated through Pyrex for 2-3 h and then the solvent was removed. The residue was chromatographed on silica gel. Elution with hexane-benzene (7:3) gave 45.4 mg, 84% of **2a** in the case of NaOH and 53.4 mg (98%) of the same product in the case of NaOMe:

Physical properties of other substitution products are shown below;

1-Cyano-4-(2-methyl-2-propenyl)naphthalene (2b); oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ 1.76 (s, 3H), 3.78 (s, 2H), 4.57 (s, 1H), 4.89 (s, 1H), 7.25-8.24 (m, 6H); ^{13}C NMR (67 MHz, $CDCl_3$), δ 22.6, 41.4, 108.8, 113.1, 117.9, 124.9, 125.6, 126.1, 127.1, 127.9, 131.9, 132.1, 132.4, 142.2, 143.1; IR (neat) 766, 1653, 2224, 2974, 3082 cm^{-1}; MS m/z 165, 166, 178, 192, 207 (M$^+$,vw). Exact mass calcd for $C_{15}H_{13}N$ 207.1048, found 207.1054.

1-Cyano-4-(3-methyl-2-butenyl)naphthalene (2c); oil; ^{1}H NMR (270 MHz, $CDCl_3$), δ 1.75 (s, 6H), 3.70 (d, H, J=7 Hz), 5.25 (t, 1H, J=7 Hz), 7.12-8.23 (m, 6H); ^{13}C NMR (270 MHz, $CDCl_3$), δ 17.9, 25.6, 31.9, 118.1, 121.1, 124.57, 124.64, 125.7, 127.2, 131.6, 132.4, 132.5, 134.2, 144.3;

IR (neat) 762, 1584, 2224, 2918, 2974, 3082 cm-1; MS m/z 166, 178, 179, 190, 191, 206, 221(M^+,vw). Exact mass calcd for $C_{16}H_{15}N$ 221.1204, found 221.1178.

A Typical Procedure for Reductive Photoallylation of 1,4-DCN in the Presence of Pyrene. An acetonitrile-methanol (4:1) solution (12.5 mL) of 1,4-DCN (25 mg, 0.14 mmol) and **1a** (0.12 mL, 0.76 mmol) in the presence of pyrene (4 mg, 0.02 mmol) was irradiated through Pyrex for 1.5 h and then the solvent was removed. The residue was chromatographed on silica gel. Elution with hexane gave 4 mg of pyrene. Elution with hexane-benzene (7:3) gave a trace amount of **2a**, that with hexane-benzene (6:4) 5 mg of 1,4-DCN, and that with hexane-benzene (5:5) 23.7 mg of **3a** (78%).

Physical properties of other reductive photoallylation products are shown.

1,4-Dicyano-1-(2-methyl-2-propenyl)-1,2-dihydronaphthalene (3b); oil; ^1H NMR (270 MHz, $CDCl_3$) δ 1.73 (s, 3H), 2.44 (dd, 2H, J=9.0, 13.9 Hz), 2.98(dd, 2H, J=4.0, 1.6 Hz), 4.76(s,1H), 5.01(dd, 1H, J=1.2, 1.6 Hz), 6.76 (dd, 1H, J=4.0, 5.2 Hz), 7.41-7.64(m, 4H) ; ^{13}C NMR (270 MHz, $CDCl_3$) δ 23.36, 32.60, 39.69, 45.15, 114.81, 115.84, 117.68, 122.21, 125.95, 126.25, 127.06, 129.32, 130.42, 132.40, 138.12, 139.15 ; IR (neat) 766, 1452, 1647, 2230, 2240, 2924, 3078 cm^{-1} ; MS m/z 152, 168, 178, 179, 234 (M^+). Exact mass calcd for $C_{17}H_{16}N_2$ 248.1313, found 248.1308.

1,4-Dicyano-1-(3-methyl-2-butenyl)-1,2-dihydronaphthalene (3c) ; oil; ^1H NMR (270 MHz, $CDCl_3$),δ 1.41 (s, 3H), 1.74 (s,3H), 2.45 (dd, 2H, J=3.7, 6.1 Hz), 2.945 (dd, 2H, J=3.7, 6.1 Hz), 4.98-5.23 (m, 2H), 6.745 (dd, 1H, J=3.7, 6.1 Hz), 7.42-7.58 (m, 4H) ; ^{13}C NMR (270 MHz, $CDCl_3$) δ 17.78, 25.93, 32.62, 36.54, 40.72, 114.73, 115.96, 116.69, 121.78, 125.93, 127.14, 129.24, 130.34, 131.12, 132.36, 138.20, 139.01 ; IR (neat) 768, 1452, 1491, 1647, 2230, 2240, 2926, 2976, 3072 cm^{-1}; MS m/z 248 (M^+).

