Photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction, Part 13. The scope and limitations of the reaction with cyanide anion as the nucleophile[1]

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Abstract: The scope of the photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction has been extended to include cyanide anion as the nucleophile. Highest yields of adducts were obtained when the alkene or diene has an oxidation potential less than ca. 1.5 V (SCE). No adducts were obtained from 2-methylpropene (**9**), oxidation potential 2.6 V. Oxidation of cyanide anion, by the radical cation of the alkene or diene, can compete with the combination. With the alkenes, 2,3-dimethyl-2-butene (**2**) and 2-methyl-2-butene (**10**), both nitriles and isonitriles were obtained; isonitriles were not detected from the reactions involving the dienes, 2-methyl-1,3-butadiene (**11**), 2,3-dimethyl-1,3-butadiene (**12**), 4-methyl-1,3-pentadiene (**13**), 2,4-dimethyl-1,3-pentadiene (**14**), and 2,5-dimethyl-2,4-hexadiene (**6**). The specificity, nitrile versus isonitrile, is explained in terms of the Hard-Soft-Acid-Base (HSAB) principle. The photo-NOCAS reaction also occurs with the allene, 2,4-dimethyl-2,3-pentadiene (**15**), cyanide combining at the central carbon. Factors influencing the regiochemistry of the combination step, Markovnikov versus *anti*-Markovnikov, have been defined. Cyanide anion adds preferentially to the less alkyl-substituted, less sterically hindered, end of an unsymmetric alkene or conjugated diene radical cation, forming the more heavily alkyl-substituted radical intermediate. High-level *ab initio* molecular orbital calculations (MP2/6-31G*//HF/6-31G*) have been used to determine the effect of alkyl substitution on the stability of the intermediates, β-cyano and β-isocyano alkyl radicals, and products, alkyl cyanides and isocyanides. The more heavily alkyl-substituted radical is not necessarily the more stable. The product ratio (Markovnikov versus *anti*-Markovnikov) must be kinetically controlled.

Key words: photochemistry, radical ions, electron transfer, nitriles, isonitriles.

Résumé : On a élargi le domaine d'application de la réaction photochimique de combinaison nucléophile–oléfine avec substitution aromatique («photo-NOCAS») de façon à inclure l'ion cyanure comme nucléophile. Les meilleurs rendements d'adduits sont obtenus lorsque le potentiel d'oxydation de l'alcène ou du diène est inférieur à environ 1,5 V («SCE»). On n'a pas obtenu d'adduits avec les 2-méthylpropène (**9**) dont le potentiel d'oxydation est de 2,6 V. L'oxydation de l'anion cyanure, par le cation radical de l'alcène ou du diène, est en compétition avec la combinaison. Avec les alcènes, 2,3-diméthylbut-2-ène (**2**) et 2-méthylbut-2-ène (**10**), on a obtenu les nitriles ainsi que les isonitriles; on n'a toutefois pas détecté d'isonitriles lors des réactions impliquant les diènes, 2-méthylpenta-1,3-diène (**11**), 2,3-diméthylbuta-1,3-diène (**12**), 4-méthylpenta-1,3-diène (**13**), 2,4-diméthylpenta-1,3-diène (**14**) et 2,5-diméthylhexa-2,4-diène (**6**). On explique la spécificité, nitrile versus isonitrile, en fonction du principe des acides et des bases durs et mous («HSAB»). La réaction de «photo-NOCAS» se produit aussi avec l'allène et le 2,4-diméthylpenta-2,3-diène (**15**); le cyanure s'attache au carbone central. On a défini que les facteurs qui influencent la régiochimie de l'étape de combinaison sont Markovnikov versus *anti*-Markovnikov. L'anion cyanure s'additionne préférentiellement à l'extrémité d'un ion radical d'alcène non symétrique ou de diène conjugué qui est la moins substituée, la moins stériquement encombrée, par des groupes alkyles; cette addition conduit à la formation du radical intermédiaire le plus substitué par des groupes alkyles. On a fait appel à des calculs d'orbitales moléculaires ab initio à niveau élevé (MP2/6-31G*// HF/6-31G*) pour déterminer l'effet de la substitution par des groupes alkyles sur la stabilité des intermédiaires, les radicaux β-cyanoalkyles et les β-isocyanoalkyles, et des produits, les cyanures et les isocyanures. Les radicaux les plus substitués ne sont pas nécessairement les plus stables. Le rapport des produits (Markovnikov versus *anti*-Markovnikov) doit donc être sous contrôle cinétique.

Mots clés : photochimie, ions radicaux, transfert d'électron, nitriles, isonitriles.

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Introduction

The scope and limitations of the photochemically induced nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction, which combines a nucleophile and an alkene or diene radical cation, substituting on an aromatic radical anion, have been defined when an alcohol (methanol) serves as nucleophile (1). A main objective of this study was to extend the scope of this reaction with cyanide anion as the nucleophile (Scheme 1).

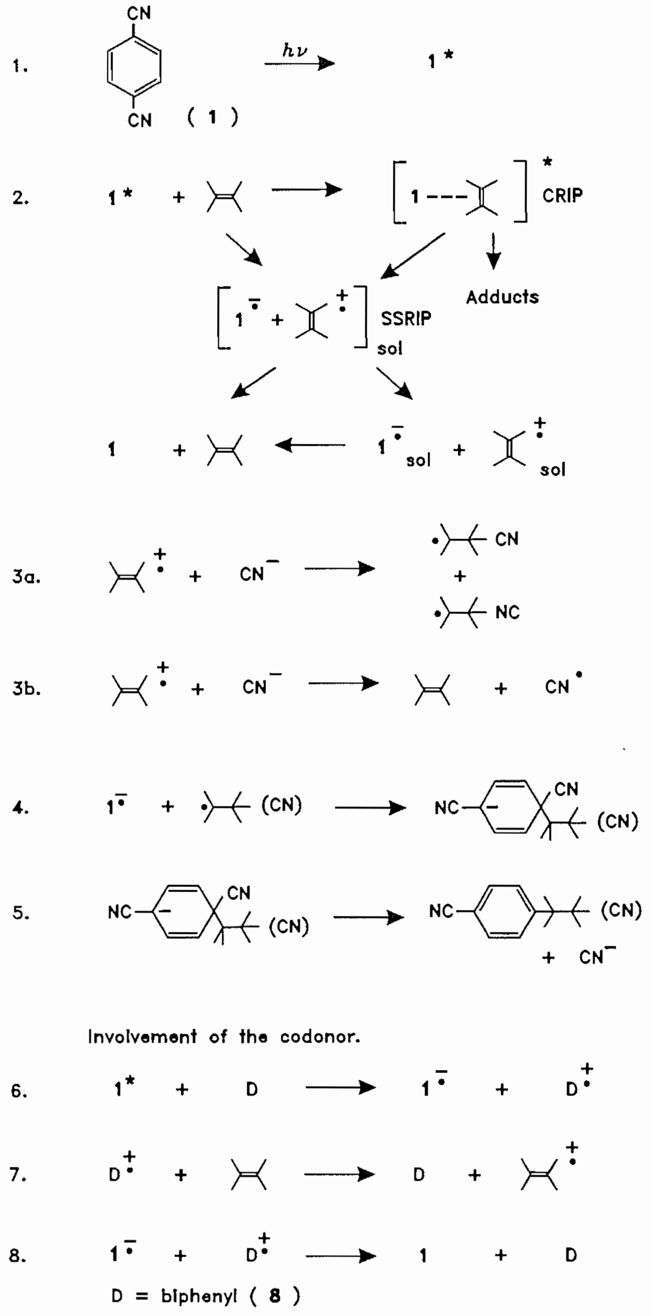
Some previous results were encouraging (1*a*–*c*). Irradiation of an acetonitrile solution (no methanol) of 1,4-dicyanobenzene (**1**) and 2,3-dimethyl-2-butene (**2**) gave primarily the expected 1:1 substitution products, 2,3-dimethyl-3-(4-cyanophenyl)-1-butene (**4**) and 2,3-dimethyl-1-(4-cyanophenyl)-2-butene (**5**), resulting from deprotonation of the alkene radical cation ($2^{+\bullet}$) followed by coupling of the resulting allylic radical with the radical anion of 1,4-dicyanobenzene ($1^{-\bullet}$). A minor product from this reaction was the photo-NOCAS adduct, 3-(4-cyanophenyl)-2,3-dimethylbutanenitrile (**3**), formed in "trace" amounts, which had incorporated cyanide anion (reaction [1]) (1*a*). The only source of cyanide anion in this reaction mixture was that generated during the aromatic substitution–rearomatization step (Scheme 1, step 5). This was the only previous report of incorporation of cyanide anion during a photo-NOCAS reaction involving an alkyl-substituted alkene.

One example of the photo-NOCAS reaction, involving cyanide anion combining with the radical cation of a conjugated diene has been reported (1*b*). Competitive formation of the nitrile was initially observed during the photo-NOCAS reaction of 2,5-dimethyl-2,4-hexadiene (**6**) and 1,4-dicyanobenzene (**1**) in acetonitrile–methanol (3:1). Subsequent irradiation of an acetonitrile solution of 2,5-dimethyl-2,4-hexadiene (**6**) and potassium cyanide, with 1,4-dicyanobenzene (**1**) serving as the electron acceptor, gave a good yield (80%) of the photo-NOCAS adduct, (*E*)-5-(4-cyanophenyl)-2,2,5-trimethyl-3-hexenenitrile (**7**) (reaction [2] (1*b*)).

