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[3+2]-Photocycloadditions of Dicyanonaphthalenes to Alkenes

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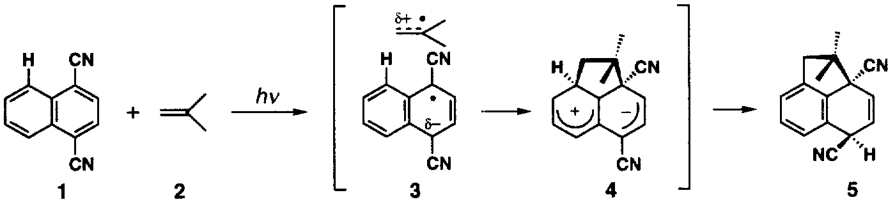
Abstract: [3+2]-Photocycloadditions of 1,2-, 1,3-, and 2,3-dicyanonaphthalenes to alkenes were found to proceed at the 1,8-, 4,5-, and 1,8-positions of the naphthalene ring of dicyanonaphthalenes, respectively. In the photoreactions of the 1,3- and 2,3-isomers [3+2]-adducts were obtained in oxidized forms and addition of $Cu(OAc)_2$ considerably improved the yields of the adducts. The observed addition sites of the alkenes are rationalized on the basis of the spin and charge densities of the radical anions of dicyanonaphthalenes.

Keywords: Photochemistry; Cycloadditions; Nitriles; Alkenes

There has been considerable interest in the photocycloadditions of arenes to alkenes from synthetic and mechanistic viewpoints [1]. Although a number of [2+2]-, [4+2]-, and [4+4]-photoadditions of arenes to alkenes or dienes has been well known, a very limited number of [3+2]-cycloadditions, five-membered ring formation, has so far been reported [2-4]. We have found a novel 1,8-photoaddition of dimethyl 1,4-naphthalenedicarboxylate and 1,4-dicyanonaphthalene (**1**) to alkenes, a formal [3+2]-cycloaddition, which proceeds stereospecifically possibly via formation of an exciplex **3** and almost synchronous two bond formation in **3** to give a zwitterionic intermediate **4** followed by proton transfer (eq 1) [5,6].



(1)

We report here that [3+2]-photocycloadditions of 1,2-, 1,3-, and 2,3-dicyanonaphthalenes (**6**, **7**, **8**) to alkenes proceed in quite general, and that observed addition sites of the alkenes may be reasonably rationalized on the basis of the spin and charge densities of the radical anions of dicyanonaphthalenes.

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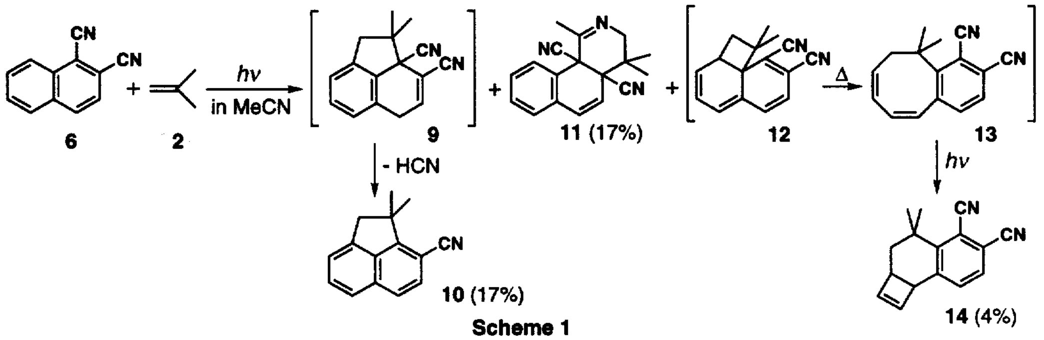
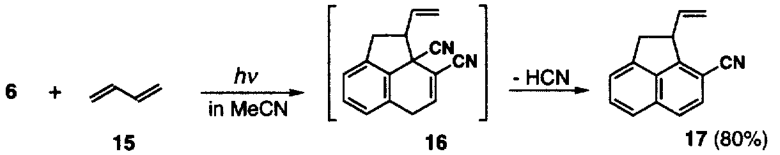


Scheme 1



(2)

Irradiation of an acetonitrile solution of **6** (4×10^{-3} mol/dm^3) and isobutene (**2**, 1 mol/dm^3) with a high-pressure Hg lamp through an uranium filter (> 320 nm) under a nitrogen atmosphere gave a [3+2]-adduct **10** at the 1,8-position of the naphthalene ring of **6** with loss of HCN, together with an acetonitrile-incorporated [2+2+2]-adduct **11** [7] and a cyclobutene derivative **14** [8], which possibly occurred from a [2+2]-photocycloaddition of **6** to **2** to give **12** followed by a thermal ring opening and a photochemical electrocyclic reaction (Scheme 1). These products were isolated by column chromatography on silica gel. Their structures were determined by their spectral properties, especially by their ^{1}H NMR spectra[2] and NOE experiments.

