REGIOSELECTIVE PHOTOALLYLATIONS OF DICYANOPOLYCYCLIC AROMATIC COMPOUNDS VIA ELECTRON TRANSFER

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Abstract: Upon irradiation with allyltrimethylsilane, dicyanopolycyclic aromatic
compounds undergo two modes of photoallylations, depending on the compounds and
the reaction conditions.   Both the photoreactions occur in a highly
regioselective manner via electron transfer.

Photoallylation by allylic silanes is the subject of a current interest
from synthetic and mechanistic viewpoints.[1-3]   Mariano and his co-workers have
reported an allylation at a C=N bond by the photoaddition of allylic silanes to
iminium salts.[1]   However, little is known about photoallylation on a nucleus of
aromatic compounds.[2]   We now report two modes of regioselective photoallyla-
tions by allyltrimethylsilane on 1,4-dicyanonaphthalene (DCN), 9,10-dicyano-
anthracene (DCA), and 9,10-dicyanophenanthrene (DCP) and related photoreaction.
The mechanistic features of these photoreactions are also discussed.

Irradiation of an acetonitrile solution containing DCN (2 mmol) and
allyltrimethylsilane (1, 10 mmol) through Pyrex filter for 5 h under nitrogen
atmosphere afforded 1-allyl-4-cyanonaphthalene (2, mp 59-60 °C, 34%), 1-allyl-
1,4-dicyano-1,2-dihydronaphthalene (3, oil, 8%), and 3,6-dicyano-4,5-benzotri-
cyclo[4.2.1.0^{3,8}]nonane (4, mp 152-153 °C, 42%).   These products were isolated
by column chromatography on silica gel.   The structures of the products were
established by spectral properties[4] and chemical transformations.

Treatment of 3 with NaOMe in MeOH afforded 2 in 90% yield.   Irradiation of
3 in CH$_3$CN through Pyrex gave 4 in a quantitative yield.   The photolysis of 3
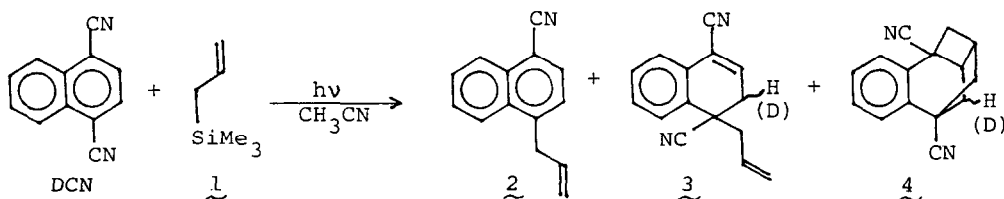
in the presence of NaOMe also gave 4 in a high yield.   Consequently, it is apparent that 2 and 3 are the primary products and 4 is the product derived from 3 under the reaction conditions.   The 400 MHz ^{1}H and ^{13}C NMR spectra of 4 showed unequivalent eight aliphatic proton and seven aliphatic carbon signals, respectively.[4,5]   The other possible structure 4', which could be formed by a [2+2] intramolecular cyclization of 3, can be excluded by the NMR data; if the compound has the structure 4', it should exhibit four kinds of aliphatic proton signals and five kinds of aliphatic carbon signals in the NMR spectra, because 4' has a symmetry plane bisecting the benzene ring.
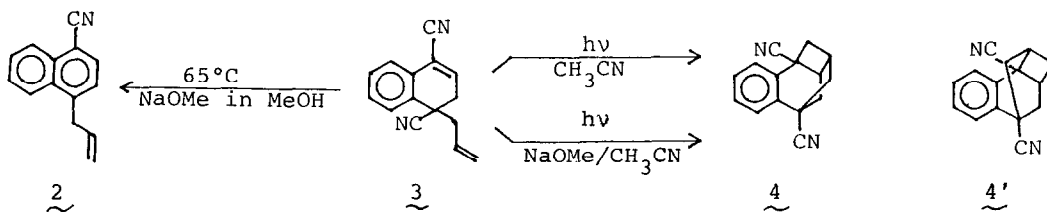
The product distribution in the photoreaction changed with irradiation time and also by the addition of additives.   The results are summarized in Table 1. The selectivity in the formation of 2 was largely enhanced by the addition of NaOMe or NaOH.   The rates of the formation of 3 and 4 were accelerated by the addition of MeOH or H_2O.   When the photoreaction was carried out in the presence of MeOD or D_2O, deuterium atom was incorporated in 3 and 4.   However, the deuterated compounds were not obtained by the photoreaction in CD_3CN.   It is therefore conceivable that a small amount of H_2O included in CH_3CN or CD_3CN is a proton source in the formation of 3 and 4.