With aryl-substituted alkenes, the products of addition of hydrogen cyanide were obtained (1*c*). For example, irradiation of an acetonitrile – 2,2,2-trifluoroethanol solution of 1,1-diphenylethylene and potassium cyanide, with 1-cyanonaphthalene or methyl 4-cyanobenzoate serving as the electron acceptor, gave the cyanation product, 3,3-diphenylpropanenitrile (reaction [3] (1*c*)). Cyanide anion serves as the nucleophile, adding to the 1,1-diphenylethylene radical cation. In this case, as with other aryl-substituted alkenes, the resulting benzylic radical intermediate is reduced to the carbanion by the radical anion of the initial electron acceptor, followed by protonation.

There is direct physical evidence for the reaction of cyanide anion with the radical cation of aryl alkenes and conjugated dienes. Flash photolysis studies have shown cyanide anion reacts (adds?) with the radical cation of aryl-substituted alkenes and conjugated dienes with rate constants approaching the diffusion-controlled limit (3). The relative rates of the reaction of substituted styrene radical cations with methanol and with cyanide anion reflect the well-established difference in nucleophilicity of these nucleophiles; the nucleophilicity, *n* (CH_3I), value for cyanide anion is 6.7 (methanol, $n = 0.0$ by definition (4)).

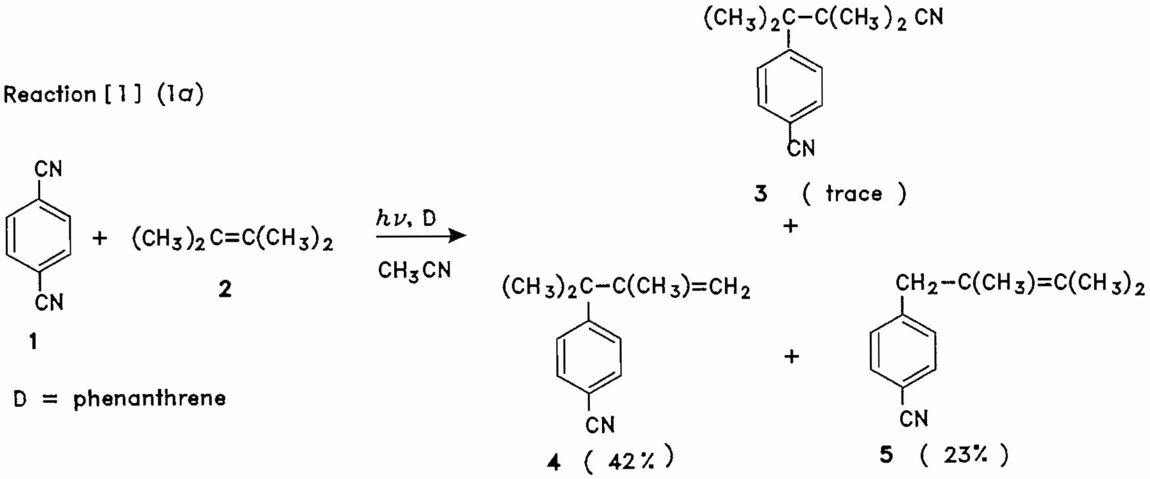
Scheme 1.



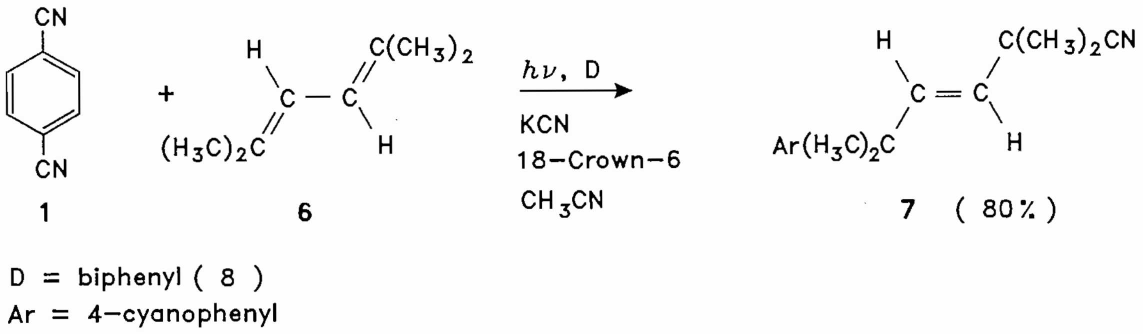
We report here results from the irradiation of acetonitrile, potassium cyanide, and solutions of several alkenes and dienes, using 1,4-dicyanobenzene (**1**) as the electron acceptor and with biphenyl (**8**) serving as a codonor. The alkenes and dienes chosen for study include: 2-methylpropene (**9**), 2-methyl-2-butene (**10**), 2,3-dimethyl-2-butene (**2**), 2,5-dimethyl-2,4-hexadiene (**6**), 2-methyl-1,3-butadiene (**11**), 2,3-dimethyl-1,3-butadiene (**12**), 4-methyl-1,3-pentadiene (**13**), 2,4-dimethyl-1,3-pentadiene (**14**), and the allene, 2,4-dimethyl-2,3-pentadiene (**15**).

Another objective of this study involved the identification of the factor(s) that influence the regiochemistry of the bonding of the nucleophile to the alkene or diene radical cation.

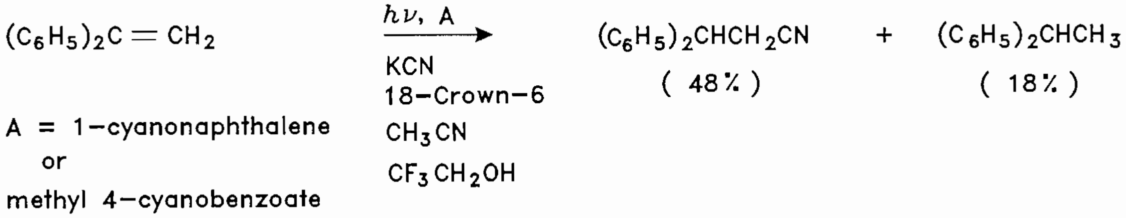
Reaction [1] (1*a*)



Reaction [2] (1*b*)



Reaction [3] (1c)



Previous work, with methanol serving as the nucleophile, has led to the following hypothesis: the nucleophile (methanol) adds to that end of the alkene or diene radical cation which leads ultimately to formation of the more stable radical intermediate — the more stable radical intermediate is not necessarily that with the most heavily alkyl substituted radical moiety. The initial intermediate, formed upon addition of methanol, is the distonic radical cation, capable of bridging and equilibration. Of course, there is no distonic radical cation intermediate formed upon addition of a negatively charged nucleophile. High-level ab initio molecular orbital calculations (MP2/6-31G*//HF/6-31G* (5, 6)) have been used to determine the relative stability of the alternative radical intermediates formed upon addition of cyanide anion to the alkene or diene radical cation. These results will be compared with those for the analogous intermediates formed upon addition of methanol (1*i*).

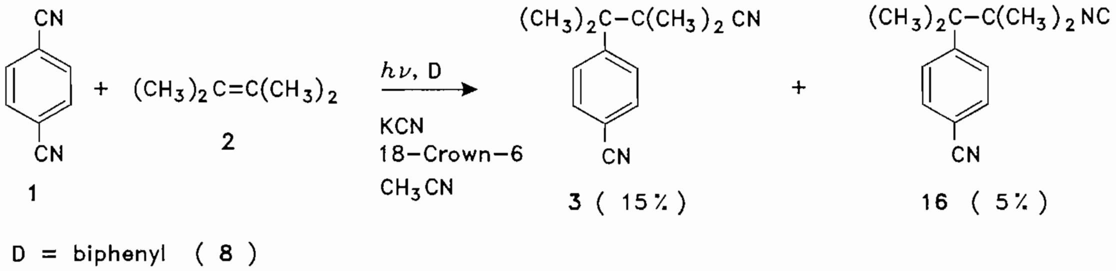
Results

The reaction conditions used for the addition of cyanide anion are similar to those reported for the reactions involving methanol as the nucleophile (1). Acetonitrile solutions of the alkene or diene, 1,4-dicyanobenzene (**1**), biphenyl (**8**) serving as a codonor, and potassium cyanide, were irradiated with a medium-pressure mercury vapour lamp through Pyrex. The solubility of the potassium cyanide in the acetonitrile was increased by the addition of 18-crown-6 ether (1,4,7,10,13,16-hexaoxacyclooctadecane). Progress of the reaction was followed by capillary column gas chromatography with a flame ionization detector (gc/fid). The first indication of the structure of the product(s) was gleaned from the mass spectrum obtained from a gas chromatograph equipped with a mass selective detector (gc/ms). The ratios of products were determined by integration of the peak areas in the gc/fid. The relative yields of isolated products were generally in agreement with these ratios. The yields were based upon the amount of 1,4-dicyanobenzene (**1**) consumed; the alkene or diene was generally present in excess.

