

The electron transfer photochemistry of allenes with cyanoarenes. Photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) and related reactions

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The photochemical reactions of 1,2,4,5-tetracyanobenzene (**1**), 1,4-dicyanobenzene (**2**) and 1,4-dicyanonaphthalene (**3**) with tetramethylallene (**4**) and 1,1-dimethylallene (**5**) in acetonitrile–methanol solution have been investigated. Both **1** and **2** give 1 : 1 : 1 arene–allene–methanol products (**7–12**) in which addition of methanol occurs exclusively at the central allene carbon with aromatic substitution at the termini. The formation of these products is rationalised on the basis of a photoinduced electron transfer mechanism described as the photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction. Cyanoarene **3** undergoes photochemical reactions initially similar to the photo-NOCAS reaction, but with addition to the arene occurring instead of substitution. The primary product (example, **22**) was not isolated since it undergoes further photochemical reactions. Compound **22** and its dimethyl analogues react *via* a photoinduced intramolecular $[2\pi + 2\pi]$ cycloaddition across the 3,4-double bond to give tricyclo 1 : 1 : 1 arene–allene–methanol adducts (**14**, **17** and **18**) or add methanol and cyclise to bicyclo 1 : 1 : 2 arene–allene–methanol adducts (**15**, **19** and **20**). The use of biphenyl (**6**) as a co-donor enhances the efficiency of all the photoinduced electron transfer reactions studied. In fact, removing **6** from the reaction mixture containing **3** and **5** diverts the reaction from the electron transfer pathway and instead gives an exciplex-mediated $[4\pi + 2\pi]$ cycloadduct, **21**. The mechanisms, with particular reference to the regiochemical selectivities observed in the photoreactions involving **5**, are discussed.

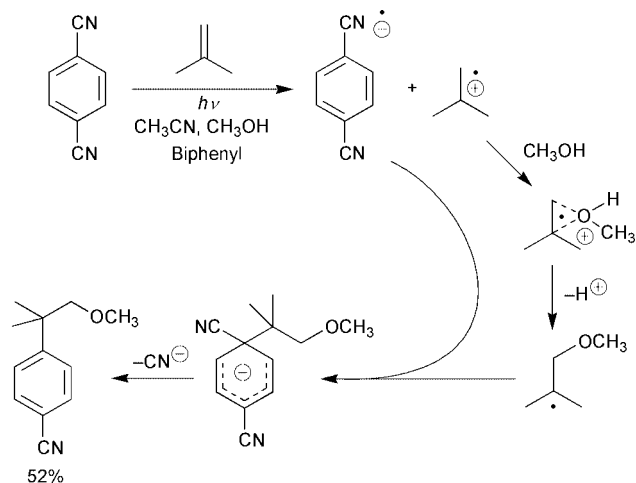
Introduction

The photochemically induced electron transfer between cyanoaromatic electron acceptors and olefinic electron donors, such as simple aliphatic alkenes, conjugated and non-conjugated dienes, and various terpenes in the presence of a variety of nucleophiles has been thoroughly investigated in the context of the photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction, and has provided invaluable mechanistic information regarding the behaviour of photogenerated radical ions.^{1–5} This reaction involves the combination of the three reagents (arene, olefin and nucleophile), generally in an *anti*-Markovnikov regioselective

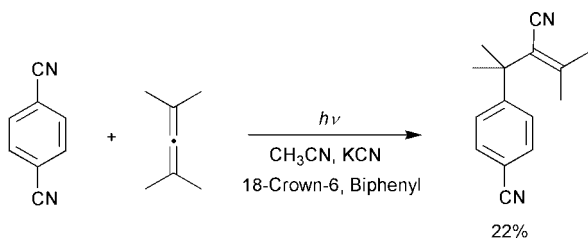
fashion (with a few exceptions). The reaction outline in Scheme 1 illustrates the mechanism utilising 2-methylpropene as the electron donor, with 1,4-dicyanobenzene and methanol as the electron acceptor and nucleophile respectively.³ The observed *anti*-Markovnikov regioselectivity is a direct consequence of the involvement of the olefin radical cation and can be either thermodynamically or kinetically controlled, depending on the nature of the nucleophile.⁴ An uncharged nucleophile such as methanol results initially in the formation of a distonic radical cation upon addition to the olefin radical cation. This distonic species is capable of equilibration with its alternative isomeric form *via* a bridged intermediate—in this case the regiochemistry is determined by the stability of the β -alkoxyalkyl radicals resulting from the irreversible deprotonation of the bridged distonic radical cations.^{4a} Alternatively, utilising a negatively charged nucleophile such as fluoride anion leads to a kinetically controlled regioselectivity in which steric and polar factors dominate. Fluoride addition occurs at the less hindered site to give the more highly substituted β -fluoroalkyl radical, even when this leads to the less stable radical intermediate.^{4b}

In this study we expand our understanding of the mechanistic and synthetic aspects of the photo-NOCAS pathway by extending the reaction to aliphatic allenes as the electron donors.

The electron transfer photochemistry of these species is relatively unexplored. To the best of our knowledge, the only studies reported in the literature are an earlier report from our laboratory⁵ and the work of Mariano.⁶ We have previously observed that irradiation of 1,4-dicyanobenzene and tetramethylallene in the presence of cyanide anion gave the photo-NOCAS product, 4-(4-cyanophenyl)-2,4-dimethylpent-2-ene-3-nitrile in 22% yield (Scheme 2).



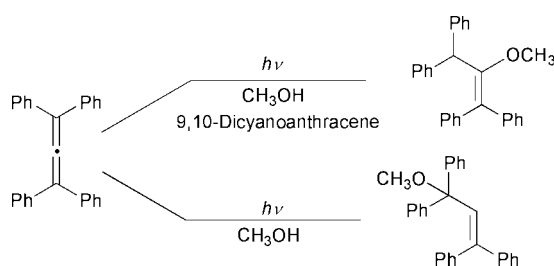
Scheme 1



Scheme 2

Mariano and co-workers conducted a more extensive study on a series of allenes utilising 2-phenyl-1-pyrrolin-1-ium perchlorate as the electron acceptor and methanol as the nucleophile. Photo-NOCAS adducts were the major products observed. Deprotonation of the allene radical cation (instead of nucleophilic trapping) followed by substitution at the pyrrolinium nucleus, and cycloaddition on the phenyl ring constituted important competing side-reactions; in the absence of a nucleophile, cycloaddition became the dominant reaction pathway.

As is typical with olefins, introduction of aryl groups on the allene inhibits substitution on the electron acceptor and leads to 1:1 allene–nucleophile adducts. This is thought to be partly due to the increased steric bulk of the intermediate allene–nucleophile adduct radical inhibiting its addition to the electron acceptor radical anion, and, more importantly, due to the lower reduction potential of the radical which provides an efficient alternative pathway by enabling it to undergo reduction to the anion by the electron acceptor radical anion. Protonation of the anion yields what is formally an *anti*-Markovnikov allene–nucleophile addition product. Thus, Klett and Johnson reported that tetraphenyl- and triphenylallene undergo a photoinduced electron transfer-mediated methanol addition to give a vinyl ether, in contrast to the allyl ether obtained upon direct irradiation (Scheme 3).⁷ These results parallel studies from our laboratory with 1,1-diphenylethene and related systems.⁸



Scheme 3

The most studied photochemical reactions of allenes are cycloadditions to ketones, cyclic enones, quinones, thiones and related systems.^{9–12} Although a photoinduced electron transfer mechanism has been proposed in one case,¹⁰ these reactions are usually thought to proceed *via* a triplet state exciplex of limited charge transfer character that collapses to a 1,4-biradical.¹¹ However, in a more recent laser flash photolysis study on thione–allene photocycloadditions, no evidence for such an exciplex precursor was found and a mechanism involving direct formation of the biradical was suggested.¹² Whatever the operating mechanism, the reaction outcome is strongly dependent both on the structure of the reactants as well as on the nature of the excited state, with $[2\pi + 2\pi]$ cyclobutane, oxetane and various $[4\pi + 2\pi]$ cycloadditions reported.

With a view to further defining the photochemical reactivity of allenes, we hereby present the results from our investigations into the photoinduced electron transfer reactions of the allenes, tetramethylallene (2,4-dimethylpenta-2,3-diene, **4**) and

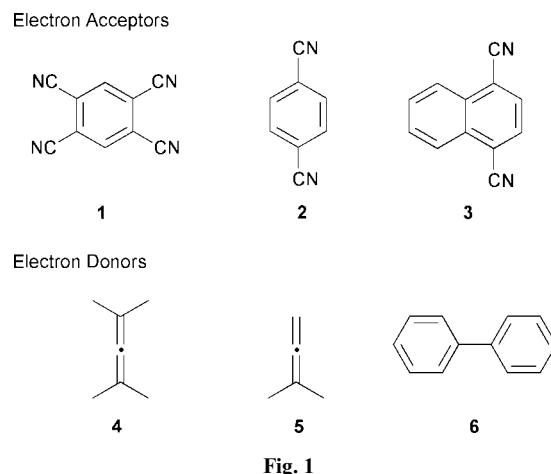


Fig. 1

Table 1 Half-wave reduction potentials (E_2^{red}) and singlet excitation energies ($E_{0,0}$) for the electron acceptors and half-wave oxidation potentials (E_2^{ox}) for the electron donors. All potentials are reported vs. SCE in CH_3CN

Compound	$E_2^{\text{red}}/\text{V}^a$	E_2^{ox}/V	$E_{0,0}/\text{eV}^a$
1,2,4,5-Tetracyanobenzene (1)	−0.65		3.83
1,4-Dicyanobenzene (2)	−1.66		4.21
1,4-Dicyanonaphthalene (3)	−1.28		3.45
Tetramethylallene (4)		+1.93 ^b	
1,1-Dimethylallene (5)		+2.23 ^c	
Biphenyl (6)		+1.85 ^d	

^a Ref. 15. ^b Ref. 5. ^c Peak potential $E^{\text{ox}} = 1.92 \text{ V}$ vs. Ag/Ag^+ in CH_3CN , cyclic voltammetry, 100 mV s^{-1} scan rate, tetraethylammonium tetrafluoroborate as supporting electrolyte.¹⁶ Corrected to E_2^{ox} by subtracting 0.03 V from the peak potential;¹⁷ referenced to SCE by adding 0.34 V . ^d Ref. 1d.

1,1-dimethylallene (3-methylbuta-1,2-diene, **5**), with the cyanoarenes, 1,2,4,5-tetracyanobenzene (**1**), 1,4-dicyanobenzene (**2**) and 1,4-dicyanonaphthalene (**3**) in the presence of methanol as nucleophile (Fig. 1).

