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The Photochemical Reaction between Dicyanobenzenes and 2,3-Dimethyl-2-butene in Acetone Solution: A Potential Route to Substituted 2,3-Dihydro-1H-inden-1-ones

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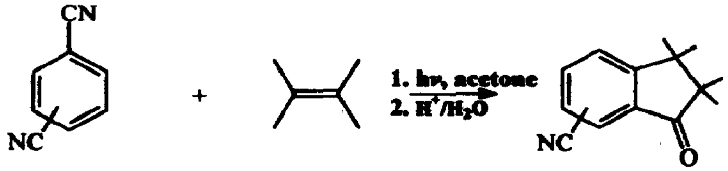
Abstract: *Irradiation of 1,3- or 1,4-dicyanobenzene in the presence of 2,3-dimethyl-2-butene, in acetone solution, affords cyano-substituted 2,3-dihydro-2,2,3,3-tetramethyl-1H-inden-1-ones in good yields.*

Over the last 25 years, the photochemical reactivity between aromatic carbonitriles and alkenes has been an area of intense research activity.[1,2] Amongst one of the important features to emerge from these studies was the strong solvent influence upon the outcome of the photoreaction. For example, irradiation of the dicyanobenzenes in the presence of 2,3-dimethyl-2-butene (1) in polar acetonitrile solution yields substitution products as a result of photoinduced electron transfer, whilst in non-polar benzene solution, no reaction is observed to occur[2]. We now wish to report a new mode of photoreactivity of the dicyanobenzenes with 1, when acetone is used as a solvent.

Irradiation of an acetone solution of 1,4-dicyanobenzene (2, 0.16 mol dm^{-3}) and 1 (0.48 mol dm^{-3}) by means of a 400W medium pressure mercury lamp through pyrex (>280nm) under a nitrogen atmosphere followed



1,4- (2)
1,3- (4)
1,2- (6)

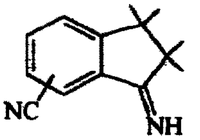
(1)

5-CN (3) 67%
6-CN (5) 68%
7-CN (7) trace

by column chromatography (silica gel) of the photolysate, resulted in the isolation of a pale-yellow crystalline material, which was identified as 5-cyano-2,3-dihydro-2,2,3,3-tetramethyl-1H-inden-1-one (**3**, 67% isolated yield).

Our structural assignment rests predominantly upon the infra-red, ^{1}H and ^{13}C NMR, and mass-spectral data[3], which also compares well with the data reported for related structures.[4] Similar results were obtained when 1,3-dicyanobenzene (**4**) was irradiated, whereas the *ortho* isomer (**6**) proved relatively unreactive. Dark control experiments established that the reaction is indeed a photochemical process.

The above new compounds are not primary photoproducts, but probably arise from hydrolysis (on silica gel?) of the imines **8-10**, themselves resulting from what is formally a [3+2] cycloaddition reaction between the dicyanobenzenes and 2,3-dimethyl-2-butene, and which involves one of the nitrile functions.



5-CN (**8**)
6-CN (**9**)
7-CN (**10**)

Imines 8-10 have proven difficult to isolate, but evidence for their existence as intermediates stems from two experimental observations. Thus, during the course of photolyses, reaction mixtures were monitored by gas-chromatography/ion-trap detection (GC/ITD), which revealed that the major product yielded prominent ions at m/e 213 and 197 (base peak). Analyses of the isolated products by GC/ITD, however, yielded different retention times, and ions at m/e 213 (M^{+}) and 198 (base peak), as expected for structures **3**, **5** and **7**. Presumably, the spectrum before isolation is that given by the imine, with the peak at m/e 213 being due to the protonated form[5], and m/e 197 corresponding to (M-15).

Further evidence for the imine intermediates stems from the monitoring of the photoreaction between **1** and **2** in acetone-d_6 by ^{1}H NMR spectroscopy. This revealed the formation of a product whose spectrum resembled that of the isolated ketone **3** very closely, except for an additional broad, exchangeable peak at *ca.* 2.9ppm.

There are to our knowledge only two reports of similar [3+2] photocycloaddition reactions between cyanoaromatics and alkyl olefins, and in these cases the solvent used was either acetonitrile,[4b] or acetonitrile/methanol mixtures.[4a] These are usually the solvents of choice for photosubstitution or photosubstitution-nucleophilic addition (i.e. photo-NOCAS[1b]) reactions of cyanoaromatics via photoinduced electron transfer pathways, as is the case for the dicyanobenzenes.[1b,2] Thus, we are the first to report that a photosubstitution mode of reactivity may be replaced by [3+2] photocycloaddition on switching to acetone solvent.