1,4-Dicyano-1-(1,1-dimethyl-2-propenyl)-1,2-dihydronaphthalene (3c') ; oil; ^1H NMR (270 MHz, $CDCl_3$), δ 1.03 (s, 3H), 1.18 (s, 3H), 3.02 (dd, 1H, J=3.1, 19.5 Hz), 3.21 (dd, 1H, J=6.7, 19.5 Hz), 5.03 (d, 1H, J=17.1 Hz), 5.16 (d, 1H, J=10.4 Hz), 5.89 (dd, 1H, J=10.7, 17.4 Hz), 6.70 (dd, 1H, J=3.1, 6.7 Hz), 7.41-7.64 (m, 4H); IR (neat) 766, 1450, 2228, 2240, 2976 cm^{-1}; MS m/z 248 (M^+). Exact mass calcd for $C_{17}H_{16}N_2$ 248.1313, found 248.1215

A Typical Procedure for Preparation of Tricyclic Compounds from 1,4-DCN and Allylic Silanes. An acetonitrile-methanol (4:1) solution (250 mL) of 1,4-DCN (500 mg, 2.8 mmol) and **1a** (25 mmol) in the presence of phenanthrene (500 mg, 2.8 mmol) was irradiated through Pyrex for 2 h and then the solvent was removed. The residue was chromatographed on silica gel. Elution with hexane gave 490 mg of phenanthrene, that with hexane-benzene (7:3) 104 mg (19%) of **2a**, and that with hexane-benzene (4:6) 446 mg (72%) of **4a**.

Physical properties of other tricyclic compounds are shown below;

3,6-Dicyano-1-methyl-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4b) ; mp 154-155 °C ; ^{1}H NMR (270 MHz, $CDCl_3$), δ 1.35 (s, 3H), 1.90 (dd, 1H, J=0.8, 11.7 Hz), 1.99 (d, 1H, J=12.5 Hz), 2.23 (dd, 2H, J=13.3, 14.5 Hz), 2.42 (dd, 1H, J=4.0, 12.5 Hz), 2.87(d, 1H, J=11.7 Hz), 3.30 (d, 1H, J=4.0 Hz), 7.34-7.73 (m, 4H) ; ^{13}C NMR (67 MHz, $CDCl_3$), δ 27.0, 34.0, 39.3, 42.8, 45.1, 48.0, 51.0, 51.9, 120.9, 121.5, 125.0, 126.7, 128.2, 129.2, 133.1, 136.8 ; IR (KBr) 1435, 1445 (sh), 1480, 2230, 2320, 2860 (sh), 2910 cm^{-1}; MS m/z 153, 168, 178, 179, 193,234 (M^+) ; Anal calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.78; H, 5.96; N, 11.65.

2,5-Dicyano-1-methyl-3,4-benzotricyclo[3.3.1.0^{2,7}]-3-nonene (5b) ; ^{1}H NMR (270 MHz, $CDCl_3$), solid; δ 1.20 (s, 3H), 1.53 (dt, 1H, J=2.0, 2.4, 12.5 Hz), 1.65 (d, 1H, J=10.1 Hz), 1.74-1.88 (m, 1H), 2.50 (dd, 2H, J=12.5, 12.9 Hz), 2.71 (tt, 1H, J=2.0, 6.6 Hz), 2.80 (t, 1H, J=6.4 Hz), 7.48-7.73 (m, 4H) ; ^{13}C NMR (67 MHz, $CDCl_3$), δ 22.8, 36.46, 36.52, 37.2, 41.7, 44.0, 45.1, 46.5, 119.7, 120.1, 121.4, 125.4, 128.3, 128.9, 129.1, 138.6; IR (oil) 1446, 1480, 2220, 2236, 2850 (sh), 2920 cm^{-1}; MS m/z 152, 169, 179, 193, 234 (M^+). Exact mass calcd for $C_{16}H_{14}N_2$ 234.1157, found 234.1214.