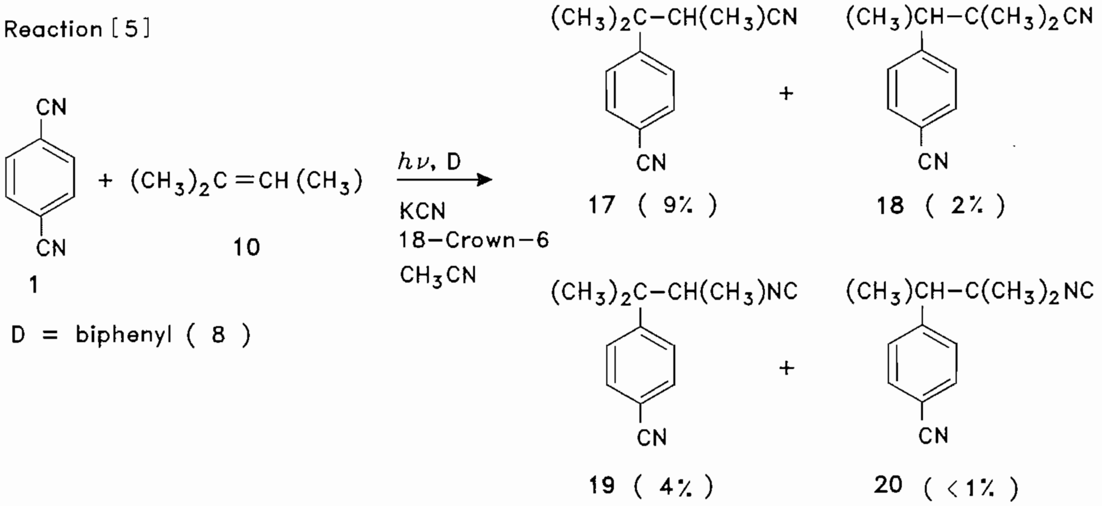
Previous results had shown the photo-NOCAS adduct, **3**, was a minor product, formed along with the 1:1 adducts, **4** and **5**, upon irradiation of an acetonitrile solution of 1,4-dicyanobenzene (**1**) and 2,3-dimethyl-2-butene (**2**) (reaction [1] (1*a*)). When an acetonitrile solution of **1**, **2**, biphenyl (**8**), and potassium cyanide was irradiated, **3** became a major product (15%). The isonitrile (**16**) was also formed (5%), along with the 1:1 adducts (**4** and **5**) (reaction [4]).

In marked contrast, no 1:1:1 adduct was detected (gc/ms) when 2-methylpropene (**9**) was subjected to these reaction conditions. However, irradiation of an acetonitrile solution of 2-methyl-2-butene (**10**), **1**, **8**, and potassium cyanide, did give the photo-NOCAS adducts, nitriles (**17**, **18**) and isonitriles (**19**, **20**), albeit in low yield (reaction [5]). The ratio of the isonitriles, **19** (*anti*-Markovnikov) : **20** (Markovnikov), determined from the integrated peak areas (gc/fid), was large (> 30:1).

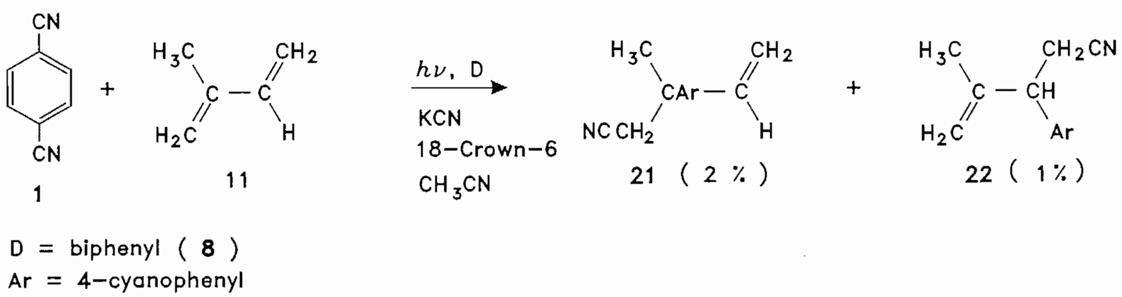
Reaction [4]



Reaction [5]



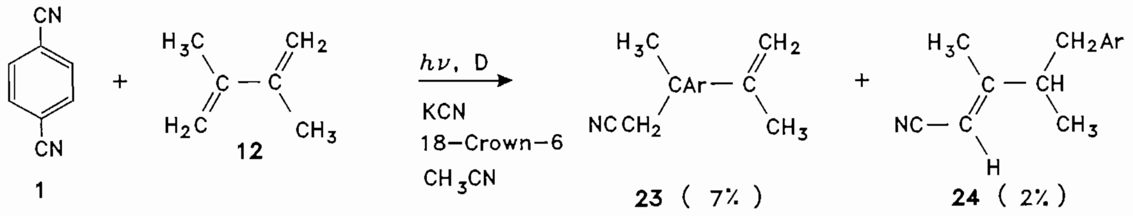
Reaction [6]



An acetonitrile solution of 2-methyl-1,3-butadiene (**11**), 1,4-dicyanobenzene (**1**), biphenyl (**8**), and potassium cyanide was irradiated; 3-(4-cyanophenyl)-3-methyl-4-pentenenitrile (**21**, 2%) and 3-(4-cyanophenyl)-4-methyl-4-pentenenitrile (**22**, 1%) were isolated in low yield (reaction [6]). Both of these adducts result from 1,2-addition to the diene; no 1,4-addition product was detected.

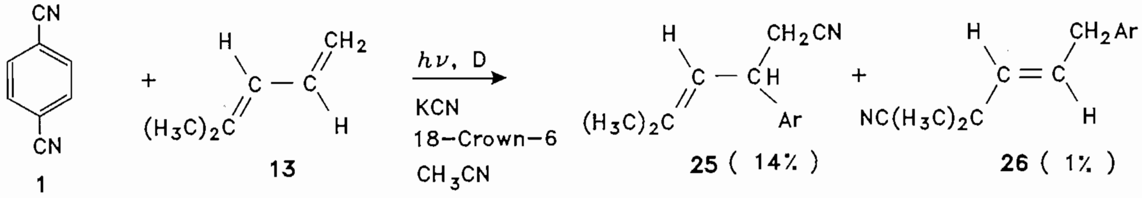
When an acetonitrile solution of 2,3-dimethyl-1,3-butadiene (**12**), **1**, **8**, and potassium cyanide was irradiated, 3-(4-cyanophenyl)-3,4-dimethyl-4-pentenenitrile (**23**, 7%) and (*E*)-5-(4-cyanophenyl)-3,4-dimethyl-2-pentenenitrile (**24**, 2%) were obtained (reaction [7]). Adduct **23** is a 1,2-addition product. No 1,4-addition product (i.e., neither (*E*)- nor (*Z*)-5-(4-cyanophenyl)-3,4-dimethyl-3-pentenenitrile) was detected; however, **24** may result from isomerization (tautomerization) of this 1,4-adduct.

Reaction [7]



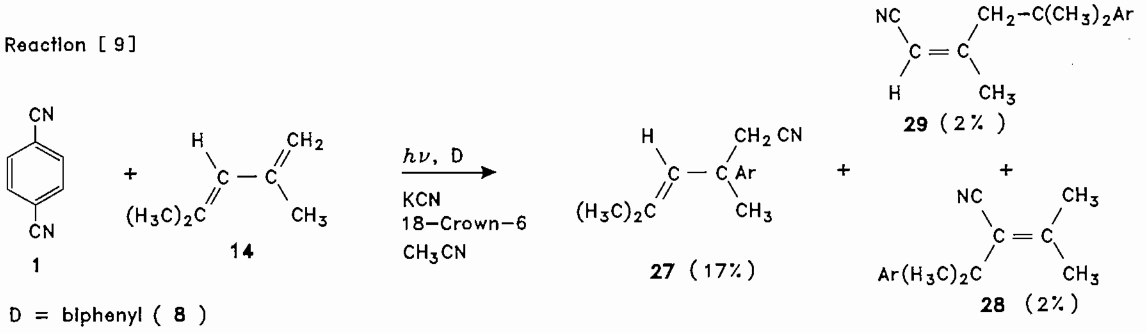
D = biphenyl (**8**)
Ar = 4–cyanophenyl

Reaction [8]



D = biphenyl (**8**)
Ar = 4–cyanophenyl

Reaction [9]



D = biphenyl (**8**)
Ar = 4–cyanophenyl

Two photo-NOCAS adducts were formed upon irradiation of a solution of 4-methyl-1,3-pentadiene (**13**), **1**, **8**, and potassium cyanide in acetonitrile (reaction [8]). The major adduct, 3-(4-cyanophenyl)-5-methyl-4-hexenenitrile (**25**, 14%), was the 1,2-addition product resulting from initial attack of the cyanide anion at the less substituted terminal end of the diene radical cation. A 1,4-addition product, (*E*)-5-(4-cyanophenyl)-2,2-dimethyl-3-pentenenitrile (**26**, 1%), resulting from initial attack of the cyanide anion at the more substituted terminal end of the diene radical cation, was the minor adduct.

When an acetonitrile solution of 2,4-dimethyl-1,3-pentadiene (**14**), **1**, **8**, and potassium cyanide was irradiated, three isomeric 1:1:1 adducts were formed: 3-(4-cyanophenyl)-3,5-dimethyl-4-hexenenitrile (**27**, 17%), 4-(4-cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile (**28**, 2%), and (*Z*)-5-(4-cyanophenyl)-3,5-dimethyl-2-hexenenitrile (**29**, 2%) (reaction [9]). The major product, **27**, is the expected photo-NOCAS adduct resulting from 1,2-addition to the less substituted terminal end of the diene radical cation. Compound **29**, like compound **24**, may result from isomerization (tautomerization) of initially formed 1,4-addition product(s).