The photoallylation was also accelerated by the addition of aromatic hydrocarbons such as phenanthrene (Phen) and pyrene, which were quantitatively recovered after the photoreaction and act as a sensitizer for the photoreaction.[6,7]

The photoreaction of DCA with 1 in CH_3CN-MeOH (9:1) afforded a 1 : 1 mixture of cis- and trans-9-allyl-9,10-dicyano-9,10-dihydroanthracenes (5) in a

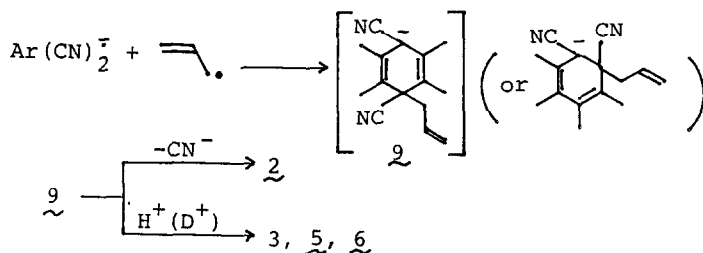Table 1. Effects of Additives in the Photoallylation of DCN by 1

Solvent	Additive	Irrad time/h	Total Yield of Products/%	Product Ratio 2 : 3 : 4		
CH_3CN		5	85	40	10	50
CH_3CN-MeOH (9:1)		3	90	20	20	60
CH_3CN-H_2O (9:1)		3	80	15	20	65
CH_3CN	NaOMe	2	70	90	5	5
CH_3CN	NaOH	2	80	90	6	4
CH_3CN-MeOH (9:1)	Phen	1	90	5	5	90

quantitative yield. The photoreaction of DCP with 1 under similar conditions gave cis- and trans-9-allyl-9,10-dicyano-9,10-dihydrophenanthrenes (6) in 80% yield. Treatment of 5 and 6 with NaOMe in MeOH in the dark gave 7 and 8 in 73% and 98% yields, respectively.
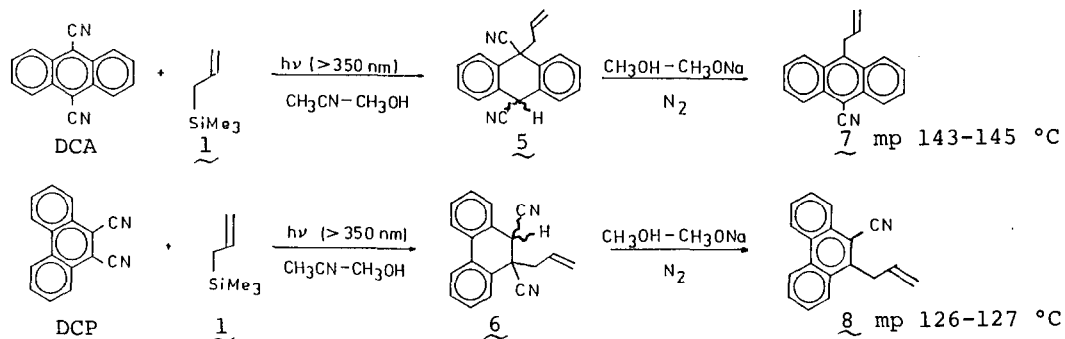
The fluorescence of DCN and DCA in CH_3CN was efficiently quenched by 1 at nearly diffusion controlled rates ($k_q \simeq 6 \times 10^9 \ mol^{-1} dm^3 s^{-1}$). Estimation of the free energy change ($\Delta G = -32.5$ and $-21.8 \ kJ \ mol^{-1}$) by the Rehm-Weller equation suggested that the electron transfer process from 1 to the excited singlet DCN and DCA should be exothermic.[8] However, the fluorescence of these dicyanoaromatics was hardly quenched by 1 in benzene, and the photoallylation did not occur in this solvent.