3,6-Dicyano-2,2-dimethyl-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4c) ; solid; ^{1}H NMR (270 MHz, $CDCl_3$), δ 0.30 (s, 3H), 1.60 (s, 3H), 2.00 (d, 1H, J=12.5 Hz), 2.23-2.32 (m, 3H), 2.53-2.64 (m, 1H), 3.71 (ddd, 1H, J=0.8, 4.4, 6.4 Hz), 7.34-7.72 (m, 4H) ; ^{13}C NMR δ 19.9, 29.1, 38.6, 40.3, 42.3, 43.7, 44.5, 46.0, 46.7, 119.7, 121.0, 124.9, 128.3, 128.8, 130.9, 136.9 ; MS m/z 69, 154, 180, 207, 248 (M^+). Exact mass calcd for $C_{17}H_{16}N_2$ 248.1313, found 248.1396.

3,6-Dicyano-9,9-dimethyl-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4c') ; solid; ^{1}H NMR (270 MHz, $CDCl_3$), δ 0.81 (s, 3H), 1.32 (s, 3H), 1.91 (dd, 2H, J=12.9, 1.6 Hz), 2.53 (m, 1H), 2.60 (dd, 1H, J=4.4, 12.9 Hz), 2.935 (dd, 1H, J=12.1, 9.3 Hz), 3.72 (dd, 1H, J=4.4, 6.4 Hz), 7.34-7.70 (m, 4H) ; ^{13}C NMR (67 MHz, $CDCl_3$), δ 20.9, 30.0, 36.76, 36.84, 37.1, 44.6, 45.7, 47.9, 53.9, 119.9, 121.2,126.66, 126.74, 127.9, 132.3, 136.0; MS m/z 248(M^+).

A Typical Procedure for Intramolecular (2π+2π) Photocycloaddition of Photoaddition Products. An acetonitrile solution (3 mL) of **3a** (6 mg, 0.03 mmol) was irradiated for 0.3 h through Pyrex under argon atmosphere and then the solvent was removed. The residue was analyzed from 270 MHz ^{1}H NMR spectral data.

Preparation of 2a from 3a. A methanol solution (10 mL) of **3a** (57.2 mg, 0.26 mmol) in the presence of NaOMe (24 mg, 0.44 mmol) was refluxed for 2 h under argon atmosphere and then the solvent was removed. The residue was chromatographed on silica gel. Elution with hexane-benzene (7:3) gave 45.6 mg (92%) of **2a**.

Preparation of 3a-d$_1$. An acetonitrile-methanol-O-d$_1$ (4:1) solution (10 mL) of 1,4-DCN (50 mg, 0.28 mmol) and **1a** (2.5 mmol) in the presence of pyrene (8 mg, 0.04 mmol) was irradiated through Pyrex for 2 h. Flash chromatography on silica gel gave **3a-d$_1$** (deuterium content was 68%).

1-Allyl-2-deuterio-1,4-dicyano-1,2-dihydronaphthalene (3a-d$_1$): ^{1}H NMR (270 MHz, CDCl$_3$) δ 2.45 (dd, 1H, J=7.9, 14.0 Hz), 2.54 (dd, 1H, J=6.7, 14.0 Hz), 2.99 (d, 1H, J=3.7 Hz), 5.14 (d, 1H, J=17.7 Hz), 5.25 (d, 1H, J=9.8 Hz), 5.69-5.84 (m, 1H), 6.75 (dd, 1H, J=3.7, 5.5 Hz), 7.41-7.59 (m, 4H).

Preparation of 4a-d$_1$. An acetonitrile-methanol-O-d$_1$ (4:1) solution (10 mL) of 1,4-DCN (50 mg, 0.28 mmol) and **1a** (2.5 mmol) in the presence of phenanthrene (50 mg, 0.28 mmol) was irradiated through Pyrex for 2 h. Flash chromatography on silica gel gave **4a-d$_1$** (deuterium content was 88%).

7-Deuterio-3,6-dicyano-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4a): ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.72(d, 1H, J=11.6 Hz), 2.20 (d, 1H, J=14.0 Hz), 2.35 (d, 1H, J=4.3 Hz), 2.54 (dd, 1H, J=9.7, 13.4 Hz), 2.97 (br q, 1H), 3.14 (dd, 1H, J=9.1, 11.0 Hz), 3.78 (dd, 1H, J=4.3, 6.1 Hz), 7.37-7.76 (m, 4H).

Preparation of 2a-d$_1$ from 3a-d$_1$. A dry dimethylformamide solution (10 mL) of **3a-d$_1$** (28 mg, 0.13 mmol, deuterium content was 68%) in the presence of NaOMe (12 mg, 0.22 mmol) was refluxed for 2 h under argon atmosphere. Flash chromatography on silica gel gave **2a-d$_1$** (deuterium content was 50%).