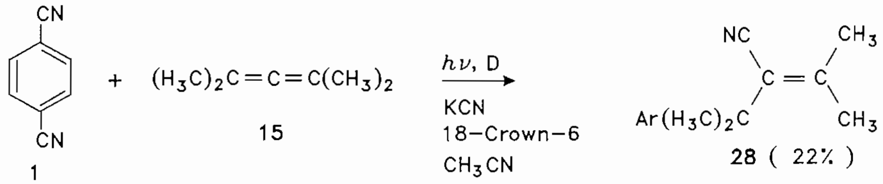
The other minor product, **28**, may result from a photo-NOCAS reaction involving the tautomeric diene, the allene 2,4-dimethyl-2,3-pentadiene (**15**), present as an impurity in the starting diene. To test this possibility a similar solution, starting with **15**, was irradiated under identical conditions; the photo-NOCAS adduct, **28**, was obtained in reasonable yield (22%) (reaction [10]).

Structural assignments

Structural assignments of the products were based primarily upon detailed analysis of ^1H and ^{13}C nmr, mass, and infrared spectra. For two of the products, 4-(4-cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile (**28**) and (*Z*)-5-(4-cyanophenyl)-3,5-dimethyl-2-hexenenitrile (**29**), structures were firmly established by X-ray crystallography on a single crystal.[3]

Irradiation of an acetonitrile solution of 1,4-dicyanobenzene (**1**), 2,3-dimethyl-2-butene (**2**), biphenyl (**8**), and potassium cyanide gave the nitrile, 3-(4-cyanophenyl)-2,3-dimethylbutanenitrile (**3**), and the isonitrile, 3-(4-cyanophenyl)-2,3-dimethyl-2-isocyanobutane (**16**) (reaction [4]).

Reaction [10]



1

15

28 (22%)

D = biphenyl (8)
Ar = 4-cyanophenyl

The structure of **3** has been established previously (1*a*). The ^1H and ^{13}C nmr, and the infrared spectra provide convincing evidence for the structure of the isonitrile, **16**. The infrared spectrum shows peaks at both the aromatic nitrile (2229 cm^{-1}) and the aliphatic isonitrile (2131 cm^{-1}) carbon–nitrogen triple-bond stretching frequencies. The ^1H and ^{13}C nmr spectra show the expected patterns; particularly informative is coupling of the signal, in the ^1H nmr spectrum, assigned to the hydrogens vicinal to the isonitrile (1.34 ppm), due to the ^{14}N nuclear spin. In the ^{13}C nmr spectrum, signals due to the isonitrile carbon (155.95 ppm) and the carbon directly bonded to the isonitrile (63.78 ppm) also show distinctive coupling due to the ^{14}N nucleus.

Major photo-NOCAS adducts resulting from the irradiation of an acetonitrile solution of 2-methyl-2-butene (**10**), 1,4-dicyanobenzene (**1**), biphenyl (**8**), and potassium cyanide were the nitriles **17** and **18** (reaction [5]). The first indication of the regiochemistry of these isomers was from the mass spectrum (gc/ms), which showed a dominant fragment of 144 *m/z* ($C_{10}H_{10}N$) for **17**, due to the arylpropyl fragment, and of 130 *m/z* (C_9H_8N) for **18**, due to the arylethyl fragment. The aliphatic region of the ^1H nmr spectrum of **17** shows a doublet (1.10 ppm) corresponding to a methyl group adjacent to a methine group. The proton of the methine group bonded to the nitrile produces a quartet at lower field (2.97 ppm). The typical AA′XX′ pattern in the aromatic region of the ^1H nmr is indicative of the 4-cyanophenyl group. In the ^{13}C nmr spectrum, the cyano-substituted methine group shows up as a doublet (37.61 ppm) and the aryl-substituted carbon appears as a singlet (40.27 ppm).

The ^1H and ^{13}C nmr spectra for compound **18** show characteristic patterns similar to those of **17**. In the aliphatic region of the ^1H nmr spectrum a doublet (1.50 ppm) corresponds to the methyl group adjacent to a methine group. The proton of the methine group, bonded to the aryl group, produces a quartet at lower field (2.77 ppm). In the ^{13}C nmr spectrum, the cyano-substituted carbon appears as a singlet (37.06 ppm) and the benzylic carbon as a doublet (48.15 ppm). The major adduct (**17**:**18**, 4.5:1) results from initial bonding of the cyanide anion to the radical cation, $\mathbf{10}^{+\cdot}$, at the less substituted alkene carbon, giving the more heavily alkyl-substituted radical intermediate, i.e., *anti*-Markovnikov addition.

The isonitriles, **19** and **20**, are minor products from reaction [5]. The ^1H and ^{13}C nmr and the infrared spectra provide convincing evidence for the structures of **19** and **20**. The first indication for the structure of these isonitriles, **19** and **20**, came from the infrared spectra, which again show peaks at both the aromatic nitrile and aliphatic isonitrile carbon–nitrogen triple-bond stretching frequencies. The ^1H and ^{13}C nmr spectra show the expected patterns, including significant coupling of the geminal and vicinal hydrogens, due to the ^{14}N nuclear spin, in the ^1H nmr of **19** and to the vicinal hydrogens in the ^1H nmr of **20**. In the ^{13}C nmr spectrum, the isonitrile carbon, as well the carbon directly bonded to the isonitrile, shows distinctive coupling to the ^{14}N nucleus.

The products resulting from irradiation of an acetonitrile solution of 2-methyl-1,3-butadiene (**11**), **1**, **8**, and potassium cyanide, were 3-(4-cyanophenyl)-3-methyl-4-pentenenitrile

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[3] Crystallographic data for **28** and **29** may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Details of data collection, structural analysis and refinement, and tables of interatomic distances and bond angles have also been deposited with the Cambridge Crystallographic Data Centre and may be obtained on request from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

(**21**) and 3-(4-cyanophenyl)-4-methyl-4-pentenenitrile (**22**) (reaction [6]). The ^{1}H and ^{13}C nmr spectra provide good evidence for the structures of **21** and **22** as photo-NOCAS 1,2-adducts. Compound **21** results from attack of cyanide anion at the more heavily substituted end of the diene radical cation (C-1), generating the more heavily substituted allylic radical. Coupling of this allylic radical at the more heavily substituted carbon, with the anion radical, $\mathbf{1}^{-\bullet}$, at the *ipso* position, generates the terminal alkene. Evidence for this regiochemistry is the two doublets and a multiplet (5.19, 5.34, and 6.02 ppm) in the vinyl proton region of the ^{1}H nmr spectrum. This spectrum also exhibits a singlet (1.61 ppm) due to the methyl group and a lower-field singlet (2.77 ppm) for the cyanomethylene group.

In the ^{13}C nmr spectrum of compound **21**, there is a triplet (29.82 ppm) indicative of a methylene carbon substituted by a cyano group. There is a lower-field singlet (43.58 ppm) that is consistent with an aryl-substituted quaternary carbon. There are also two low-field singlets (117.18 and 118.44 ppm) consistent with two distinctive cyano groups. The ^{13}C nmr spectrum also exhibits a triplet (115.34 ppm) for the terminal vinyl methylene and a doublet for the vinyl methine (141.93 ppm), additional evidence for the mono-substituted alkene.

Compound **22** was identified as 3-(4-cyanophenyl)-4-methyl-4-pentenenitrile, which would result from initial attack of cyanide anion at the less substituted end of the diene radical cation. The presence of the disubstituted alkene is supported by two apparent singlets in the vinyl proton region (4.99 and 5.11 ppm) assigned to the geminal protons. The ^{1}H nmr spectrum also exhibits a singlet (1.61 ppm) indicative of the methyl group and an ABX pattern (2.72, 2.85, and 3.66 ppm) for the protons of the methylene group, next to a cyano group, and of the benzylic, allylic methine group.

The ^{13}C nmr spectrum of compound **22** exhibits a triplet (22.43 ppm) that is indicative of the methylene group substituted by the cyano group. There is a lower-field doublet (48.55 ppm) that is consistent with an aryl-substituted methine group. And there are two singlets (117.83 and 118.95 ppm) supporting two cyano groups. The ^{13}C nmr spectrum also exhibits a triplet (113.21 ppm) for the terminal vinyl methylene and a singlet (143.18 or 145.06 ppm) due to the quaternary vinyl carbon, further supporting the existence of the disubstituted alkene.

When an acetonitrile solution of 2,3-dimethyl-1,3-butadiene (**12**), **1**, **8**, and potassium cyanide was irradiated, 1:1:1 adducts **23** and **24** were produced (reaction [7]). Compound **23** was identified as 3-(4-cyanophenyl)-3,4-dimethyl-4-pentenenitrile, a 1,2-addition product. The ^{1}H and ^{13}C nmr spectra were similar to those of **21**; however, there are only two singlets in the vinyl region of the ^{1}H nmr spectrum (5.07 and 5.15 ppm), indicative of a terminal, disubstituted alkene. In the ^{13}C nmr spectrum, there are signals due to a vinyl quaternary carbon (147.00 or 148.84 ppm) and a vinyl methylene (113.06 ppm).

Compound **24** was identified as (*E*)-5-(4-cyanophenyl)-3,4-dimethyl-2-pentenenitrile, which may result from isomerization (tautomerization) of the initially formed 1,4-adduct, 5-(4-cyanophenyl)-3,4-dimethyl-3-pentenenitrile. The ^{1}H and ^{13}C nmr spectra of **24** both support the assigned structure. The ^{1}H nmr spectrum shows a doublet (1.08 ppm) that represents a methyl group bonded to a methine group, a singlet (2.06 ppm) due to the methyl group bonded to a vinyl carbon, and multiplets of an ABC second-order pattern (2.62, 2.69, and 2.82 ppm) for the protons of the benzylic methylene group and the allylic methine group. One olefinic proton appears as a singlet (5.05 ppm) and the typical AA′XX′ pattern in the aromatic region of the ^{1}H nmr spectrum is indicative of the 4-cyanophenyl group.