Results and discussion

Photochemistry of 1,2,4,5-tetracyanobenzene (**1**)

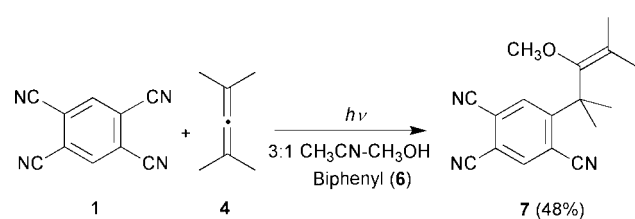
The singlet excited state of 1,2,4,5-tetracyanobenzene (**1**) possesses an exceptionally high reduction potential ($E_2^{\text{red}}(\mathbf{1}^*) = E_2^{\text{red}}(\mathbf{1}) + E_{0,0}(\mathbf{1}) = 3.18 \text{ V}$, Table 1), making it a very effective electron acceptor for photoinduced electron transfer (PET). The reason why **1** has not received as much attention as an electron acceptor in PET studies as other cyanoarenes, such as 1,4-dicyanobenzene (**2**) and 9,10-dicyanoanthracene, is mainly due to the pronounced stability (low oxidation potential) of its radical anion. This renders it a poor photosensitiser since its radical anion is generally incapable of being oxidised back to the neutral starting material in order to complete the photosensitisation cycle.¹³ Nevertheless, it has proven to be very successful in PET reactions that do not require photosensitisation but rather involve the electron acceptor as a reactant. Albini and co-workers have exploited the properties of this electron acceptor in a variety of photochemical reactions with electron donors, some of which were previously inaccessible due to their relatively high oxidation potentials.¹⁴ We were thus interested in investigating how **1** would perform in a photo-NOCAS system.

In our study, the electron donors have moderately high oxidation potentials (Table 1). As seen in Table 2, the free energy of the PET process involving **1** and the electron donors is highly exergonic in all cases, and electron transfer is expected to proceed at a diffusion-controlled rate.

Irradiation of **1** in the presence of tetramethylallene (**4**) in 3:1 acetonitrile–methanol through a Pyrex filter ($\lambda > 280$ nm) led to 24% consumption of **1** after 45 min of irradiation (Reaction 1, Table 3). The only chromatographable product formed in detectable amounts (39%) was a 1:1:1 arene–allene–methanol adduct, identified as 4-(2,4,5-tricyanophenyl)-3-methoxy-2,4-dimethylpent-2-ene (**7**) by spectroscopic methods and comparison with similar products.^{6b} In particular, the photoproduct was distinguished from another possible isomer, 3-(2,4,5-tricyanophenyl)-4-methoxy-2,4-dimethylpent-2-ene, by consideration of the allylic C-4 resonance in the ¹³C NMR spectrum. The observed signal occurred at too high field (45.2 ppm) for it to be representative of an allylic carbon bearing a methoxy group.

The inclusion of biphenyl (**6**) as a co-donor in the photochemical mixture had a beneficial effect on both the efficiency and yield of the photoreaction, boosting the rate of consumption to 50% after 45 min of irradiation and increasing the yield of photoproduct **7** to 48% (Reaction 2, Table 3; Scheme 4).

The role of co-donors such as **6** is not fully understood. There are numerous reports in the literature in which PET reac-



Scheme 4

Table 2 Free energy (ΔG_{PET}) for the photoinduced electron transfer process between the singlet excited states of the electron acceptors and the ground state of the electron donors

Electron acceptor	Electron donor	$\Delta G_{\text{PET}}/\text{kJ mol}^{-1}$ ^a
1	6	-134
1	4	-126
1	5	-97
2	6	-73
2	4	-65
2	5	-36
3	6	-36
3	4	-29
3	5	0

^a Calculated using the Weller equation: $\Delta G_{\text{PET}} = F(E_2^{\text{ox}} - E_2^{\text{red}} - E_{0,0} - e/4\pi\epsilon a)$.¹⁸ The Coulombic attraction term $F/4\pi\epsilon a$ was calculated as 5.4 kJ mol⁻¹ by assuming an encounter distance a of 7 Å.^{1a}

Table 3 Photochemical reactions between the cyanoarenes **1–3** and the allenes **4** and **5**. Reaction conditions: 1 kW medium-pressure Hg lamp, Pyrex filter, 5 °C, 45 min irradiation time, 3:1 acetonitrile–methanol (except where indicated otherwise)

Reaction number	Acceptor (% consumed)	Donor	Co-donor (% recovered)	Products (% yield)
1	1 (24)	4	—	7 (39)
2	1 (50)	4	6 (94)	7 (48)
3	1 (23)	5	—	8 (7), 9 (1)
4	1 (61)	5	6 (98)	8 (37), 9 (5)
5	2 (10)	4	—	10 (7)
6	2 (46)	4	6 (98)	10 (42)
7	2 (7)	5	—	11 (21), 12 (8), 13 (8)
8	2 (43)	5	6 (95)	11 (36), 12 (4), 13 (10)
9	3 (10)	4	—	14 (11), 16 (5)
10	3 (75)	4	6 (100)	14 (54), 16 (24)
11	3 (85)	5	—	17 (8), 18 (22), 21 (26)
12	3 (95)	5	6 (94)	17 (8), 18 (18), 19 (22), 20 (20)
13 ^a	3 (84)	5	—	21 (38)
14 ^b	3 (88)	5	—	21 (42)

^a In acetonitrile. ^b In benzene.

tions are enhanced by the addition of an appropriate co-donor, generally an aromatic hydrocarbon.¹⁹

Typically, the oxidation potential of the co-donor D is higher than that of the donor substrate Q but lower than the reduction potential of the excited state of the electron acceptor A* so that both steps shown in Scheme 5 will be exergonic. The resulting



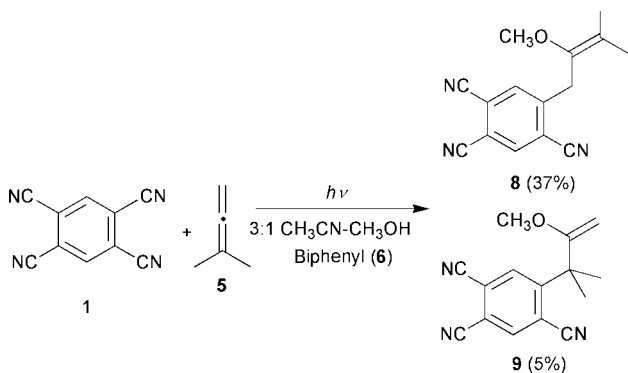
Scheme 5

reaction enhancement is a consequence of the slower rate of back electron transfer (BET) for the A^{·-}–D^{·+} pair as opposed to that of the A^{·-}–Q^{·+} pair, a phenomenon attributed to a smaller reorganisation energy for D^{·+} going back to D.²⁰ Reducing the rate of BET prolongs the lifetime of the radical ion pair, allowing the two species to become efficiently solvated and to diffuse apart as free, solvated radical ions.

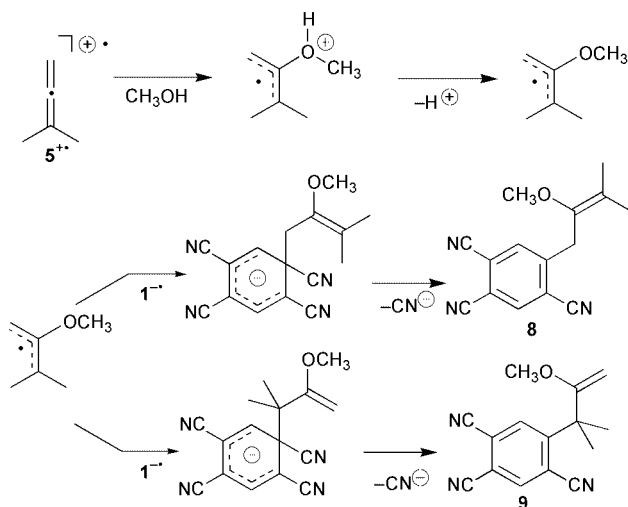
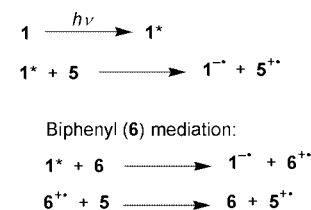
However, in many cases, including the present one, the oxidation potential of the co-donor D is lower than that of the donor substrate Q, which implies that the second step in Scheme 5 is endergonic. Despite this, a marked enhancement in the photochemical reaction is commonly observed.²¹ The prevalent explanation put forward to account for this is that the co-donor radical cation D^{·+} and the donor Q lie in equilibrium with a small amount of the donor radical cation Q^{·+} and the co-donor D; consumption of Q^{·+} drives the equilibrium forward generating more Q^{·+}. Alternatively, this may be viewed as the formation of a π -complex between D^{·+} and Q that imparts substantial charge onto Q.²²

Biphenyl (**6**) also enhances the photochemical reaction between 1,2,4,5-tetracyanobenzene (**1**) and 1,1-dimethylallene (**5**), resulting in 61% consumption of **1** after 45 min of irradiation and the formation of two isomeric 1:1:1 arene–allene–methanol adducts, 1-(2,4,5-tricyanophenyl)-2-methoxy-3-methylbut-2-ene (**8**, 37%) and 3-(2,4,5-tricyanophenyl)-2-methoxy-3-methylbut-1-ene (**9**, 5%) (Reactions 3 and 4, Table 3; Scheme 6). The two products are readily distinguished by the presence of two distinct resonances in both the ¹H and ¹³C NMR spectra representing the magnetically non-equivalent methyl groups in **8**; a situation not encountered in **9**. Furthermore, **9** exhibits two doublets (²J = 3.6 Hz) in the ¹H NMR spectrum characteristic of the two geminal olefinic protons.

The formation of photoproducts **7**, **8** and **9** can be readily explained by means of a photo-NOCAS mechanism.^{1–5} The mechanism, exemplified for 1,1-dimethylallene (**5**) as the electron donor, is illustrated in Scheme 7. Electron transfer, either



Scheme 6



Scheme 7

directly to the excited singlet state of **1** from the ground state of the allene **5**, or mediated by biphenyl (**6**), leads to the formation of the cyanoarene radical anion, $1^{\cdot-}$, and the allene radical cation, $5^{\cdot+}$. The latter adds methanol, exclusively at the central carbon, to give a β -methoxyallyl radical. No products arising from addition of methanol to a terminal allenyl carbon are observed. The absence of such products is clear evidence that the allene radical cation does not add to the cyanoarene radical anion *via* a radical coupling mechanism while still within the geminate radical ion pair, prior to nucleophilic trapping. If this mechanism were operational we would not expect to observe the aryl moiety attached to a terminal allenyl carbon since this would generate a highly unstable vinyl cation. This alternative mode of reactivity was suggested in early studies on these types of photoreactions,²³ but was largely disfavoured in subsequent work,²⁴ with the exception of a few special cases.²⁵ The observed reaction enhancement upon addition of biphenyl (**6**) is further proof against this alternative mechanism: generating the allene radical cation and the cyanoarene radical anion in separate stages should inhibit geminate radical ion pair reactions and increase the probability of interception of the allene radical cation by methanol prior to its addition onto the aromatic ring.