1-Allyl-4-cyano-3-deuterionaphthalene (2a-d$_1$): ^{1}H NMR (270 MHz, CDCl$_3$) δ 3.87 (d, 2H, J=6 Hz), 5.06-5.20 (m, 2H), 6.00-6.15 (m,1H), 7.62 (t, 1H, J=7.4 Hz), 7.68 (t, 1H, J=7.4 Hz), 7.83 (s, 1H), 8.09 (d, 1H, J=7.4 Hz), 8.25 (d, 1H, J=7.4 Hz).

X-ray Structure Determination. The intensity data were measured on a CAD-4 Enraf-Nonius diffractometer with graphite-monochromated MoK radiation (λ=0.71069 A) by a ω-2θ scan technique. A crystal of size 0.32 x 0.56 x 0.56 mm or 0.49 x 0.53 x 0.49 mm was selected for diffraction measurements for **4a** or **4b**, respectively. A total 3044 and 3578 independent reflections were measured for 1<θ<26, of which 2341 and 1730 were considered to be observed [I 3 (I)] for **4a** and **4b**, respectively. The structure was solved by direct methods using MULTAN 82 and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were refined with isotropic thermal parameters. There are no significant features in the final difference Fourier map.

Crystal data:

3,6-Dicyano-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4a). $C_{15}H_{11}N_2$, M=219.3, orthorhombic, space group $P2_1/b2_1/c2_1/a$,a=9.611(22) A, b=13.780(2) A, c=17.284(4) A, V=2288.7 A^3, Z=8, D_{calcd}=1.27 g cm^{-3}, D_{obs}=1.26 g cm^{-3}, R_w=0.068, R=0.065:

3,6-Dicyano-1-methyl-4,5-benzotricyclo[4.2.1.0^{3,8}]-4-nonene (4b). $C_{16}H_{14}N_2$, M= 234.3, monoclinic, space group P12(1)/n1, a=8.826(1) A, b=9.755(13) A, c=15.984(2) A,V=1324.2 A3, Z=4, D_{calcd}=1.175 g cm^{-3}, D_{obs}=1.180 g cm^{-3}, R_w=0.080, R=0.092.

Acknowledgement. This work is partially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan. We thank Shin-Etsu Chemical Co. Ltd., for gift of chlorotrimethylsilane and Asai Germanium Research Institute for gift of tetrachlorogermane. We also thank T. Tamai (Osaka Municipal Technical Research Institute) for measurements of HRMS and M. Ansho (Miyazaki University) for assistance of X-ray measurements.

Supplementary Material Available. X-ray crystallographic data for compounds **4a** (23 pages) and **4b** (24 pages). Ordering information is given on any current masthead page.

REFERENCES AND NOTES

(1) a) University of Osaka Prefecture. b) Miyazaki University.

(2) Review articles; Mattes, S. L.; Farid, S. *Organic Photochemistry*, ed by Padwa, A; Marcel Dekker Inc.; New York, **1983**, *6*, 233; Mariano, P. S.; Stavinoha, J. L.; *Synthetic Organic Photochemistry*, ed by Horspool, W. M., Plenum Press,; New York, **1984**, 145; Chanon, M. *Bull. Chem. Soc. Fr.* **1985**, 209; Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401; Mattay, J. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 825; *Photoinduced Electron Transfer*, Part A-D, ed by Fox, M. A.; Chanon, M., Elsevier,; Amsterdam, **1988**; Mattay, J. *Synthesis*, **1989**, 233; Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron*, **1990**, *46*, 6193; *Photoinduced Electron Transfer I-III*: *Topics in Current Chemistry* 156, 158, 159, ed by Mattay, J., Springer-Verlay,; Berlin, **1990-1991.**

(3) Ohga, K.; Mariano, P. S. *J. Am. Chem. Soc.* **1982**, *104*, 617; Harding, T. T.; Ullrich, J. W.; Chiu, F. T.; Chen, S.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3362; Chen, S.; Ullrich, J. W.; Mariano, P. S. *J. Am. Chem. Soc.*, **1983**, *105*, 6160; Ohga, K.; Yoon, U. C.; Mariano, P. S.*J. Org. Chem.* **1984**, *49*, 213; Ullrich, J. W.; Chiu, F. T.; Harding, T.T.; Mariano, P. S. *Ibid.* **1984**, *49*, 220; Chiu, F. T.; Ullrich, J. W.; Mariano, *Ibid.* **1984**, *49*, 228; P. S. Borg, B. M.; Mariano, P. S. *Tetrahedron Lett.*, **1986**, *27*, 2821; Hasegawa, E.; Xu, W,; Mariano, P. S.; Yoon, U. C.; Kim, J. U. *J. Am. Chem. Soc.*, **1988**, *110*, 8099.