The *E*-configuration was assigned on the basis of the observed nuclear Overhauser effect (nOe). When the signal due to the allylic methyl group was irradiated a small nOe was observed in the signal of the methine and methylene hydrogens (ABC second-order pattern) and of the *ortho*-aryl H's. Irradiation of the signal due to the vinyl hydrogen caused a large nOe on the signals due to the methine and methylene hydrogens (ABC second-order pattern) and the *ortho*- and *meta*-aryl hydrogens.

In the ^{13}C nmr spectrum, there are distinctive carbon shifts, further supporting the structure proposed for compound **24**. The signal at 95.89 ppm is distinctive for an alkene methine group, cyano substituted (7). The quaternary alkene carbon β to the cyano group absorbs at 167.39 ppm. There are also two low-field singlets (116.84 and 118.74 ppm) supporting two different cyano groups. These chemical shifts were reproduced using the Advanced Chemical Development's ^{13}C nmr spectra simulation program; the calculated values are in good agreement with the observed chemical shifts.[4]

When an acetonitrile solution of 4-methyl-1,3-pentadiene (**13**), **1**, **8**, and potassium cyanide was irradiated, two photo-NOCAS adducts, **25** and **26**, were obtained (reaction [8]). Compound **25** was identified as the *anti*-Markovnikov 1,2-addition product, 3-(4-cyanophenyl)-5-methyl-4-hexenenitrile. This regioisomer is the result of initial bonding of cyanide anion at the less substituted end of the diene radical cation, $\mathbf{13}^{+\bullet}$, generating the more heavily alkyl-substituted allylic radical intermediate. The presence of the trisubstituted alkene is supported by a doublet (5.35 ppm, $J = 9.3$ Hz) in the vinyl proton region of the ^{1}H nmr spectrum, which represents coupling to the allylic methine proton. The ^{1}H nmr spectrum also exhibits two singlets (1.69 and 1.77 ppm), indicative of the two nonequivalent methyl groups bonded to the alkene, and an ABX multiplet (2.66, 2.70, and 3.97 ppm) for the protons of the methylene group next to a cyano group and that of the benzylic, allylic methine group.

The ^{13}C nmr spectrum of compound **25** exhibits a triplet (24.90 ppm) indicative of the methylene group substituted by the cyano group. There is a lower-field doublet (40.56 ppm) that is consistent with an aryl-substituted methine carbon. There are two low-field singlets (117.92 and 118.64 ppm) consistent with two cyano groups. The ^{13}C nmr spectrum also exhibits a doublet (123.08 ppm), for the vinyl methine group, and a singlet (136.94 ppm), for the quaternary vinyl carbon, further supporting the presence of the trisubstituted alkene.

Compound **26** was identified as the 1,4-addition product, (*E*)-5-(4-cyanophenyl)-2,2-dimethyl-3-pentenenitrile, resulting from attack of the cyanide anion at the more heavily substituted terminal end of the diene. The first indication of the

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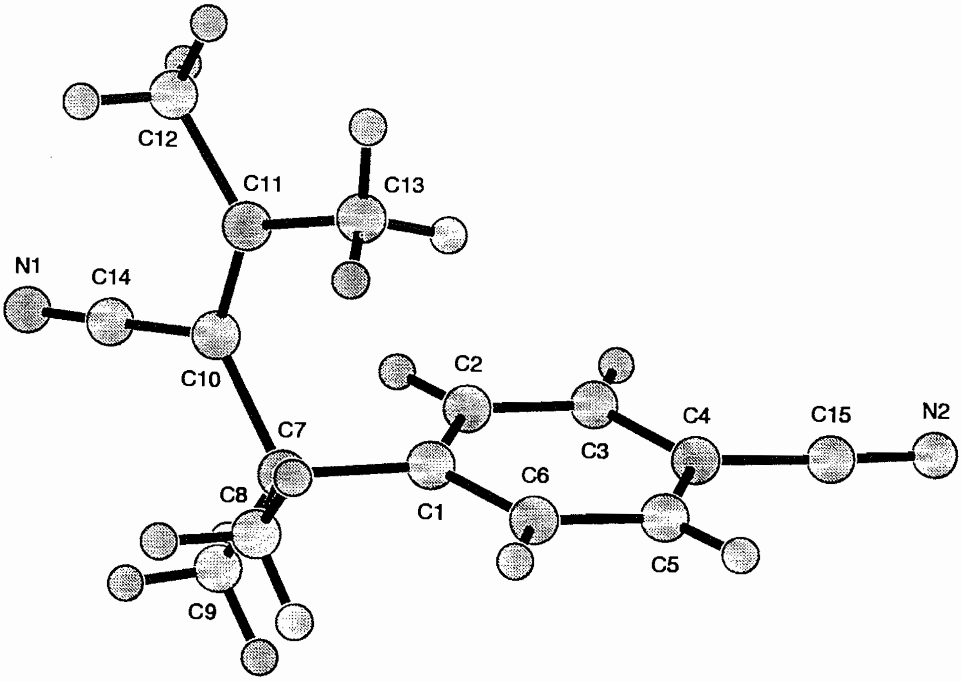
[4] Software available from: Advanced Chemical Development, Inc., 141 Adelaide Street, West, Suite 1501, Toronto, ON M5H 3L5, Canada.

Fig. 1. X-ray crystal structure of 4-(4-cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile (**28**).



regiochemistry of this isomer was obtained from the mass spectrum (gc/ms), which shows a dominant fragment of 142 *m/z* ($C_{10}H_8N$) due to loss of the cyanopropyl fragment. There is a singlet (1.41 ppm) in the aliphatic region of the ^1H nmr spectrum, representing the two chemically equivalent methyl groups, a lower-field doublet (2.47 ppm) indicating the presence of an aryl-substituted allylic methylene group, and an AA′XX′ pattern in the aromatic region indicative of the 4-cyanophenyl group. A doublet of triplets and a doublet (6.40 and 6.55 ppm, respectively) appear in the vinyl region, each with a coupling constant (15.9 Hz) typical of a *trans* configuration. The infrared spectrum shows a peak at the C-H bending frequency (973 cm^{-1}) further supporting the *trans* configuration for this alkene. In the ^{13}C nmr spectrum of **26**, there is a singlet (32.65 ppm) due to the quaternary carbon substituted by a cyano group and a triplet (44.32 ppm) for the methylene carbon substituted by the aryl group.

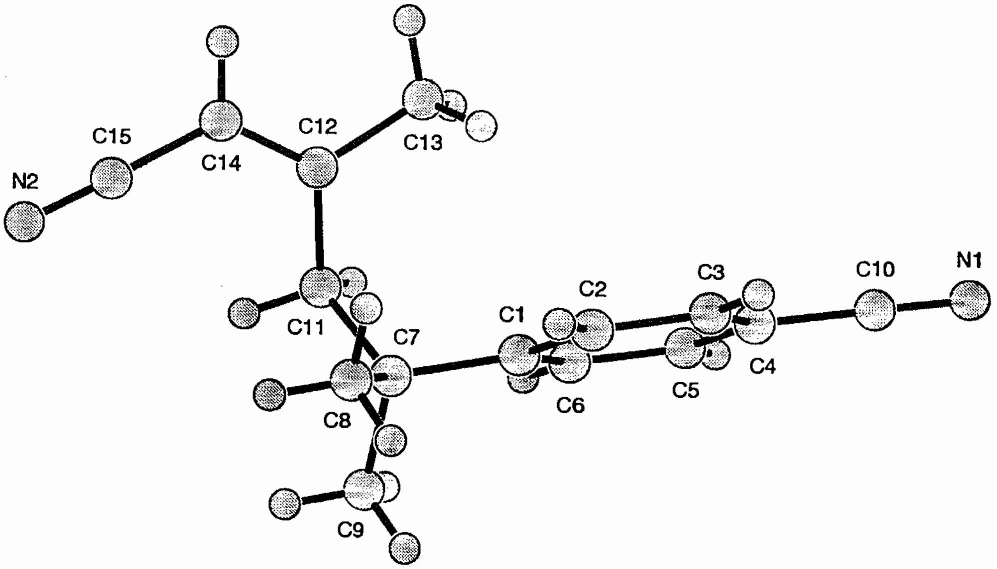
Irradiation of an acetonitrile solution of 2,4-dimethyl-1,3-pentadiene (**14**), **1**, **8**, and potassium cyanide gave three 1:1:1 adducts: **27**, **28**, and **29** (reaction [9]). Compound **27** was identified as the *anti*-Markovnikov 1,2-addition product, 3-(4-cyanophenyl)-3,5-dimethyl-4-hexenenitrile. Initial attack of cyanide anion at the less substituted end of the diene radical cation, $14^{+\bullet}$, gives the more heavily alkyl-substituted allylic radical intermediate. The presence of the trisubstituted alkene is supported by a broad singlet in the vinyl proton region (5.54 ppm) of the ^1H nmr spectrum. The ^1H nmr spectrum also exhibits three singlets (1.14, 1.64, and 1.76 ppm) indicative of the two nonequivalent methyl groups bonded to the alkene and the allylic methyl group. Also in the ^1H nmr spectrum, an AB apparent singlet was observed (2.68 ppm) for the diastereotopic protons of the methylene group bearing the cyano group.