The final stage in the mechanism involves the addition of the β -methoxyallyl radical to the *ipso* position of $1^{\cdot-}$, which, as expected, is the site of highest spin density (Fig. 2). This is

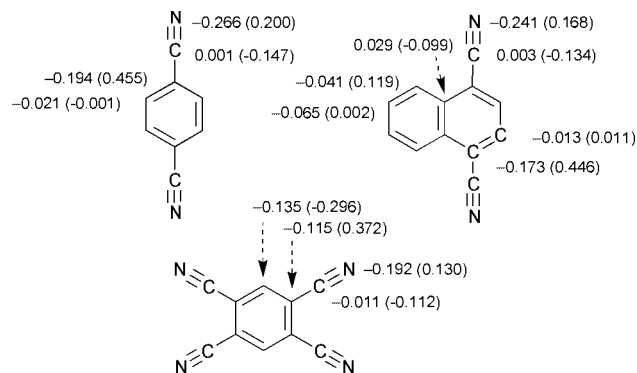
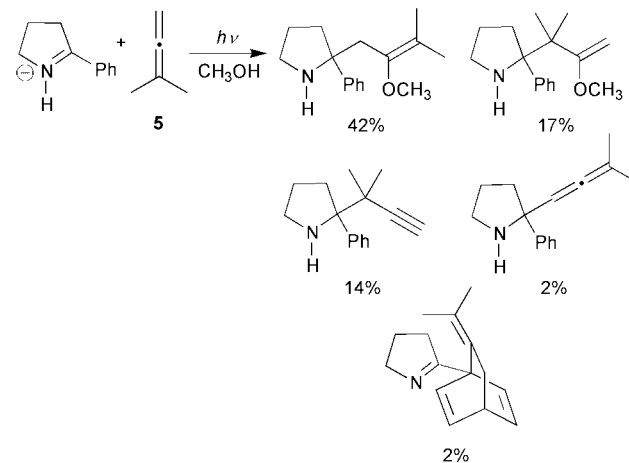


Fig. 2 Atomic charge densities with hydrogens summed into heavy atoms and total atomic spin densities (in parentheses) for the radical anions of electron acceptors **1–3** calculated by the semi-empirical AM1 method.

followed by rearomatisation of the adduct anion *via* expulsion of a cyanide ion to yield the final photo-NOCAS product. The unsymmetrical β -methoxyallyl radical derived from 1,1-dimethylallene (**5**) provides two distinct sites of reactivity. The predominance of photoproduct **8** (**8**:**9** = 7) in the reaction mixture indicates that the addition of the β -methoxyallyl radical to the cyanoarene radical anion is sterically controlled, with the less heavily substituted radical site being more reactive; a situation typical of radical coupling reactions.²⁶ This observation is analogous to that reported by Mariano in which reaction at the less substituted site of the β -methoxyallyl radical of $5^{\cdot+}$ is favoured by a factor of 2.5 (Scheme 8).⁶

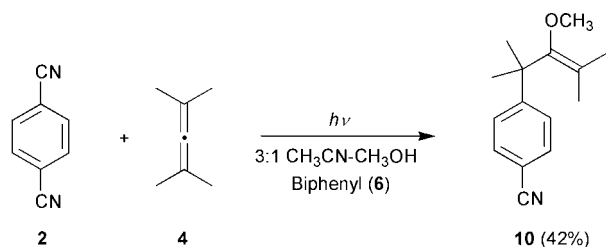


Scheme 8

Photochemistry of 1,4-dicyanobenzene (**2**)

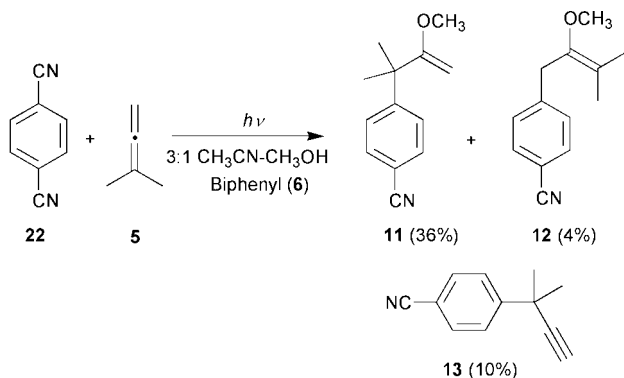
1,4-Dicyanobenzene (**2**) behaves similarly to the tetracyano analogue **1**. The reduction potential of the singlet excited state (2.55 V) is somewhat lower than that of 1^* ; nevertheless, electron transfer with the electron donors **4–6** is expected to be highly exergonic (Table 2) and proceed at a diffusion-controlled rate. However, the photoreaction with tetramethylallene (**4**) is inefficient in the absence of a co-donor (Reaction 5, Table 3). A single photo-NOCAS product, identified as 4-(4-cyanophenyl)-3-methoxy-2,4-dimethylpent-2-ene (**10**), is obtained in low yield (7%). Addition of biphenyl (**6**) to the reaction mixture greatly improves the reaction, resulting in 46% consumption of **1** after 45 min of irradiation and an enhanced yield of **10** of 42% (Reaction 6, Table 3; Scheme 9).

In analogy to the reaction between 1,2,4,5-tetracyanobenzene (**1**) and 1,1-dimethylallene (**5**), photolysis of **2** in the presence of **5** delivered two photo-NOCAS products, arising from reaction at the non-equivalent ambident termini of the unsymmetrical β -methoxyallyl radical derived from **5**. In this



Scheme 9

case, however, the major product after 45 min of irradiation was 3-(4-cyanophenyl)-2-methoxy-3-methylbut-1-ene (**11**), obtained in 36% yield when biphenyl (**6**) was used as co-donor (Reaction 8, Table 3; Scheme 10). This is the product arising



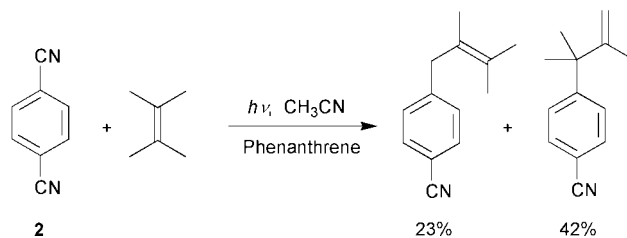
Scheme 10

from reaction at the more sterically hindered terminus of the β -methoxyallyl radical. The isomeric 1-(4-cyanophenyl)-2-methoxy-3-methylbut-2-ene (**12**), which is the analogue of the major product in the similar reaction involving **1** (Reactions 3 and 4, Table 3), was detected only in trace amounts (4%). Its identity was tentatively established based solely on its GC–MS characteristics; unfortunately, we were unable to isolate this compound.

We have considered the possibility that this switch in product ratio might be due to the adventitious consumption of **12**. The dimethylvinyl ether moiety is an electron-rich centre and is expected to possess a low oxidation potential (for comparison, E_2^{ox} for (*Z*)-2-methoxybut-2-ene is 1.73 V, SCE).²⁷ This would enable it to undergo electron transfer with 2^* in preference to **5** ($E_2^{\text{ox}} = 2.23$ V, SCE). Although GC monitoring of the photo-reaction does show changes in the product ratio as the reaction progresses, at no point during the reaction does the product ratio favour isomer **12**. The ratio of **11**:**12** varies from *ca.* 3.5 after 2 minutes to *ca.* 10 after 115 minutes of irradiation time. Nevertheless, the photolability of these products bearing vinyl ether moieties might account for the non-quantitative yields of the reactions.

This alteration in regiochemistry has interesting implications for the behaviour of the allylic radical intermediates. It appears that, in the absence of steric crowding at the cyanoarene reaction site (as in the case of **2**), the allylic radical will react preferentially from the more highly substituted allylic terminus, which is expected to bear a greater portion of the spin density. A similar regiochemical outcome has been observed in the PET-induced substitution reaction of 2,3-dimethylbut-2-ene and 1,4-dicyanobenzene (**2**), which proceeds *via* a very similar allylic radical, generated by deprotonation of the alkene radical cation (Scheme 11).^{1a,f,4b,23b}

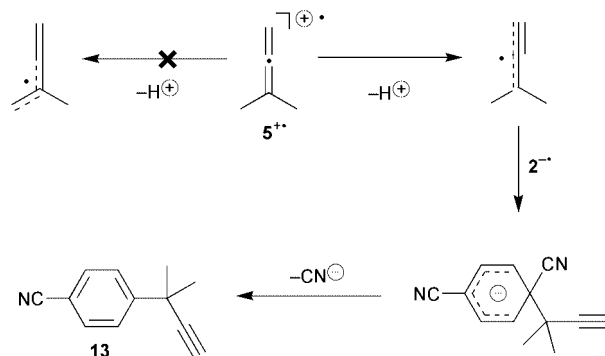
However, increasing the steric crowding at the *ipso*-position of the cyanoarene (as in the case of **1**) causes the allylic radical to react preferentially from the less substituted terminus. The fact that, in these reactions, both isomers are present, albeit in drastically different proportions, suggests that the two



Scheme 11

regiochemical reaction pathways must differ only slightly in their activation energy barriers. Which pathway is favoured will depend on a fine balance between various contributing factors such as steric hindrance and spin density distribution. A recent study on the PET-induced addition of allylic radicals (formed *via* deprotonation of alkene radical cations) to phenoxy radicals (*via* proton abstraction from 1,4-benzoquinone radical anions) has shown similar trends as regards the regiochemical selectivity of non-symmetrical allylic radicals—in the absence of *ortho*-substituents on the phenoxy moiety, reaction occurred exclusively at the more highly substituted allylic terminus, but increasing the steric bulk of the *ortho*-substituents clearly favoured reaction at the less-substituted allylic terminus.³⁰