From these results, we propose the electron transfer mechanism as shown in Scheme 1 for the photoallylations of dicyanoaromatics $Ar(CN)_2$. The first step is one-electron transfer from 1 to the excited singlet dicyanoaromatics $Ar(CN)_2^*$ to produce the radical ion pair ($Ar(CN)_2^{-\bullet}\cdots1^{+\bullet}$) which dissociates to the radical anion $Ar(CN)_2^{-\bullet}$ and the radical cation $1^{+\bullet}$. The attack of allyl radical generated from $1^{+\bullet}$ toward $Ar(CN)_2^{-\bullet}$ gives the anionic intermediate 9 which collapses to the substitution product by loss of cyanide ion or affords the reductive allylation products upon protonation. The choice for these two processes depends upon the aromatic stabilization of dicyanoaromatics. The large rings such as DCA and DCP, which have lower resonance energy per π-electron, preferentially undergo the addition reaction to give only the reductive allylation products. On the other hand, the dicyanobenzenes, which have higher resonance energy per π-electron, preferentially undergo the substitution reaction to give only the substitution products. The naphthalene derivative is intermediate between these two groups of compounds and gives a mixture of the reductive allylation and substitution products. The proposed mechanism is consistent with the fact that in the photoreaction of DCN with 1, the addition of a proton source such as MeOH or H_2O enhances the formation of 3 and 4, but the addition of NaOMe or NaOH enhances the formation of 2. The role of aromatic hydrocarbons in the photoreaction is probably to suppress a back-electron transfer from $Ar(CN)_2^{-\bullet}$ to $1^{+\bullet}$.
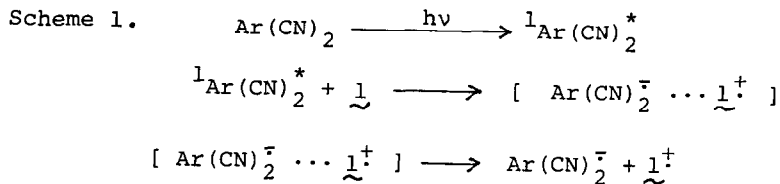
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Scheme 1. $Ar(CN)_2 \xrightarrow{h\nu} {}^1Ar(CN)_2^*$

$${}^1Ar(CN)_2^* + \underset{\sim}{1} \longrightarrow [\; Ar(CN)_2^{\bar{}} \cdots \underset{\sim}{1}^{\cdot +} \;]$$

$$[\; Ar(CN)_2^{\bar{}} \cdots \underset{\sim}{1}^{\cdot +} \;] \longrightarrow Ar(CN)_2^{\bar{}} + \underset{\sim}{1}^{\cdot +}$$

$$Ar(CN)_2^{\bar{}} + \overset{}{\diagup}{\cdot} \longrightarrow \left[\text{(structure)} \right] \left(or\ \text{(structure)} \underset{\sim}{9} \right)$$

$$\underset{\sim}{9} \xrightarrow[\;\; H^+(D^+)\;\;]{-CN^-} \begin{array}{l} \underset{\sim}{2} \\ \underset{\sim}{3},\ \underset{\sim}{5},\ \underset{\sim}{6} \end{array}$$

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4. Compound $\underset{\sim}{3}$: IR ν_{max} 3045, 2920, 2240(C≡N, sh), 2230(C≡N), 1655(C=C) cm^{-1}; m/e 220(M$^+$); ^{1}H NMR δ(CDCl$_3$) 2.54(2H, d, J=7 Hz), 2.95(2H, d, J=5 Hz), 5.25(2H, d, J=3 Hz), 5.4-6.1(1H, m), 6.70(1H, t), 7.2-7.6(4H, m).   Compound $\underset{\sim}{4}$: IR ν_{max}(KBr) 2950, 2910, 2220(C≡N, vw); m/e 220(M$^+$); ^{1}H NMR (400 MHz) δ(CDCl$_3$) 1.72(1H), 2.04(1H), 2.20(1H), 2.34(1H), 2.54(1H), 2.99(1H), 3.14(1H), 3.78(1H), 7.39(2H), 7.53(1H), 7.74(1H); ^{13}C NMR (400 MHz) δ(CDCl$_3$) 35.13(1H, d), 37.02(1H, s), 40.29(1H, t), 41.49(1H, t), 44.75(1H, s), 45.44(1H, d), 45.68(1H, d), 121.02(1H, s), 121.23(1H, s), 137.34(1H, s).

5. The structure of $\underset{\sim}{4}$ was further confirmed by the X-ray diffraction study by Professor K. Shima at Miyazaki University and will be reported in a full paper.   The authors are grateful to Professor Shima for this X-ray diffraction study.

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(Received in Japan 21 September 1985)