The ^{13}C nmr spectrum of compound **27** exhibits a triplet (33.44 ppm) indicative of the methylene group substituted by the cyano group. There is a lower-field singlet (41.90 ppm) that is consistent with an aryl-substituted quaternary carbon. There are also two singlets (117.63 and 118.71 ppm) supporting two cyano groups. The ^{13}C nmr spectrum also exhibits a doublet (129.15 ppm) for the vinyl methine group and the quaternary vinyl carbon shows up as a singlet (137.27 ppm), further indicating the trisubstituted alkene.

Compound **28**, 4-(4-cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile, was identified as a possible product of the allene, 2,4-dimethyl-2,3-pentadiene (**15**), which could be an impurity in the starting diene. The ^1H nmr spectrum exhibits three singlets (1.31, 1.58, and 2.11 ppm), indicative of the four methyl groups; the singlet at 1.58 ppm represents the pair of magnetically equivalent methyl groups. The ^{13}C nmr spectrum of compound **28** exhibits a singlet (41.08 ppm) that indicates a quaternary carbon substituted by the 4-cyanophenyl group. There are also three singlets (118.26, 118.32, and 118.71 ppm) supporting two types of cyano groups and the quaternary vinyl carbon, cyano substituted. The ^{13}C nmr spectrum also exhibits a singlet (154.57 or 155.69 ppm) representing a quaternary vinyl carbon, alkyl substituted. The overall structure of **28** was firmly established by X-ray analysis of a single crystal (Fig. 1).[3]

Compound **29** was identified as (**Z**)-5-(4-cyanophenyl)-3,5-dimethyl-2-hexenenitrile, which, we believe, results from the tautomerization of the initially formed 1,4-addition product, 5-(4-cyanophenyl)-3,5-dimethyl-3-hexenenitrile. The ^1H and ^{13}C nmr spectra are consistent with this structure for compound **29**. The ^1H nmr spectrum shows two high-field singlets (1.39 and 1.46 ppm) indicative of the three methyl groups; the singlet at 1.46 ppm is due to the two magnetically equivalent methyl groups. There is a low-field singlet (2.79 ppm) due to the allylic methylene group and a singlet (5.17 ppm) for the vinyl proton. In the ^{13}C nmr spectrum, a doublet (99.24 ppm) is distinctive for the alkene methine group, cyano substituted

Fig. 2. X-ray crystal structure of (*Z*)-5-(4-cyanophenyl)-3,5-dimethyl-2-hexenenitrile (**29**).



(7). The alkene carbon β to the cyano group shows up at low field (162.15 ppm). There are two singlets (117.21 and 118.79 ppm) supporting two types of cyano groups. The *Z*-configuration, as well as the overall structure of **29**, was firmly established by X-ray analysis on a single crystal (Fig. 2).^{3}

Discussion

There is a dramatic increase in yield of the photo-NOCAS adduct(s), incorporating cyanide anion, through the series of alkenes: 2-methylpropene (**9**) (0%) < 2-methyl-2-butene (**10**) < 2,3-dimethyl-2-butene (**2**) (20%), and through the series of conjugated dienes: 2-methyl-1,3-butadiene (**11**) (3%) < 2,3-dimethyl-1,3-butadiene (**12**) < 4-methyl-1,3-pentadiene (**13**) < 2,4-dimethyl-1,3-pentadiene (**14**) < 2,5-dimethyl-2,4-hexadiene (**6**) (80%!). Increasing alkyl substitution on the alkene or diene correlates with increased yields of photo-NOCAS adduct(s) incorporating cyanide anion. This trend was not evident in the analogous reactions involving alcohol (methanol) as the nucleophile. The observed dependence in yield of photo-NOCAS adduct(s), through these series, can be attributed to the concomitant decrease in the oxidation potential of the alkene and diene associated with increasing alkyl substitution (Table 1).

The determination of the oxidation potential of cyanide anion, by electrochemical methods, is complicated by ion-pair formation, solvent interaction, adsorption on the electrode, etc. (9, 10). Under some conditions, oxidation begins at an electrode potential as low as +0.6 V (SCE) (9); however, the best estimate of the half-wave potential ($E_{1/2}^{\mathrm{ox}}$, $\mathrm{CN^-/CN^\bullet}$) is +1.65 V (SCE, DMF) (9*d*). Therefore, nucleophilic attack of cyanide anion on the radical cation of an alkene or diene that has an oxidation potential greater than ca. +1.5 V will be accompanied by electron transfer; oxidation of the cyanide anion to the cyano radical by the alkene or diene radical cation will compete with the combination. Similar results have been reported for the anodic cyanation of aromatic compounds where the highest yields of mono-cyanation products were obtained on aromatic substrates with oxidation potentials less than +1.3 V (SCE) (9*a*,*b* and 10*a*,*b*).

Table 1. Oxidation potentials of alkenes and dienes.

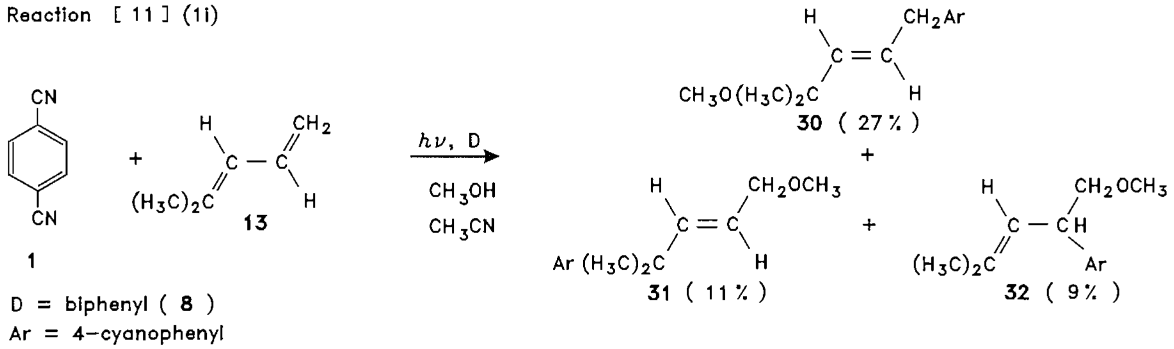
Alkene/diene	$E_{1/2}^{\mathrm{Ox}}$ (V,SCE)	Reference
2-Methylpropene (**9**)	2.64	1*d*
2-Methyl-2-butene (**10**)	2.03	1*e*
2,3-Dimethyl-2-butene (**2**)	1.62	1*d*
2-Methyl-1,3-butadiene (**11**)	2.25	1*b*
2,3-Dimethyl-1,3-butadiene (**12**)	2.16	1*b*
4-Methyl-1,3-pentadiene (**13**)	1.51	This work[a]
2,4-Dimethyl-1,3-pentadiene (**14**)	1.52	This work[a]
2,5-Dimethyl-2,4-hexadiene (**6**)	1.24	1*b*
2,4-Dimethyl-2,3-pentadiene (**15**)	1.93	This work[a]
1,1-Diphenylethylene	1.82	2*a*

[a] The anodic wave was irreversible; the half-wave potential was taken as 0.028 V before the peak potential (8).

The ultimate fate of the cyano radical is not known. Certainly the cyano radical is very reactive; it reacts at essentially the diffusion-controlled rate with alkanes and alkenes, with itself, with cyanide anion, and with acetonitrile (11).

Since the first examples of the photo-NOCAS reaction, the regiochemistry of the initial bonding step has been termed *anti*-Markovnikov; that is, the nucleophile (methanol) adds to that end of the radical cation which is less heavily substituted, less sterically hindered, to give the more heavily substituted (more stable?) radical intermediate (1). The (superficial) analogy with the mechanism for free-radical addition to alkenes and dienes is obvious (12).

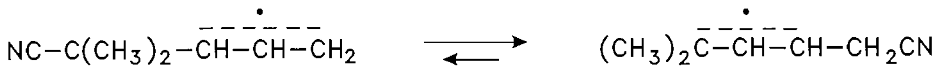
Usually the more heavily alkyl-substituted radical is also the more stable; however, there are exceptions. Compare the product ratios, Markovnikov *vs.* *anti*-Markovnikov, for the cyanide and methanol addition to the radical cation of 4-



methyl-1,3-pentadiene ($13^{+\cdot}$) (reactions [8] and [11] (1*i*)). The major photo-NOCAS adduct isolated from reaction [8] is **25** (14%), the *anti*-Markovnikov adduct; the Markovnikov adduct, **26**, is a minor (1%) product. Relevant isodesmic reactions, [8*a*] and [8*b*], are in agreement; both high-level ab initio molecular orbital calculations (MP2/6-31G*//HF/6-31G*) and heats of formation based upon the empirically derived Benson's rules indicate that the more heavily substituted allylic radical, $\mathbf{25a}^{\cdot}$, is the more stable. The cyanide anion bonds preferentially to the less substituted, less sterically hindered, end of the radical cation, $\mathbf{13}^{+\cdot}$ which yields the more stable radical intermediate.