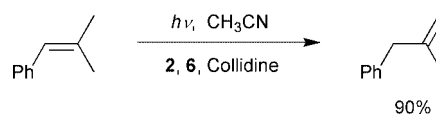
The only other product evident in the chromatogram of the reaction between **2** and **5** was 3-(4-cyanophenyl)-3-methylbut-1-yne (**13**, 10%). This is thought to form *via* deprotonation of the allenyl radical cation $5^{+\cdot}$, according to the mechanism in Scheme 12. It is interesting to note that deprotonation in $5^{+\cdot}$



Scheme 12

occurs exclusively from the allenyl sp^2 -carbon site rather than from the methyl sp^3 -carbon centre, a phenomenon attributed to kinetic acidity.^{6b,31}

Deprotonation of alkene radical cations is commonly observed as the major reaction pathway in the absence of a nucleophile. In the case of aliphatic alkenes, the allylic radical formed upon deprotonation usually substitutes, from either ambident end, at the *ipso*-position of the cyanoarene radical anion to give 1:1 arene–alkene products (Scheme 11).^{1a,f,4b,23b} With aromatic alkenes, the allylic radical does not substitute but instead gets reduced to the allylic anion, which can then get protonated at either end of the allylic moiety to regenerate the starting material or to give a deconjugated tautomer (Scheme 13).³²



Scheme 13

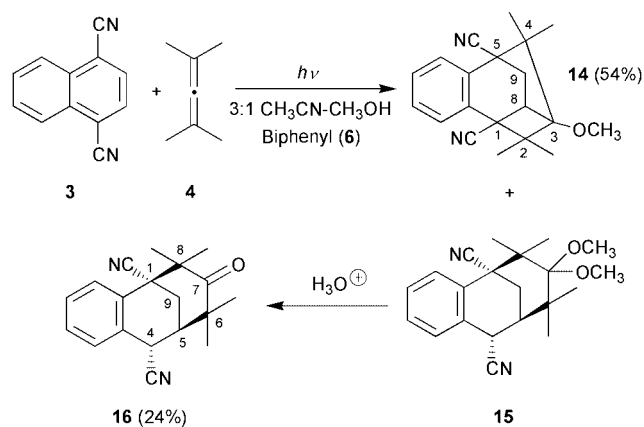
Alkene radical cations are generally not acidic enough for deprotonation to compete effectively with nucleophilic trapping by strong nucleophiles such as methanol.^{32b} Deprotonation only becomes competitive in the presence of weaker nucleophiles

such as fluoride anion which also has substantial basic character.^{4b} In contrast, the increased acidity of allene radical cations does allow deprotonation to compete with nucleophilic addition. In addition to the results obtained in this work, Mariano and co-workers also observed appreciable amounts of 1:1 products derived from deprotonation of the allene radical cation (Scheme 8).⁶ Similarly, Klett and Johnson reported the formation of a deprotonation product (1,3,3-triphenylpropyne) in their PET study on triphenylallene.^{7b} Both of these reactions were conducted in pure methanol.

Photochemistry of 1,4-dicyanonaphthalene (3)

1,4-Dicyanonaphthalene (**3**) possesses the lowest excited state reduction potential (2.17 V, Table 1) among the electron acceptors chosen for this investigation. This is mainly due to its low singlet excitation energy, $E_{0,0}$. Nevertheless, the free energies for PET are still sufficiently exergonic to ensure an efficient electron transfer process, except in the case of 1,1-dimethylallene (**5**) for which the free energy is isoergic (Table 2). As in the previous experiments, biphenyl (**6**) was found to enhance the reactions (Table 3).

Thus, the photolysis of **3** and tetramethylallene (**4**) in the presence of **6** gave two crystalline products upon chromatographic workup which were identified as 1,5-dicyano-3-methoxy-2,2,4,4-tetramethyl-6,7-benzotricyclo[3.2.2.0^{3,8}]nonane (**14**, 54%) and *cis*-1,4-dicyano-6,6,8,8-tetramethyl-7-oxo-2,3-benzo-*cis*-bicyclo[3.3.1]nonane † (**16**, 24%) (Reaction 10, Table 3; Scheme 14).



Scheme 14

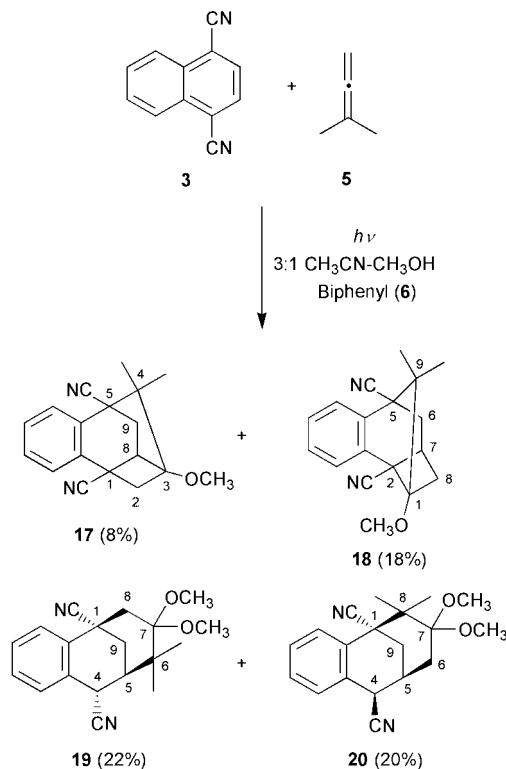
The structural assignments of both products were confirmed by X-ray crystallographic analyses since spectroscopic interpretation was not trivial. In particular, the absence of vicinal coupling constants in the ¹H NMR spectra of both products was quite misleading. In the case of **14**, only one of the two geminal C-9 protons appeared, as expected, as a doublet of doublets (2.71 ppm, ²*J* = 12.8 Hz, ³*J* = 4.6 Hz); the other showed up as a simple doublet (1.88 ppm, ²*J* = 12.8 Hz) and as a consequence the vicinal C-8 proton appeared as a doublet (3.45 ppm, ³*J* = 4.6 Hz) as well. The Karplus equation predicts that a vicinal coupling constant is reduced to a minimum when the dihedral angle between the coupled protons is approximately 90°;³³ crystallographic analysis of **14** suggested a value of 76° for one dihedral angle between the C-8 proton and one of the C-9 protons. The other dihedral angle is estimated as 47°. The observed coupling of 4.6 Hz would then represent the coupling at this 47° angle, in a situation where 0° is approximately 8 Hz.

† The IUPAC names for the parent hydrocarbons that form the basis of structures **14–21** are tetracyclo[8.2.1.0^{2,7}.0^{8,11}]trideca-2(7),3,5-triene (**14**, **17**), tricyclo[7.3.1.0^{2,7}]trideca-2(7),3,5-triene (**15**, **16**, **19**, **20**), tetracyclo[7.3.1.0^{2,11}.0^{3,8}]trideca-3(8),4,6-triene (**18**) and tricyclo[6.2.2.0^{2,7}]dodeca-2,4,6-triene (**21**).

This is a reasonable value in view of the presence of electron withdrawing substituents next to the tricyclic ring protons which may contribute to a reduction in the coupling constants.^{33a,34}

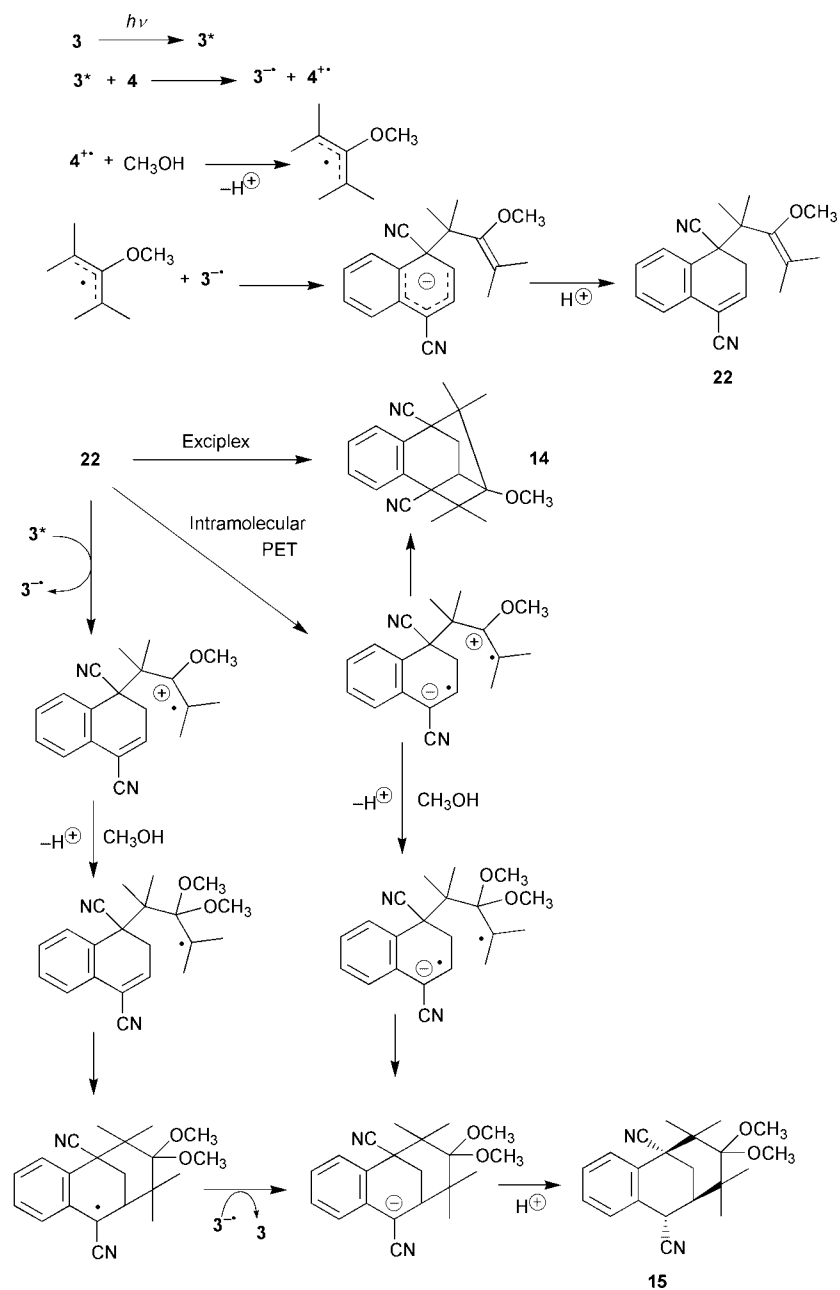
The bicyclo-ring ¹H NMR resonances in **16** also displayed some peculiarities that made reliable structural elucidation difficult. One of the C-9 proton signals appeared at 3.26 ppm as a doublet of doublets of doublets, displaying a geminal coupling of 14.5 Hz to the other C-9 proton and a vicinal coupling of 4.0 Hz to the C-5 proton, as well as a long-range w-coupling of 1.5 Hz to the C-4 proton. All the couplings to the C-5 proton (2.61 ppm) were either zero or small so that its resonance appeared as a broad singlet. Furthermore, the low-field C-4 proton (4.19 ppm) was a broad apparent singlet that failed to exhibit the vicinal coupling to the C-5 proton and the w-coupling to the C-9 proton at 3.26 ppm. Compound **16** is most probably the hydrolysis product of acetal **15** (*vide infra*), although we were unable to isolate **15** from the reaction mixture.