The [3+2]-photocycloadditions of **6** also proceeded to dienes. Thus, the reaction with 1,3-butadiene (**15**, 1 mol/dm^3) gave a [3+2]-adduct **17** at the 1,8-position of the naphthalene ring of **6** in 80% yield (eq 2). There were no evidences of the formation of the [3+2]-adducts at the 4,5-positions of the naphthalene ring of **6** despite the careful examinations of the reaction mixture.

On the other hand, photoreactions of the **7** with aliphatic alkenes were rather complex, but gave [3+2]-adducts in oxidized forms in relatively low yields. However, when the reactions were carried out in the presence of an oxidant, such as $Cu(OAc)_2$, the yields of the adducts were considerably improved. For example, the photoreaction of **7** (3×10^{-3} mol/dm^3) with 1-hexene (**18**, 0.8 mol/dm^3) in the presence of $Cu(OAc)_2$ (3×10^{-3} mol/dm^3) gave an oxidized [3+2]-adduct **20** at the 4,5-position of the naphthalene ring of **7** and a cyclobutene derivative **23** in yields of 68% and 9%, although that in the absence of $Cu(OAc)_2$ afforded **20** and **23** in yields of 22% and 4%, respectively (Scheme 2). In these reactions there were no evidences of the formation of the [3+2]-adduct at the 1,8-position despite the careful examinations of the reaction mixture.

[3+2]-Photoadditions of **7** were found to proceed with retention of the stereochemistry of

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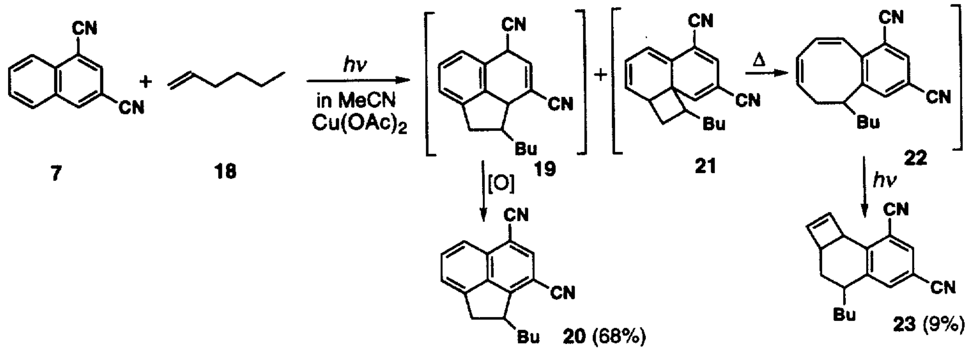
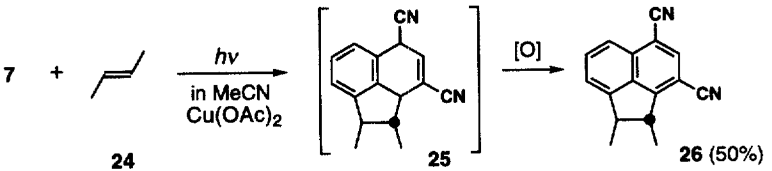
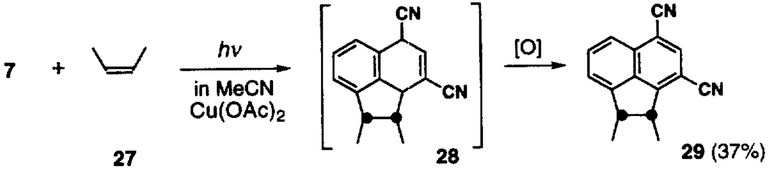
[2] ^{1}H NMR ($CDCl_3$, 270 MHz): **10**; δ 1.65 (s, 6H), 3.33 (s, 2H), 7.36-7.68 (m, 5H): **11**; δ 1.32 (s, 3H), 1.55 (s, 3H), 1.83 (dd, *J* = 1.2, 2.4 Hz, 3H), 3.50 (dd, *J* = 2.4, 8.6 Hz, 1H), 3.72 (dd, *J* = 1.4, 8.6 Hz, 1H), 5.86 (d, *J* = 9.8 Hz, 1H), 6.71 (d, *J* = 9.8 Hz, 1H), 7.18 (m, 1H), 7.46 (m, 2H), 7.93 (m, 1H): **14**; 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).