The major photo-NOCAS adduct from reaction [11] is **30**, the Markovnikov adduct. The product ratio, **30** (Markovnikov):**31** + **32** (*anti*-Markovnikov), is 1.4:1. Both ab initio molecular orbital calculations and empirically derived heats of

[8*a*]

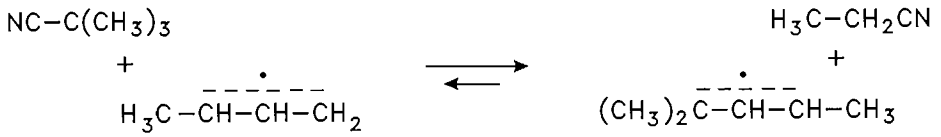


$$NC{-}C(CH_3)_2{-}\overline{CH{-}\overset{\bullet}{C}H{-}CH_2} \rightleftharpoons (CH_3)_2\overline{C{-}\overset{\bullet}{C}H{-}CH}{-}CH_2CN$$

26a• **25a•**

ΔH (kJ mol^{-1}) −4.7 (calcd.)^{a}

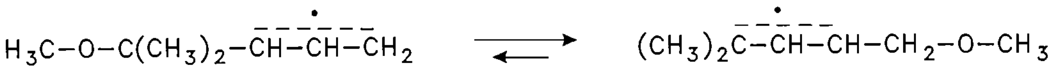
[8*b*]



$$NC{-}C(CH_3)_3 + H_3C{-}\overline{CH{-}\overset{\bullet}{C}H{-}CH_2} \rightleftharpoons H_3C{-}CH_2CN + (CH_3)_2\overline{C{-}\overset{\bullet}{C}H{-}CH}{-}CH_3$$

ΔH (kJ mol^{-1}) −3.3 (calcd.)^{a} −16.0 (calcd.)^{b}

[11*a*]

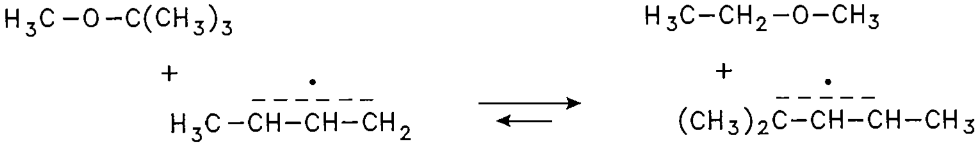


$$H_3C{-}O{-}C(CH_3)_2{-}\overline{CH{-}\overset{\bullet}{C}H{-}CH_2} \rightleftharpoons (CH_3)_2\overline{C{-}\overset{\bullet}{C}H{-}CH}{-}CH_2{-}O{-}CH_3$$

30a• **31a•**

ΔH (kJ mol^{-1}) +5.1 (calcd.)^{a} +5.8 (calcd.)^{b}

[11*b*]



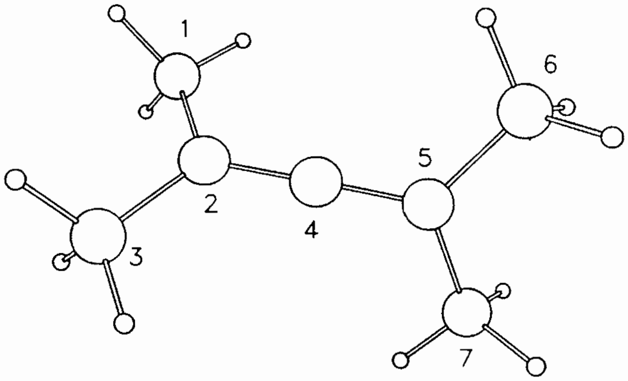
$$H_3C{-}O{-}C(CH_3)_3 + H_3C{-}\overline{CH{-}\overset{\bullet}{C}H{-}CH_2} \rightleftharpoons H_3C{-}CH_2{-}O{-}CH_3 + (CH_3)_2\overline{C{-}\overset{\bullet}{C}H{-}CH}{-}CH_3$$

ΔH (kJ mol^{-1}) +2.0 (calcd.)^{a} +0.8 (calcd.)^{b}

[a] MP2/6-31G*//HF/6-31G*

[b] Benson's rules.

Table 2. Calculated (MP2/6-31G*//HF/6-31G*) Mulliken charge (charge on hydrogens summed in with bound carbon) and spin density for the radical cation of 2,4-dimethyl-2,3-pentadiene (**15**$^{+\bullet}$).



Atom	Charge	Spin	Structure
1	0.186	-0.029	∠ 2,4,5 180°
2	0.059	0.361	Dihedral ∠ 1,2,3,4 180°
3	0.186	-0.029	Dihedral ∠ 1,2,5,6 55.2°
4	0.138	0.267	
5	0.059	0.361	Total energy (Hartree)
6	0.186	-0.029	-272.625 62 au
7	0.186	-0.029	

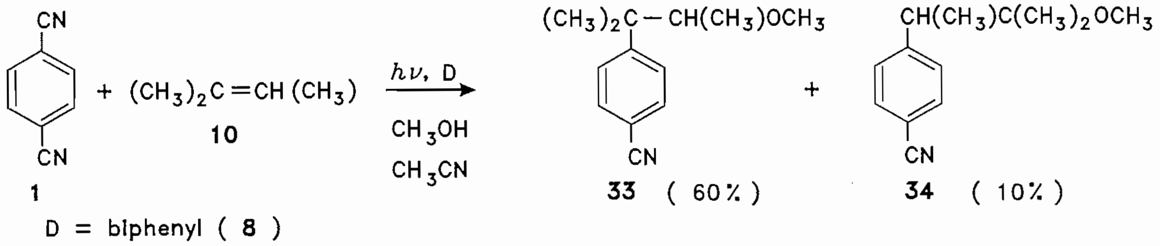
formation indicate that, in this case, the more heavily substituted allylic radical, **31a**$^{\bullet}$, is **not** the more stable (isodesmic reactions [11*a*] and [11*b*] (1*i*)). The effect of alkyl substitution on the carbon bearing the ether-oxygen obviously has a greater influence on the stability of this intermediate than does alkyl substitution on the allylic radical moiety. Of course, the total structure of the intermediate must be considered, not just the radical moiety. Upon addition of this neutral nucleophile, methanol, the initially formed distonic radical cation allows equilibration of the intermediates; steric factors, which generally influence the rate of addition, are less important.

There are previous reports of nucleophilic addition to the radical cation of an allene (13). Formation of 4-(4-cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile (**28**) indicates cyanide anion addition to the central carbon of the radical cation of 2,4-dimethyl-2,3-pentadiene (**15**$^{+\bullet}$) (reaction [10]). Nucleophilic attack at the central carbon of this radical cation is as expected; the molecular orbital calculations (MP2/6-31G*//HF/6-31G*) indicate the positive charge density is greater at the central carbon than at the terminal carbons (Table 2). In marked contrast, the spin density is greater at the termini than at the central carbon. Nucleophilic attack at the less sterically hindered central carbon also yields (ultimately) the stabilized allylic radical. The lack of isonitrile from this reaction is indicative that this allene radical cation is reacting as a "soft" electrophile; this is consistent with the delocalized charge. The calculated structure for the radical cation, **15**$^{+\bullet}$, is in good agreement with the experimentally determined structure and with lower level molecular orbital calculations (14).

The two photo-NOCAS reactions involving 2-methyl-2-butene (**10**), reactions [5] and [12] (1*b*), allow the comparison of the regiochemistry of the combination with cyanide anion, yielding both nitriles, **17** and **18**, and isonitriles, **19** and **20**, and, with methanol, yielding the ethers, **33** and **34**. The ratios of isomeric adducts (*anti*-Markovnikov:Markovnikov) are, for the nitriles, 4:1, for the isonitriles, >30:1, and, for the ethers, 6:1 (1*e*)). Relevant isodesmic reactions are summarized in Table 3.

For the nitriles, the two possible intermediates are directly compared in reaction [a]. The difference in total energy calculated by the ab initio molecular orbital method (MP2/6-31G*//HF/6-31G*) is still in agreement with the observed product

Reaction[12](1e)



D = biphenyl (**8**)

Table 3. Isodesmic reactions.

	ΔH (kJ mol^{-1})		
R	MP2/6-31G*//HF/6-31G*[a]	Benson's rules[b]	Experimental[c]
[a]	R—$(CH_3)_2C$—$\dot{C}H(CH_3)$	$\rightleftharpoons$	$(CH_3)_2\dot{C}$—$CH(CH_3)$—R
-CN	−5.6		
-NC	+0.9		
-OCH_3	−6.4	−2.1	
[b]	R—$(CH_3)_2C$—CH_3 + H_3C—$\dot{C}H(CH_3)$	$\rightleftharpoons$	H_3C—$CH(CH_3)$—R + $(CH_3)_2\dot{C}$—CH_3
-CN	−3.5	−10.6	
-NC	+2.0		
-OCH_3	−4.1	−1.9	−6.7
[c]	R—$(CH_3)_2C$—CH_2CH_3	$\rightleftharpoons$	$(CH_3)_2CH$—$CH(CH_3)$—R
-CN	+3.5	−2.5	
-NC	+9.5		
-OCH_3	+5.0	+6.3	
[d]	$CH_3)_2CH$—$\dot{C}H(CH_3)$	$\rightleftharpoons$	$(CH_3)_2\dot{C}$—CH_2CH_3
	−9.8	−8.1	
[e]	R—$(CH_3)_2C$—CH_2CH_3 + $(CH_3)_2CH$—$\dot{C}H(CH_3)$	$\rightleftharpoons$	$(CH_3)_2CH$—$CH(CH_3)$—R + $(CH_3)_2\dot{C}$—CH_2CH_3
-CN	−6.3	−10.6	
-NC	−0.3		
-OCH_3	−4.8	−1.8	
[f]	R—$C(CH_3)_3$	$\rightleftharpoons$	$(CH_3)_2CCH_2$—R
-CN	+8.4		
-NC	+21.6		
-OCH_3	+15.3	+21.3	

[a] Ab initio molecular orbital calculations (MP2/6-31G*//HF/6-31G*) (5, 6).

[b] Empirically derived heats of formation, Benson's empirical rules (15).