The photolysis of **3** and 1,1-dimethylallene (**5**) led to a more complex mixture of products due to the regiochemical possibilities arising from the involvement of the unsymmetrical allene. When biphenyl (**6**) was used we were able to isolate the four major products from the photochemical mixture: two 1:1:1 arene–allene–methanol tricyclic products, 1,5-dicyano-3-methoxy-4,4-dimethyl-6,7-benzotricyclo[3.2.2.0^{3,8}]nonane (**17**, 8%) and 2,5-dicyano-1-methoxy-9,9-dimethyl-3,4-benzotricyclo[3.3.1.0^{2,7}]nonane (**18**, 18%), and two 1:1:2 arene–allene–methanol bicyclic products, *cis*-1,4-dicyano-7,7-dimethoxy-6,6-dimethyl-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**19**, 22%) and *trans*-1,4-dicyano-7,7-dimethoxy-8,8-dimethyl-2,3-benzo-*cis*-bicyclo[3.3.1]nonane † (**20**, 20%) (Reaction 12, Table 3; Scheme 15).



Scheme 15

Spectroscopic identification of the products **17–20** was further complicated by the possibility of regioisomers. Therefore, the characterisation of these products relied mainly on their X-ray crystallographic analyses. The ¹H and ¹³C NMR spectra of the tricyclic product **17** were very similar to those of **14**. In the ¹³C NMR spectrum, the two lower-field methyl carbons (26.0 and 27.0 ppm) and one of the high-field



Scheme 17. In this earlier study, however, the product ratio implies that addition of the allylic radical to the *ipso*-position of the arene radical anion occurs predominantly from the less substituted end. This contrasts with our current results and lends support to the hypothesis that the regiochemical control in these reactions is very sensitive to the controlling factors and is, therefore, hard to predict reliably.

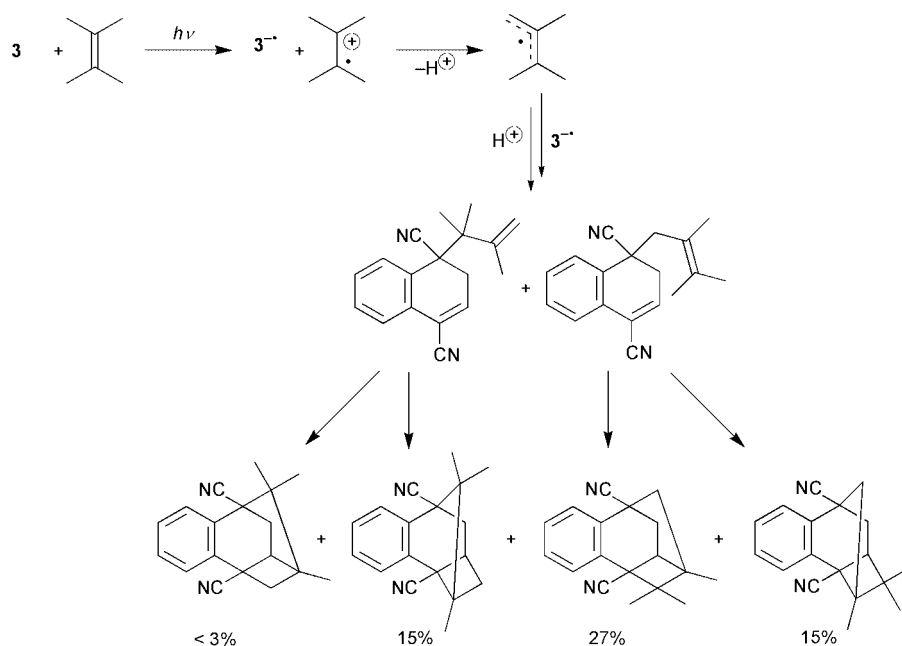
The effect of biphenyl (**6**) on the photochemical reaction between **3** and **5** merits some attention. As shown in Table 2, the free energy for the PET process between **3** and **5** is isoergic, so that electron transfer is disfavoured when no co-donor mediation is possible. The major product **21** is formally a $[4\pi + 2\pi]$ photocycloadduct, formed *via* the addition of an allene double bond across the 5,8-positions of the naphthalene ring. It is clearly a product arising directly from the exciplex and precludes the formation of separated radical ions, since a solvent-separated radical cation of **5** would invariably add methanol or alternatively undergo deprotonation prior to reaction with the arene radical anion. In fact, the formation of this cycloadduct is insensitive to solvent polarity and proceeds as efficiently in benzene (Reaction 14, Table 3) as it does in methanol or acetonitrile (Reaction 13, Table 3). It is surprising

that addition occurs across the 5,8-positions rather than across the 1,4-positions. Most of the spin and charge densities are expected to reside at the cyano-substituted ring-carbon atoms and an exciplex of substantial charge transfer character would involve the allene complexing preferentially with the cyano-substituted ring. However, exciplex formation is known to be very sensitive to steric interactions and the unusual regiochemistry that is observed is most likely a consequence of steric inhibitions exerted by the cyano substituents.

Conclusions

The photoinduced nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction has been successfully extended to include the reactions between aliphatic allenes and cyanoarenes. Although the yields are only moderate, the reactions mentioned represent simple and straightforward one-pot synthetic methods for the products shown, which, to the best of our knowledge, are all new compounds.

More importantly, this study has provided us with further support for establishing an accurate mechanistic scheme for the photo-NOCAS reaction, which we have used in a lot of our



Scheme 18

previous work as a mechanistic framework for understanding the behaviour of photogenerated radical ions.^{1,3-5} The strict regiochemical control, involving the exclusive addition of the nucleophile to the central allenic carbon and the cyanoarene to the terminal one, supplements earlier studies from our laboratory with conjugated dienes^{1f} and firmly establishes the sequence of mechanistic events in the photo-NOCAS reaction, with nucleophilic trapping of the olefin radical cation occurring prior to addition to the cyanoarene radical anion.

The drastic variations in the regiochemical selectivity observed in the reactions involving 1,1-dimethylallene (**5**) highlight the difficulty in predicting the preferred site of reactivity in non-symmetrical allylic radicals. The reaction outcome is most likely determined by a fine balance between two opposing factors: steric hindrance at the reaction site and spin density distribution in the allylic radical.

The reactions involving 1,4-dicyanonaphthalene (**3**) indicate that the photo-NOCAS reaction takes a different course with dinuclear cyanoaromatics, favouring addition of the olefin–nucleophile adduct radical to the cyanoarene over substitution, most probably a consequence of a lower rearomatization energy. In these cases, the primary photochemical products were too photoreactive to be detected; the isolated materials resulted from intramolecular $[2\pi + 2\pi]$ cycloaddition and nucleophile addition–cyclisation reactions of these elusive primary products.

Experimental

General information

Photochemical reactions were monitored and analysed by gas chromatography–mass spectrometry (GC–MS) using an HP 5890 gas chromatograph with an SPB-5 (Supelco) bonded 5% diphenylsiloxane–95% dimethylsiloxane fused silica WCOT column (25 m \times 0.20 mm, 0.33 μ m film thickness) and an HP 5970 mass selective detector. Quantitative gas chromatographic analysis was performed on a Perkin-Elmer AutoSystem XL gas chromatograph equipped with an autosampler, flame ionization detector (FID) and an MDN-5S (Supelco) bonded and crosslinked (5% phenyl) methylpolysiloxane fused silica WCOT column (30 m \times 0.25 mm, 0.5 μ m film thickness).

Preparative separation of product mixtures was performed using flash chromatography on a 15 cm \times 5 cm silica gel (Aldrich, 230–400 mesh, 60 Å) column.³⁷ When necessary, this

was followed by preparative, centrifugally accelerated, radial, thin-layer chromatography of the partially purified mixtures using a Chromatotron (Harrison Research) on 4, 2 or 1 mm silica gel (Aldrich, TLC grade 7749 with gypsum binder and fluorescent indicator) plates. The mobile phases were typically hexanes with increasing amounts of ethyl acetate. Collected fractions were analysed by TLC using silica gel plates (Aldrich, 250 μ m plate thickness, 5–17 μ m, 60 Å , with fluorescent indicator) and/or GC–MS.

All ^1H and ^{13}C NMR spectra were acquired on a Bruker AC 250F spectrometer at 250.13 MHz for ^1H and 62.90 MHz for ^{13}C . Chemical shifts are reported in ppm relative to tetramethylsilane ($\delta = 0$ ppm) in ^1H NMR spectra and chloroform- d ($\delta = 77.0$ ppm) or acetonitrile- d_3 ($\delta = 1.39$ ppm) in ^{13}C NMR spectra. Coupling constants (J values) are reported in Hz. The multiplicities of the decoupled ^{13}C NMR signals were determined by J-Modulated Spin-Echo (J-MOD) experiments. Infrared spectra were recorded as films on sodium chloride plates on a Nicolet 510P FT-IR spectrophotometer and are reported in wavenumbers (cm^{-1}). Melting points were determined using a Cybron Corporation Thermolyne apparatus equipped with a digital thermocouple (± 0.1 $^\circ\text{C}$) and are corrected. Elemental analysis was carried out by Canadian Microanalytical Service Ltd., Delta, BC. High-resolution mass spectrometry for exact mass determination was performed on a CEC 21-110 mass spectrometer using an electron-impact energy of 70 eV.