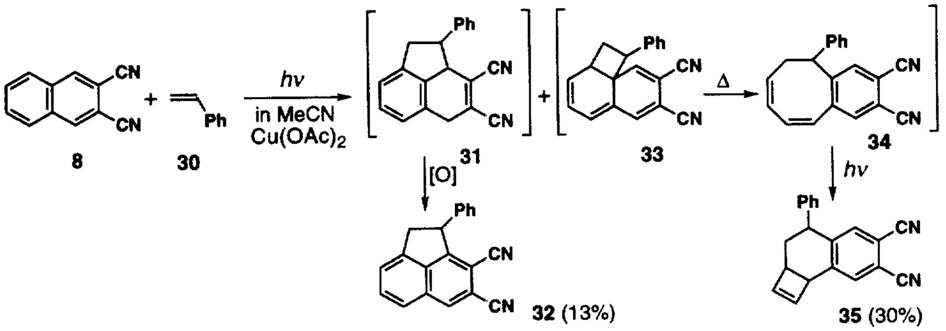
Scheme 2



(3)



(4)



Scheme 3

alkenes. Thus, irradiation of **7** with *trans*-2-butene (**24**, 1 mol/dm^3) in the presence of Cu(OAc)$_2$ (3×10^{-3} mol/dm^3) gave **26**, while that with *cis*-2-butene (**27**, 1 mol/dm^3) afforded **29** (eq 3,4). No cis-trans isomerized adducts were observed on irradiation with **24** and **27**.

Although no photoreactions of **8** with aliphatic alkenes were observed in the absence and in the presence of Cu(OAc)$_2$ possibly due to the poor electron acceptability of **8** ($E^{\mathrm{red}} = -1.55$ *V* in 0.1 mol/dm^3 Bu$_4$NClO$_4$/MeCN vs. Ag/0.01 mol/dm^3 AgClO$_4$) compared with those of **1** (-1.21 *V*), **6** (-1.01 *V*), and **7** (-1.16 *V*), a photoaddition to styrene (**30**, 1×10^{-2} mol/dm^3) was found to proceed to give an oxidized [3+2]-adduct **32** in yields of 8% and 13%, together with a cyclobutene derivative **35** as the major product in yields of 29% and 30%, in the absence and in the presence of Cu(OAc)$_2$ (3×10^{-3} mol/dm^3), respectively (Scheme 3).

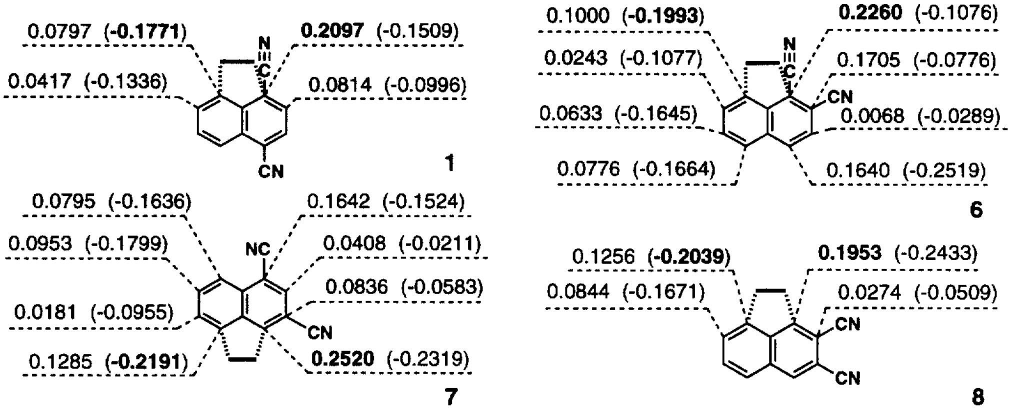


Chart 1. Spin and charge (in parenthesis) densities of the radical anions of 1,4-, 1,2-, 1,3-, and 2,3-dicyanonaphthalenes (**1**, **6**, **7**, **8**) by PM3 calculations.

In summary, [3+2]-photocycloadditions were confirmed to be quite general in the photoreactions of isomeric dicyanonaphthalenes with alkenes. In the cases of the photoreactions of the 1,3- and 2,3-isomers **7**,**8** addition of $Cu(OAc)_2$ was found to be an effective method of improving the yields of the oxidized [3+2]-adducts. In competition with the [3+2]-cycloadditions cyclobutene formations and an acetonitrile-incorporated [2+2+2]-addition were observed depending on the structures of dicyanonaphthalenes and alkenes.

An interesting feature of the [3+2]-cycloadditions of dicyanonaphthalenes is that the addition sites, at which the additions of the alkenes occur, depend largely on the structures of dicyanonaphthalenes. The difference between the addition site of the 1,8-position for the 1,2-isomer **6** and that of the 4,5-position for the 1,3-isomer **7** seems to be unique. Based on the proposed mechanism for the [3+2]-cycloaddition (eq 1), the key step determining the addition sites may be the almost synchronous two-bond formation in the exciplex, radical coupling and electrophilic attack of the cationic center of the alkene moiety, and thus the spin and charge densities of the radical anions of dicyanonaphthalenes can play an important role in determining the addition sites. As a result, the spin and charge densities obtained by PM3 calculations (Chart 1) are found to excellently rationalize the observed addition sites. Thus, the highest spin density of the radical anion of **6** is observed at the 1-position and the negative charge density of the 8-position is considerably high. On the contrary the spin of the radical anion of **7** localizes at the 4-position and the negative charge density of the 5-position is considerably high.

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