(4) Mizuno, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1984**, *26*, 461; Mizuno, K.; Toda, S.; Otsuji, Y. *Chem. Lett.* **1987**, 203; *Nippon Kagaku Kaishi*, **1987**, 1183; Mizuno, K.; Terasaka, K.; Yasueda, M.; Otsuji, Y. *Chem. Lett.* **1988**, 145; Mizuno, K.; Yasueda, M.; Otsuji, Y. *Ibid.* **1988**, 229; Mizuno, K.; Nakanishi, K.; Otsuji, Y. *Ibid.* **1988**, 1833; Mizuno, K.; Nakanishi, K.;

Chosa, J.; Nguyen, T.; Otsuji, Y. *Tetrahedron Lett.*, **1989**, *28*, 3689; Mizuno, K.; Kobata, K.; Maeda, R.; Otsuji, Y. *Chem. Lett.*, **1990**, 1821.

(5) Eaton, D. F. *J. Am. Chem. Soc.* **1980**, *102*, 3280; *Ibid* **1981**, *103*, 7235; Kubo, Y.; Imaoka, T.; Shiragami, T.; Araki, T. *Chem. Lett.* **1986**, 1749; Maruyama, K.; Imahori, H.; Osuka, A.; Takuwa, A.; Tagawa, A. *Chem. Lett.* **1986**, 1719; Mochida, K.; Kochi, J. K.; Chen, K. S.; Wan, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2927; Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.*, **1985**, 1781; Watanabe, H.; Kato, M.; Tabei, E.; Kawabata, H.; Hirai, N.; Sato, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 166; Kyushin, S.; Ehara, Y.; Nakadaira, Y.; Ohashi, M. *Ibid.* **1989**, 279.

(6) Preliminary results: Mizuno, K.; Terasaka, K.; Ikeda, M.; Otsuji, Y. *Tetrahedron Lett.* **1984**, *26*, 5819.

(7) Photosubstitution of 1,4-DCN by use of alkylborate: Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.*, **1985**, *107*, 6710; *Tetrahedron Lett.*, **1986**, *27*, 4261.

(8) Photosubstitution, photoaddition, and photocycloaddition of 1,4-DCN by use of alkylbenzene derivatives: Albini, A.; Fasani, E.; Oberti, R. *Tetrahedron*, **1982**, *38*, 1027; Albini, A.; Fasani, E.; Sulpizio, A. *J. Am. Chem. Soc.*, **1984**, *106*, 3562; Anbini, A.; Fasani, E.; Mella, M. *Ibid.*, **1986**, *108*, 4119.

(9) Photocycloaddition of 1,4-DCN by use of 2,3-dimethyl-2-butene: Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron,T. S. *Pure Appl. Chem.*, **1980**, *52*, 2609.

(10) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(11) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd. W. P.; Mattes, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8973; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *Ibid.* **1991**, *113*, 3601.

(12) Nakadaira, Y.; Otani, S.; Kyushin, S.; Ohashi, M.; Sakurai, H.; Funada, Y.; Sakamoto, K.; Sekiguchi, A. *Chem. Lett.* **1991**, 601.

(13) Pac, C.; *Pure Appl. Chem.* **1986**, *58*, 1249; Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265; *Ibid.*, **1981**, *103*, 4499; Steichen, D. S.; Foote, C. S. *Ibid.*, **1981**, *103*, 1855; Schaap, A. P.; Lopez, L.; Gagnon, S. D. *Ibid.*, **1983**, *105*, 663; Schaap, A. P.; Siddiqui, S.; Gagnon, D.; Lopez, S. D. *Ibid.*, **1983**, *105*, 5149 and references cited therein.

(14) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 2589; Sommer, L. H.; Tyler, L.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2872; Abel, E. W.; Rowley, R. J. *J. Organomet. Chem.* **1975**, *84*, 199.

(15) Heiss, L.; Paulus, E. F.; Rehling, H. *Liebig. Ann. Chem.* **1980**, 1583.

(16) Murov, S. L. *Handbook of Photochemistry*, Marcel Dekker,; New York, **1973**, p. 94 and p. 119.