X-Ray crystallography ‡

Single crystal X-ray crystallographic structure determinations were performed at room temperature on a Rigaku AFC5R diffractometer equipped with a 12 kW rotating anode generator utilising graphite monochromated Cu- $K\alpha$ (compounds **14**, **16** and **19**) or Mo- $K\alpha$ (**17**, **18**, **20** and **21**) radiation. All data were corrected for Lorentz and polarization effects, while an empirical absorption correction (ψ scan; **14** and **17**) and/or a correction for secondary extinction (**14**, **18** and **20**) were applied as necessary. All calculations were formed using the teXsan crystallographic software package,³⁸ except for the refinements of compounds **16** and **19** which were carried out using SHELXL-97.³⁹ Problems with acquiring crystals of suitable

‡ CCDC reference number 188/278. See <http://www.rsc.org/suppdata/p2/b0/b007205m/> for crystallographic files in .cif format.

size, shape and/or quality sometimes meant that not enough data could be collected for a full anisotropic refinement of the heavy atoms in a structure. In consequence, compounds **17** and **21** were refined totally isotropically, compounds **16**, **19** and **20** were refined with some atoms anisotropic and other atoms isotropic, while compounds **14** and **18** were refined with all heavy atoms anisotropic. In all cases the reflection to parameter ratio was maintained at 5.0 or greater. Disorder was observed in only one structure (**20**) where the methoxy carbon (C34) was split over two positions, each with an occupancy of one half. In all structures, hydrogen atoms were placed in geometrically calculated positions and not refined.

Materials

1,4-Dicyanobenzene (98%, Aldrich) was purified by treatment with Norite in methylene chloride, followed by sublimation and recrystallisation from 95% ethanol. 1,4-Dicyanonaphthalene was prepared and purified as indicated previously.⁴⁰ Biphenyl (99%, Aldrich) was recrystallised from methanol. 1,2,4,5-Tetracyanobenzene (Pfaltz and Bauer), tetramethylallene (97%, Aldrich), and 1,1-dimethylallene (98%, Aldrich) were used as received. Acetonitrile was distilled twice, first from sodium hydride and then from phosphorus pentoxide. It was then passed through a column of basic alumina, refluxed over calcium hydride for 24 h under a nitrogen atmosphere, fractionally distilled and stored over 3 Å molecular sieves (Aldrich). Methanol was purified by reflux and distillation over magnesium and stored over 3 Å molecular sieves (Aldrich). Hexanes for preparative chromatography were distilled prior to use while ethyl acetate was used without further purification.

Irradiations

Investigative irradiations were performed in 2 cm³ sample volumes in 20 cm × 0.5 cm tubes using a 1 kW medium-pressure mercury-arc lamp (CGE) fitted with a quartz water-cooled jacket immersed in a bath at 5 °C. Reactions used for quantitative analyses were performed in 10 cm³ sample volumes in 20 cm × 1 cm tubes while large-scale preparative photochemical reactions were carried out in 60–160 cm³ volumes in several 20 cm × 2 cm tubes. Tube distance from lamp axis was ca. 6 cm. All irradiations were carried out behind Pyrex ($\lambda > 280$ nm). Reaction details reported below are for the 10 cm³ quantitative-analysis samples. All yields were calibrated with respect to consumed cyanoarene. All quantitative-analysis GLC runs were done in triplicate and used an internal standard method for calibration. Pure samples of all products were isolated from large-scale photoreactions (60–160 cm³) identical in composition to the reactions reported below.

Irradiation of a solution of 1,2,4,5-tetracyanobenzene (1), tetramethylallene (4) and biphenyl (6) in 3:1 acetonitrile-methanol. A solution of 1,2,4,5-tetracyanobenzene (**1**, 0.02 mol dm⁻³), tetramethylallene (**4**, 0.05 mol dm⁻³) and biphenyl (**6**, 0.05 mol dm⁻³) in 3:1 acetonitrile-methanol (10 cm³) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 50% of **1** was consumed, yielding 48% of 4-(2,4,5-tricyanophenyl)-3-methoxy-2,4-dimethylpent-2-ene (**7**). 94% of **6** was recovered after irradiation. In the absence of **7**, only 24% of **1** was consumed after 45 minutes, yielding 39% of **7**.

4-(2,4,5-Tricyanophenyl)-3-methoxy-2,4-dimethylpent-2-ene (**7**). Colourless blocks, mp 166.9–167.6 °C (from hexanes) (Found: C, 72.9; H, 5.8; N, 15.1. C₁₇H₁₇N₃O requires C, 73.1; H, 6.1; N, 15.0%); ν_{\max} (film; NaCl)/cm⁻¹ 3114 (m), 3042 (s), 2990 (s), 2970 (m), 2942 (s), 2916 (m), 2237 (s), 1492 (m), 1445 (m), 1371 (m), 1202 (m), 1193 (m), 1155 (m), 1131 (s), 1120 (s), 1077 (s), 936 (m) and 924 (s); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.00 (3 H, s), 1.62 (6 H, s), 1.73 (3 H, s), 3.73 (3 H, s), 7.94 (1 H, s) and

8.03 (1H, s); δ_{C} (62.90 MHz; CDCl₃) 18.8 (q), 19.4 (q), 28.2 (q), 45.2 (s), 61.4 (q), 113.6 (s), 113.8 (s), 114.41 (s), 114.42 (s), 117.0 (s), 119.1 (s), 119.2 (s), 130.4 (d), 139.0 (d), 153.5 (s), 160.4 (s); m/z 279 (M⁺, 13%), 264 (100), 248 (86), 234 (81) and 194 (49).

Irradiation of a solution of 1,2,4,5-tetracyanobenzene (1), 1,1-dimethylallene (5) and biphenyl (6) in 3:1 acetonitrile-methanol. A solution of 1,2,4,5-tetracyanobenzene (**1**, 0.02 mol dm⁻³), 1,1-dimethylallene (**5**, 0.05 mol dm⁻³) and biphenyl (**6**, 0.05 mol dm⁻³) in 3:1 acetonitrile-methanol (10 cm³) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 61% of **1** was consumed, yielding 37% of 1-(2,4,5-tricyanophenyl)-2-methoxy-3-methylbut-2-ene (**8**) and 5% of 3-(2,4,5-tricyanophenyl)-2-methoxy-3-methylbut-1-ene (**9**). 98% of **6** was recovered after irradiation. In the absence of **6**, 23% of **1** was consumed after 45 minutes, yielding 7% of **8** and 1% of **9**.

1-(2,4,5-Tricyanophenyl)-2-methoxy-3-methylbut-2-ene (**8**). Pale yellow plates, mp 122.3–123.6 °C (from hexanes); ν_{\max} (film; NaCl)/cm⁻¹ 3111 (w), 3043 (m), 2993 (m), 2936 (s), 2831 (m), 2240 (s), 1682 (w), 1603 (m), 1489 (s), 1454 (m), 1386 (m), 1257 (m), 1196 (m), 1132 (s), 1016 (s) and 913 (m); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.75 (3 H, s), 1.76 (3 H, s), 3.48 (3 H, s), 3.83 (2 H, s), 7.82 (1 H, s) and 8.02 (1 H, s); δ_{C} (62.90 MHz; CDCl₃) 17.2 (q), 19.1 (q), 32.2 (t), 57.6 (q), 113.7 (s), 114.2 (s), 114.5 (s), 114.7 (s), 117.8 (s), 119.3 (s), 121.1 (s), 134.9 (d), 136.7 (d), 144.0 (s) and 149.8 (s); m/z 251 (M⁺, 63%), 236 (76), 220 (100), 166 (86), 139 (61) and 85 (49) (M⁺, 251.1061. C₁₅H₁₃N₃O requires *M*, 251.1058).

3-(2,4,5-Tricyanophenyl)-2-methoxy-3-methylbut-1-ene (**9**). Pale yellow plates, mp 129.6–130.8 °C (from hexanes); ν_{\max} (film; NaCl)/cm⁻¹ 3108 (w), 3041 (m), 2971 (m), 2944 (w), 2239 (m), 1609 (s), 1452 (m), 1370 (m), 1295 (m), 1279 (m), 1196 (m), 1175 (m), 1166 (m), 1148 (m), 1049 (s), 928 (s) and 811 (m); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.66 (6 H, s), 3.52 (3 H, s), 4.28 (1 H, d, *J* 3.6), 4.32 (1 H, d, *J* 3.6), 7.90 (1 H, s) and 8.01 (1 H, s); δ_{C} (62.90 MHz; CDCl₃) 27.5 (q), 45.4 (s), 55.4 (q), 83.5 (t), 113.6 (s), 114.3 (s), 114.5 (s), 115.3 (s), 116.9 (s), 119.1 (s), 132.8 (d), 138.9 (d), 156.8 (s) and 165.4 (s); m/z 251 (M⁺, 29%), 236 (100), 220 (30), 204 (75) and 57 (79) (M⁺, 251.1076. C₁₅H₁₃N₃O requires *M*, 251.1058).

Irradiation of a solution of 1,4-dicyanobenzene (2), tetramethylallene (4) and biphenyl (6) in 3:1 acetonitrile-methanol. A solution of 1,4-dicyanobenzene (**2**, 0.02 mol dm⁻³), tetramethylallene (**4**, 0.05 mol dm⁻³) and biphenyl (**6**, 0.05 mol dm⁻³) in 3:1 acetonitrile-methanol (10 cm³) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 46% of **2** was consumed, yielding 42% of 4-(4-cyanophenyl)-3-methoxy-2,4-dimethylpent-2-ene (**10**). 98% of **6** was recovered after irradiation. In the absence of **6**, only 10% of **2** was consumed after 45 minutes, yielding 7% of **10**.

4-(4-Cyanophenyl)-3-methoxy-2,4-dimethylpent-2-ene (**10**). Colourless oil; ν_{\max} (film; NaCl)/cm⁻¹ 2974 (m), 2934 (m), 2838 (w), 2227 (s), 1605 (m), 1503 (m), 1465 (m), 1449 (m), 1198 (m), 1152 (m), 1127 (s), 1108 (s), 1072 (s), 1020 (m), 992 (m) and 838 (m); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.01 (3 H, s), 1.48 (6 H, s), 1.68 (3 H, s), 3.66 (3 H, s) and 7.41–7.59 (4 H, m, AA'BB'); δ_{C} (62.90 MHz; CDCl₃) 19.0 (q), 19.4 (q), 29.2 (q), 45.1 (s), 60.9 (q), 109.0 (s), 118.2 (s), 119.1 (s), 126.5 (d), 132.1 (d), 155.9 (q) and 156.7 (q); m/z 229 (M⁺, 67%), 214 (48), 197 (47), 182 (100), 116 (65) and 70 (48) (M⁺, 229.1467. C₁₅H₁₉NO requires *M*, 229.1457).

Irradiation of a solution of 1,4-dicyanobenzene (2), 1,1-dimethylallene (5) and biphenyl (6) in 3:1 acetonitrile-methanol. A solution of 1,4-dicyanobenzene (**2**, 0.02 mol dm⁻³), 1,1-dimethylallene (**5**, 0.05 mol dm⁻³) and biphenyl (**6**, 0.05 mol dm⁻³) in 3:1 acetonitrile-methanol (10 cm³) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 43%

of **2** was consumed, yielding 36% of 3-(4-cyanophenyl)-2-methoxy-3-methylbut-1-ene (**11**), 4% of 1-(4-cyanophenyl)-2-methoxy-3-methylbut-2-ene (**12**) and 10% of 3-(4-cyanophenyl)-3-methylbut-1-yne (**13**). In the absence of **6**, only 7% of **2** was consumed after 45 minutes, yielding 21% of **11**, 8% of **12** and 8% of **13**.