The mechanism for formation of imines **8-10** is not clear. Arnold and co-workers[4a] have proposed, and given spectroscopic evidence for, a charge-transfer (CT) mechanism in their system, which involved acetonitrile-methanol mixtures as solvent. In fact, careful scrutiny of the UV absorption spectrum of 1,4-dicyanobenzene (**2**) in acetone solution has revealed the appearance of a long wavelength tail (cutoff *ca.* 375nm) when 2,3-dimethyl-2-butene (**1**) was added. However, the possibility of involvement of the triplet state in the mechanism for the cycloaddition cannot be ruled out at this stage.[6] It is unlikely that a pathway that involves the formation of solvent-separated radical ions is operative in the relatively non-polar acetone solvent.[7]

The lack of reactivity of 1,2-dicyanobenzene (**6**) was unexpected. Presumably, steric factors are responsible for this anomalous behaviour. This hypothesis is supported by the fact that, in the UV studies mentioned above, the long-wavelength tailing was less pronounced in the case of **6**, when compared to **2**. Therefore, it is plausible that steric/ electronic factors are preventing formation of a CT complex in this case.

In conclusion, the reactions reported here represent a new mode of photoreactivity between the dicyanobenzenes and **1**. Ongoing studies in our laboratory are focusing on mechanistic details, as well as examining other cyanoaromatic/alkene combinations so as to determine whether this type of reaction is a general one when acetone is used as the solvent. Indeed, preliminary results indicate that benzonitrile undergoes a similar cycloaddition reaction when irradiated in acetone solution, in the presence of **1**. The outcome of these, and other studies will be presented in the full paper.

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References

1. See, for example: a) Kubo, Y.; Noguchi, T.; Inoue, T. *Chem. Lett.* **1992**, 2027. b) Arnold, D.R.; Du, X. *J. Am. Chem. Soc.* **1989**, *111*, 7666. c) Lewis, F.D.; DeVoe, R.J. *Tetrahedron* **1982**, *38*, 1069. d) McCullough, J.J.; MacInnis, W.K.; Lock, C.J.L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4644. e) Arnold, D.R.; Wong, P.C.; Maroulis, A.J.; Cameron, T.S. *Pure & Appl. Chem.* **1980**, *52*, 2609. f) Cantrell, T.S. *J. Org. Chem.* **1977**, *42*, 4238, and references cited therein.

2. Borg, R.M.; Arnold, D.R.; Cameron, T.S. *Can. J. Chem* **1984**, *62*, 1785.

3. Spectral and other data for **3** and **5**: **3**: mp 106^{0}C; ^{1}H NMR (250 MHz, $CDCl_3$, ppm vs. TMS) 1.11 (s, 6H), 1.26 (s, 6H), 7.66 (dd, 1H, J = 7.7 Hz), 7.80 (dd, 1H, J = 7.7 Hz), 7.79 (s, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$, ppm vs. TMS) 21.4 (q), 26.1 (q), 45.1 (s), 54.1 (s), 117.6 (s), 118.2 (s), 124.7 (d), 127.6 (d), 131.2 (d), 136.6 (s), 161.6 (s), 204.5 (s). IR (KBr) 2965, 2225, 1720, 1603, 1380, 842 cm^{-1}. Mass spec. (GC/ITD, m/e (rel.int.)) 198 (100), 199 (53), 213 (33). Anal. calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.70; H, 7.10; N, 6.61. **5**: mp 137^{0}C; ^{1}H NMR (250 MHz, $CDCl_3$, ppm vs. TMS) 1.10(s, 6H), 1.25 (s, 6H), 7.61 (dd, 1H, J = 0.6, 8.0 Hz), 7.86 (dd, 1H, J = 1.6, 8.0 Hz), 8.01 (dd, 1H, J= 0.6, 1.6 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$, ppm vs. TMS) 21.4 (q), 26.0 (q), 45.5 (s), 53.9 (s), 111.7 (s), 118.1 (s), 124.5 (d), 128.2 (d), 134.2 (s), 137.5 (d), 165.7 (s), 204.5 (s). IR (KBr) 2983, 2226, 1722, 1610, 1367, 847 cm^{-1}. Mass spec. (GC/ITD, m/e (rel. int.)) 198 (100), 199 (46), 213 (30). Anal. calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 79.01; H, 7.10; N, 6.66.

4. a) McMahon, K; Arnold, D.R. *Can. J. Chem* **1992**, *71*, 450. b) Ohashi M.; Aoyagi, N.; Miyama, T.; Kyushin, S.; Yamada, S. *J. Chem. Soc. Perkin Trans. 1* **1990**, 189.

5. Prominent protonated molecular ion peaks are a well-known feature of ion-trap detectors. See: Vella, A.J. *Org. Mass Spec.* **1992**, *27*, 145.

6. The [3+2] photochemical cycloaddition of 3-cyano-5,5-dimethyl-2-cyclohexenone to alkyl olefins has been shown to occur via an excited triplet pathway. See: Saito, I.; Shimozoni, K.; Matsuhara, T. *J. Org. Chem.* **1982**, *47*, 4356.

7. It is interesting to note that the irradiation of 4-cyanopyridine in the presence of alkyl olefins in acetone solution has been reported to yield substitution products, similar to those obtained for the dicyanobenzenes in acetonitrile via a radical ion mechanism (ref 2). No imine/ketone formation was observed in either case. See: Bernardi, R.; Caronna, T.; Morocchi, S.; Traldi, P.; Vittimberga, B.M. *J. Chem. Soc. Perkin Trans. 1* **1981**, 1607.

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