3-(4-Cyanophenyl)-2-methoxy-3-methylbut-1-ene (**11**). Colourless oil; ν_{\max} (film; NaCl)/cm⁻¹ 2975 (s), 2926 (s), 2852 (m), 2228 (s), 1606 (s), 1505 (s), 1465 (m), 1175 (m), 1095 (m) and 840 (m); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.46 (6 H, s), 3.47 (3 H, s), 4.09 (1 H, d, *J* 2.8), 4.21 (1 H, d, *J* 2.8) and 7.40–7.59 (4 H, m, AA'BB'); δ_{C} (62.90 MHz; CDCl₃) 27.7 (q), 44.2 (s), 55.1 (q), 80.6 (t), 109.6 (s), 119.1 (s), 126.8 (d), 131.9 (d), 153.6 (s) and 168.9 (s); *m/z* 201 (M⁺, 29%), 186 (56), 169 (83), 154 (100) and 116 (87) (M⁺, 201.1159). C₁₂H₁₁N requires *M*, 201.1154).

1-(4-Cyanophenyl)-2-methoxy-3-methylbut-2-ene (**12**). *m/z* 201 (M⁺, 66%), 186 (26), 154 (55) and 116 (100).

3-(4-Cyanophenyl)-3-methylbut-1-yne (**13**). Colourless oil; ν_{\max} (film; NaCl)/cm⁻¹ 3297 (s), 2979 (s), 2933 (m), 2229 (s), 1607 (m), 1504 (m), 1457 (w), 1403 (w), 1364 (w), 1244 (w), 1096 (m), 1019 (w) and 839 (s); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.61 (6 H, s), 2.40 (1 H, s) and 7.60–7.70 (4 H, m, AA'BB'); δ_{C} (62.90 MHz; CDCl₃) 31.2 (q), 36.2 (s), 70.9 (d), 89.4 (s), 110.5 (s), 118.9 (s), 126.4 (d), 132.2 (d) and 151.7 (s); *m/z* 169 (M⁺, 5%), 154 (100) and 127 (38) (M⁺, 169.0898). C₁₂H₁₁N requires *M*, 169.0891).

Irradiation of a solution of 1,4-dicyanonaphthalene (3), tetramethylallene (4) and biphenyl (6) in 3:1 acetonitrile-methanol. A solution of 1,4-dicyanonaphthalene (**3**, 0.02 mol dm⁻³), tetramethylallene (**4**, 0.05 mol dm⁻³) and biphenyl (**6**, 0.05 mol dm⁻³) in 3:1 acetonitrile-methanol (10 cm³) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 75% of **3** was consumed, yielding 54% of 1,5-dicyano-3-methoxy-2,2,4,4-tetramethyl-6,7-benzotricyclo-[3.2.2.0^{3,8}]nonane (**14**) and 24% of *cis*-1,4-dicyano-6,6,8,8-tetramethyl-7-oxo-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**16**). 100% of **6** was recovered after irradiation. In the absence of **6**, only 10% of **3** was consumed after 45 minutes, yielding 11% of **14** and 5% of **16**.

1,5-Dicyano-3-methoxy-2,2,4,4-tetramethyl-6,7-benzotricyclo-[3.2.2.0^{3,8}]nonane (**14**). Colourless plates, mp >163 °C (decomp.) (from hexanes); ν_{\max} (film; NaCl)/cm⁻¹ 2991 (s), 2957 (s), 2837 (w), 2236 (m), 1489 (s), 1449 (s), 1392 (m), 1378 (m), 1264 (m), 1153 (s), 1145 (s), 1121 (m), 1095 (m), 1072 (s), 1050 (m), 1018 (m) and 758 (s); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 0.62 (3 H, s), 1.08 (3 H, s), 1.49 (3 H, s), 1.69 (3 H, s), 1.88 (1 H, d, *J* 12.8), 2.71 (1 H, dd, *J* 12.8, 4.6), 3.40 (3 H, s), 3.45 (1 H, d, *J* 4.6) and 7.75–8.55 (4 H, m); δ_{C} (62.90 MHz; CDCl₃) 22.0 (q), 23.5 (q), 26.0 (q), 27.0 (q), 34.7 (t), 42.3 (s), 47.3 (d), 54.79 (s), 54.82 (s), 55.1 (q), 57.0 (s), 89.1 (s), 119.6 (s), 119.8 (s), 127.3 (d), 128.1 (d), 128.7 (d), 129.1 (d), 130.4 (s) and 135.7 (s); *m/z* 306 (M⁺, 0.6%), 259 (12), 238 (41), 127 (89), 95 (86) and 69 (100).

Crystal data: C₂₀H₂₂N₂O, *M* = 306.41, monoclinic, *a* = 9.927(1), *b* = 11.116(1), *c* = 15.3609(7) Å, β = 103.868(5)°, *V* = 1645.6(2) Å³, *T* = 296 K, space group *P2₁/n* (no. 14), *Z* = 4, μ (Cu-K α) = 6 cm⁻¹, 3010 reflections measured, 2831 unique (*R*_{int} = 0.031). The final *R* and *R*_w were 0.041 and 0.039 respectively and are based on 1432 observed reflections (*I* > 3.00 σ (*I*)) and 209 parameters.

cis-1,4-Dicyano-6,6,8,8-tetramethyl-7-oxo-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**16**). Colourless needles, mp 252.9–253.8 °C (from methanol); ν_{\max} (film; NaCl)/cm⁻¹ 2970 (m), 2964 (m), 2904 (m), 2239 (m), 1701 (vs), 1491 (m), 1477 (m), 1464 (m), 1447 (m), 1390 (m), 1371 (m), 1043 (m) and 767 (s); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 1.05 (3 H, s), 1.14 (3 H, s), 1.46 (3 H, s), 1.62 (3 H, s), 2.61 (1 H, br s), 2.82 (1 H, dd, *J* 14.5, 2.4), 3.26 (1 H, ddd, *J* 14.5, 4.0, 1.5), 4.19 (1 H, br s) and 7.26–7.60

(4 H, m); δ_{C} (62.90 MHz; CDCl₃) 23.6 (q), 24.5 (q), 26.9 (t), 30.2 (q), 33.1 (d), 43.7 (d), 46.5 (s), 46.7 (s), 51.4 (s), 120.2 (s), 120.6 (s), 125.9 (s), 128.6 (d), 130.2 (d), 130.3 (d), 131.4 (d), 131.7 (s) and 213.5 (s); *m/z* 292 (M⁺, 2%), 113 (100) and 95 (25).

Crystal data: C₁₉H₂₀N₂O, *M* = 292.38, monoclinic, *a* = 6.227(1), *b* = 16.056(1), *c* = 15.917(1) Å, β = 92.21(1)°, *V* = 1590.3(3) Å³, *T* = 296 K, space group *Cc* (no. 9), *Z* = 4, μ (Cu-K α) = 6 cm⁻¹, 1482 reflections measured, 1421 unique (*R*_{int} = 0.029). The final *R* and *wR*₂ were 0.049 and 0.168 respectively and are based on 808 observed reflections (*I* > 3.00 σ (*I*)) and 139 parameters.

Irradiation of a solution of 1,4-dicyanonaphthalene (3), 1,1-dimethylallene (5) and biphenyl (6) in 3:1 acetonitrile-methanol.

A solution of 1,4-dicyanonaphthalene (**3**, 0.02 mol dm⁻³), 1,1-dimethylallene (**5**, 0.05 mol dm⁻³) and biphenyl (**6**, 0.05 mol dm⁻³) in 3:1 acetonitrile-methanol (10 cm³) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 95% of **3** was consumed, yielding 8% of 1,5-dicyano-3-methoxy-2,2-dimethyl-6,7-benzotricyclo[3.2.2.0^{3,8}]nonane (**17**), 18% of 2,5-dicyano-1-methoxy-9,9-dimethyl-3,4-benzotricyclo[3.3.1.0^{2,7}]nonane (**18**), 22% of *cis*-1,4-dicyano-7,7-dimethoxy-6,6-dimethyl-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**19**) and 20% of *trans*-1,4-dicyano-7,7-dimethoxy-8,8-dimethyl-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**20**). 94% of **6** was recovered after irradiation.

1,5-Dicyano-3-methoxy-4,4-dimethyl-6,7-benzotricyclo-[3.2.2.0^{3,8}]nonane (**17**). Colourless plates, mp 126.4–127.2 °C (from hexanes-ethyl acetate); ν_{\max} (film; NaCl)/cm⁻¹ 2981 (s), 2943 (s), 2832 (w), 2238 (m), 1489 (m), 1452 (s), 1278 (m), 1155 (s), 1115 (s), 1106 (m), 1088 (m) and 1073 (s); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 0.83 (3 H, s), 1.43 (3 H, s), 1.82 (1 H, d, *J* 12.8), 2.23 (1 H, d, *J* 12.2), 2.71 (1 H, dd, *J* 12.8, 4.5), 3.12 (1 H, d, *J* 12.2), 3.27 (3 H, s), 3.51 (1 H, d, *J* 4.5) and 7.38–7.70 (4 H, m); δ_{C} (62.90 MHz; CD₃CN) 22.3 (q), 23.7 (q), 31.2 (s), 35.6 (t), 42.1 (t), 50.5 (d), 52.7 (q), 52.9 (s), 55.9 (s), 84.8 (s), 120.8 (s), 122.3 (s), 127.5 (d), 127.6 (d), 129.0 (d), 130.6 (d), 133.1 (s) and 136.7 (s); *m/z* 278 (M⁺, 2%), 152 (9), 99 (93) and 67 (100) (M⁺, 278.1416). C₁₈H₁₈N₂O requires *M*, 278.1419).

Crystal data: C₇₂H₇₂N₈O₄ [4 (C₁₈H₁₈N₂O)], *M* = 1113.41, orthorhombic, *a* = 14.294(5), *b* = 16.505(6), *c* = 25.334(5) Å, *V* = 5977(3) Å³, *T* = 296 K, space group *Pca*2₁ (no. 29), *Z* = 4, μ (Mo-K α) = 0.78 cm⁻¹, 6310 reflections measured. The final *R* and *R*_w were 0.082 and 0.080 respectively and are based on 1679 observed reflections (*I* > 3.00 σ (*I*)) and 336 parameters.

2,5-Dicyano-1-methoxy-9,9-dimethyl-3,4-benzotricyclo-[3.3.1.0^{2,7}]nonane (**18**). Colourless blocks, mp 148.7–149.8 °C (from hexanes); ν_{\max} (film; NaCl)/cm⁻¹ 2976 (s), 2940 (m), 2838 (w), 2240 (m), 1486 (s), 1455 (s), 1392 (w), 1373 (w), 1276 (m), 1236 (s), 1220 (s), 1208 (m), 1151 (s), 1131 (s), 1072 (m), 1057 (s), 1026 (m) and 760 (s); δ_{H} (250.13 MHz; CDCl₃; Me₄Si) 0.43 (3 H, s), 1.43 (3 H, s), 1.71 (1 H, ddd, *J* 12.8, 7.2, 1.2), 2.20 (1 H, d, *J* 10.7), 2.50 (1 H, d, *J* 12.8), 2.62 (1 H, t, *J* 7.2), 2.99 (1 H, ddd, *J* 10.7, 7.2, 1.2), 3.54 (3 H, s) and 7.27–7.65 (4 H, m); δ_{C} (62.90 MHz; CDCl₃) 21.2 (q), 21.3 (q), 32.2 (d), 34.1 (t), 34.2 (t), 42.3 (s), 48.3 (s), 49.6 (s), 54.5 (d), 84.6 (s), 118.4 (s), 119.6 (s), 123.1 (d), 125.2 (d), 128.2 (s), 128.4 (d), 128.7 (d) and 136.7 (s); *m/z* 278 (M⁺, 4%), 237 (11), 178 (22), 99 (80) and 67 (100).

Crystal data: C₁₈H₁₈N₂O, *M* = 278.35, orthorhombic, *a* = 12.214(2), *b* = 13.305(3), *c* = 9.083(2) Å, *V* = 1476.0(4) Å³, *T* = 296 K, space group *P2₁2₁2₁* (no. 19), *Z* = 4, μ (Mo-K α) = 0.8 cm⁻¹, 2481 reflections measured. The final *R* and *R*_w were 0.040 and 0.043 respectively and are based on 1071 observed reflections (*I* > 3.00 σ (*I*)) and 191 parameters.

cis-1,4-Dicyano-7,7-dimethoxy-6,6-dimethyl-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**19**). Colourless blocks, mp 167.5–168.4 °C (from methanol); ν_{\max} (film; NaCl)/cm⁻¹ 2990 (m), 2967 (m), 2951 (m), 2835 (m), 2237 (m), 1466 (m), 1448 (m), 1137 (s), 1125 (s), 1112 (s), 1054 (s), 1038 (m), 1030 (m), 979 (m)

and 910 (m); δ_{H} (250.13 MHz; CDCl_3 ; Me_4Si) 1.23 (3 H, s), 1.29 (3 H, s), 2.13 (3H, s), 2.18–2.31 (3 H, m), 2.37 (1 H, dt, J 13.4, 5.2), 2.62 (1 H, ddd, J 13.4, 3.7, 0.9), 3.14 (3 H, s), 4.30 (1 H, s) and 7.27–7.32 (4 H, m); δ_{C} (62.90 MHz; CDCl_3) 23.6 (q), 25.0 (q), 29.5 (t), 31.4 (d), 37.0 (s), 37.2 (t), 42.5 (s), 46.6 (d), 47.4 (q), 50.1 (q), 100.1 (s), 122.0 (s), 122.4 (s), 127.0 (d), 127.9 (d), 128.7 (d), 129.0 (d), 130.8 (s) and 133.9 (s); m/z 310 (M^+ , 8%), 279 (18), 267 (15), 180 (33), 99 (77), 88 (100) and 67 (31).

Crystal data: $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$, $M = 310.39$, monoclinic, $a = 13.917(1)$, $b = 8.5864(6)$, $c = 14.304(1)$ Å, $\beta = 105.596(7)^\circ$, $V = 1646.3(2)$ Å³, $T = 296$ K, space group $P2_1/n$ (no. 14), $Z = 4$, $\mu(\text{Cu-K}\alpha) = 6.5$ cm⁻¹, 1165 reflections measured, 989 unique ($R_{\text{int}} = 0.024$). The final R and $wR2$ were 0.058 and 0.184 respectively and are based on 860 observed reflections ($I > 3.00\sigma(I)$) and 113 parameters.

trans-1,4-Dicyano-7,7-dimethoxy-8,8-dimethyl-2,3-benzo-*cis*-bicyclo[3.3.1]nonane (**20**). Colourless blocks, mp 122.9–124.6 °C (from hexanes); ν_{max} (film; NaCl)/cm⁻¹ 2990 (m), 2949 (m), 2834 (m), 2239 (m), 1492 (m), 1449 (m), 1171 (m), 1129 (s), 1122 (s), 1096 (m), 1073 (m), 1053 (s), 1044 (s) and 972 (m); δ_{H} (250.13 MHz; CDCl_3 ; Me_4Si) 1.23 (3 H, s), 1.42 (3 H, s), 1.99 (1 H, dd, J 15.0, 4.9), 2.14 (1 H, ddd, J 14.7, 4.0, 1.8), 2.46 (1 H, dt, J 14.7, 2.0), 2.70 (3 H, s), 2.71–2.77 (2 H, m), 3.21 (3 H, s), 4.37 (1 H, d, J 6.1) and 7.25–7.65 (4 H, m); δ_{C} (62.90 MHz; CDCl_3) 20.3 (q), 24.1 (q), 29.3 (d), 31.3 (t), 32.2 (t), 37.1 (d), 47.15 (s), 47.17 (s), 49.9 (q), 50.0 (q), 100.7 (s), 120.2 (s), 122.3 (s), 126.3 (d), 127.0 (d), 128.6 (d), 129.5 (d), 131.1 (s) and 133.5 (s); m/z 310 (M^+ , 33%), 279 (100), 267 (94) and 88 (56).

Crystal data: $\text{C}_{38}\text{H}_{44}\text{N}_4\text{O}_4$ [$2(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)$], $M = 620.78$, monoclinic, $a = 16.452(3)$, $b = 9.016(2)$, $c = 23.003(2)$ Å, $\beta = 95.35(1)^\circ$, $V = 3397.3(9)$ Å³, $T = 296$ K, space group $P2_1/a$ (no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.8$ cm⁻¹, 2987 reflections measured, 2685 unique ($R_{\text{int}} = 0.063$). The final R and R_w were 0.059 and 0.055 respectively and are based on 1622 observed reflections ($I > 3.00\sigma(I)$) and 300 parameters.

Irradiation of a solution of 1,4-dicyanonaphthalene (3) and 1,1-dimethylallene (5) in 3:1 acetonitrile–methanol. A solution of 1,4-dicyanonaphthalene (**3**, 0.02 mol dm⁻³) and 1,1-dimethylallene (**5**, 0.05 mol dm⁻³) in 3:1 acetonitrile–methanol (10 mL) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 85% of **3** was consumed, yielding 8% of 1,5-dicyano-3-methoxy-2,2-dimethyl-6,7-benzotricyclo[3.2.2.0^{3,8}]nonane (**17**), 22% of 2,5-dicyano-1-methoxy-9,9-dimethyl-3,4-benzotricyclo[3.3.1.0^{2,7}]nonane (**18**) and 26% of 7-isopropylidene-5,6-(1',4'-dicyanobenzo)bicyclo[2.2.2]oct-2-ene (**21**).

7-Isopropylidene-5,6-(1',4'-dicyanobenzo)bicyclo[2.2.2]oct-2-ene (**21**). Colourless blocks, mp 178.1–178.9 °C (from hexanes); ν_{max} (film; NaCl)/cm⁻¹ 3081 (w), 3066 (w), 2978 (m), 2915 (s), 2855 (m), 2233 (s), 1474 (m), 1436 (m), 1400 (s), 1374 (m), 1335 (s), 1251 (m), 1175 (m), 1158 (m), 1123 (m) and 826 (s); δ_{H} (250.13 MHz; CDCl_3 ; Me_4Si) 1.55 (3 H, s), 1.91 (3 H, s), 2.04 (1 H, d, J 15.3), 2.30 (1 H, d, J 15.3), 4.54 (1 H, m), 5.24 (1 H, dd, J 5.5, 1.8), 6.61 (2 H, m) and 7.44 (2 H, s); δ_{C} (62.90 MHz; CDCl_3) 20.2 (q), 21.7 (q), 32.1 (t), 39.9 (d), 43.5 (d), 110.3 (s), 110.8 (s), 116.29 (s), 116.32 (s), 125.4 (s), 126.0 (s), 128.3 (d), 128.5 (d), 133.4 (d), 134.6 (d), 148.5 (s) and 149.2 (s); m/z 246 (M^+ , 82%), 231 (100), 178 (22) and 68 (72).

Crystal data: $\text{C}_{17}\text{H}_{14}\text{N}_2$, $M = 246.31$, orthorhombic, $a = 13.37(1)$, $b = 25.49(1)$, $c = 7.920(7)$ Å, $V = 2698(3)$ Å³, $T = 296$ K, space group $Pbca$ (no. 61), $Z = 8$, $\mu(\text{Mo-K}\alpha) = 0.7$ cm⁻¹, 2657 reflections measured. The final R and R_w were 0.083 and 0.087 respectively and are based on 460 observed reflections ($I > 3.00\sigma(I)$) and 77 parameters.

Irradiation of a solution of 1,4-dicyanonaphthalene (3) and 1,1-dimethylallene (5) in acetonitrile. A solution of 1,4-dicyanonaphthalene (**3**, 0.02 mol dm⁻³) and 1,1-dimethylallene (**5**, 0.05 mol dm⁻³) in acetonitrile (10 mL) was irradiated for 45 minutes.

Calibrated GC-FID analysis indicated that 84% of **3** was consumed, yielding 38% of 7-isopropylidene-5,6-(1',4'-dicyanobenzo)bicyclo[2.2.2]oct-2-ene (**21**).

Irradiation of a solution of 1,4-dicyanonaphthalene (3) and 1,1-dimethylallene (5) in benzene. A solution of 1,4-dicyanonaphthalene (**3**, 0.02 mol dm⁻³) and 1,1-dimethylallene (**5**, 0.05 mol dm⁻³) in benzene (10 mL) was irradiated for 45 minutes. Calibrated GC-FID analysis indicated that 88% of **3** was consumed, yielding 42% of 7-isopropylidene-5,6-(1',4'-dicyanobenzo)bicyclo[2.2.2]oct-2-ene (**21**).

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