[c] Experimentally determined heats of formation (16).

ratio; the *tertiary*-alkyl radical is more stable than the *secondary*-alkyl radical. The isodesmic reactions [b] and [e] are consistent. The ab initio calculations indicate that the nitrile with greater alkyl substitution on the carbon bearing the cyano group is slightly more stable (reaction [c]); as a result, the difference in stability between the *tertiary*- and *secondary*-alkyl radicals (reaction [d]) dominates.

For the isonitriles, the small difference in total energy of the two possible intermediates calculated by the ab initio molecular orbital method is now inconsistent with the observed product ratio (**19**:**20**, >30:1). In fact, in this case, the isodesmic reactions [a] and [b] indicate a preference for formation of the Markovnikov addition product (**20**). The isodesmic reaction [e] shows only a slight preference for the *tertiary*-alkyl radical. The isodesmic reaction [c] provides the explanation; increased alkyl substitution on the carbon bearing the isonitrile group is now significantly stabilizing, comparable to the effect of increased alkyl substitution on the alkyl radical.

For the ethers, the difference in total energy of the two possible β-alkoxyalkyl radicals (isodesmic reactions [a], [b], and [e]), calculated by the ab initio molecular orbital method is in good agreement with the observed product ratio; the *tertiary*-β-alkoxyalkyl radical is more stable than the *secondary*-β-alkoxyalkyl radical. The *tertiary* ether, methyl 2-methyl-2-butyl ether, is more stable than the *secondary* ether, methyl 3-methyl-2-butyl ether (isodesmic reaction [c]); however, the difference in stability between the *tertiary* and *secondary* alkyl radicals is even greater (isodesmic reaction [d]). Consequentially, the combined isodesmic reaction [e] is exothermic, consistent with the observed product ratio (1*e*,*i*).

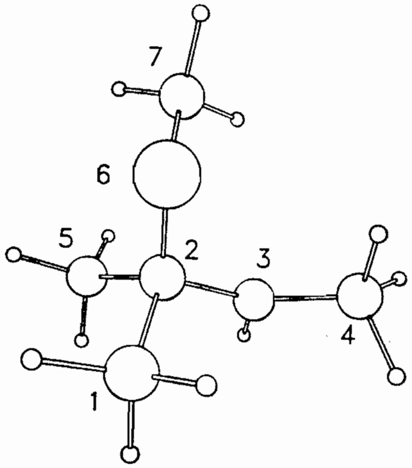
These differences in the effect of alkyl substitution on the stability of the β-cyano, β-isocyano, and β-methoxy, alkyl radicals must be due to the difference in electron demand (the inductive effect) of the cyano, isocyano, and methoxy groups. The calculated (MP2/6-31G*//HF/6-31G*) charge and spin density distributions from Mulliken and natural population

Table 4. Calculated (MP2/6-31G*//HF/6-31G*) Mulliken charge (charge on hydrogens summed in with bound carbon) and spin density.[a]

2-Methyl-2-butene – methanol radical (C-2 bonded) **34a**$^{\bullet}$

Atom	Charge	Spin
1	0.00 (0.00)	0.01 (0.01)
2	0.31 (0.27)	−0.13 (−0.07)
3	0.00 (0.07)	1.23 (1.02)
4	0.01 (−0.03)	−0.16 (−0.01)
5	0.03 (0.02)	0.03 (0.04)
6 (O)	−0.64 (−0.67)	0.01 (0.01)
7	0.30 (0.32)	0.01 (0.00)

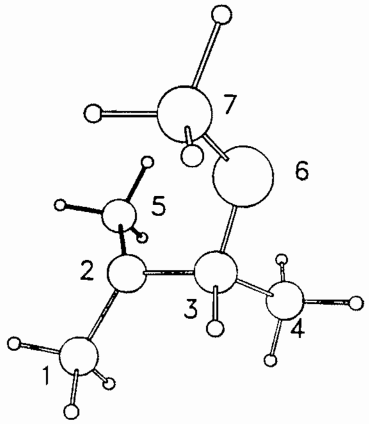
<u>Structure</u>
Length 3–6 2.4 Å
Dihedral ∡ 2,3,4,H 159.6°
Dihedral ∡ 6,2,3,4 48.4°
<u>Total energy (Hartree)</u>
−310.526 14 au



2-Methyl-2-butene – methanol radical (C-3 bonded) **33a**$^{\bullet}$

Atom	Charge	Spin
1	−0.01 (−0.02)	−0.16 (−0.01)
2	0.01 (0.07)	1.20 (1.03)
3	0.30 (0.30)	−0.13 (−0.06)
4	0.02 (0.01)	0.04 (0.04)
5	−0.01 (−0.03)	−0.16 (0.01)
6 (O)	−0.62 (−0.66)	0.01 (0.01)
7	0.30 (0.33)	0.01 (0.00)

<u>Structure</u>
Length 2–6 2.4 Å
Dihedral ∡ 1,2,3,5 155.6°
Dihedral ∡ 6,3,2,1 156.5°
<u>Total energy (Hartree)</u>
−310.528 57 au



2-Methyl-2-butene – nitrile radical (C-2 bonded) **18a**$^{\bullet}$

Atom	Charge	Spin
1	0.08 (0.07)	0.04 (0.04)
2	−0.10 (−0.20)	−0.14 (−0.08)
3	0.05 (0.12)	1.23 (1.08)
4	0.03 (−0.02)	−0.16 (−0.09)
5	0.08 (0.07)	0.01 (0.01)
6	0.32 (0.33)	0.04 (0.04)
7 (N)	−0.47 (−0.38)	−0.03 (−0.03)

<u>Structure</u>
∡ 2,6,7 179.4°
Length 3–6 2.45 Å
Dihedral ∡ 2,3,4,H 158.1°
Dighedral ∡ 6,2,3,4 49.2°
<u>Total energy (Hartree)</u>
−288.347 30 au

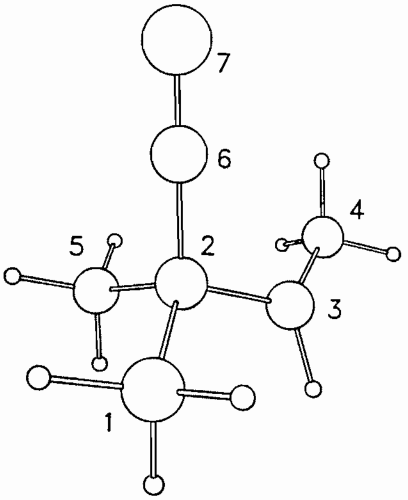
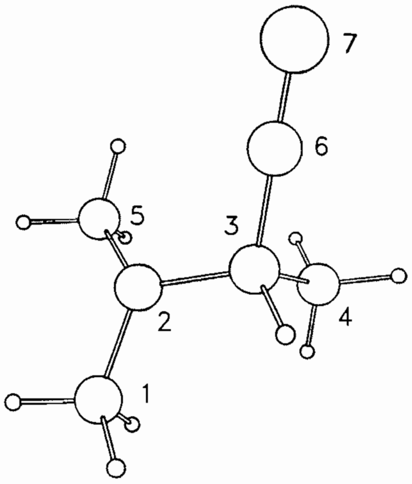


Table 4 (*continued*).

2-Methyl-2-butene – nitrile radical (C-3 bonded) **17a**•

Atom	Charge	Spin
1	0.01 (–0.02)	–0.16 (–0.09)
2	0.06 (0.12)	1.20 (1.04)
3	–0.01 (–0.11)	–0.15 (–0.08)
4	0.08 (0.06)	0.05 (0.05)
5	0.02 (–0.01)	–0.16 (–0.09)
6	0.31 (0.33)	0.05 (0.04)
7 (N)	–0.47 (–0.38)	–0.04 (–0.03)

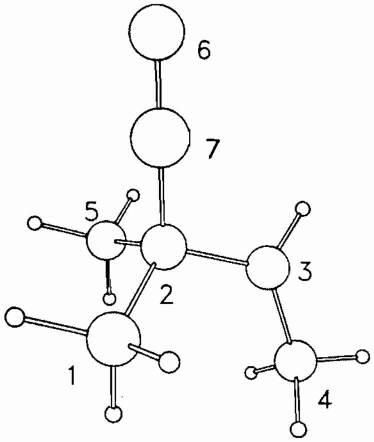
Structure
∡ 3,6,7 179.4°
Length 2–6 2.47 Å
Dihedral ∡ 1,2,3,5 155°
Dihedral ∡ 1,2,3,6 54.0°
Total energy (Hartree)
–288.349 44 au



2-Methyl-2-butene – isonitrile radical (C-2 bonded) **20a**•

Atom	Charge	Spin
1	0.08 (0.06)	0.04 (0.04)
2	0.13 (0.09)	–0.13 (–0.07)
3	0.05 (0.11)	1.23 (1.08)
4	0.02 (–0.02)	–0.16 (–0.09)
5	0.08 (0.05)	0.01 (0.01)
6	0.03 (0.35)	–0.02 (–0.02)
7 (N)	–0.38 (–0.65)	0.02 (0.02)

Structure
∡ 2,7,6 179.4°
Length 3–7 2.41 Å
Dihedral ∡ 2,3,4,H 156.7°
Dihedral ∡ 7,2,3,4 46.4°
Total energy (Hartree)
–288.311 70 au



2-Methyl-2-butene – isonitrile radical (C-3 bonded) **19a**•

Atom	Charge	Spin
1	0.01 (–0.02)	–0.16 (–0.09)
2	0.05 (0.12)	1.19 (1.03)
3	0.21 (0.17)	–0.11 (–0.06)
4	0.07 (0.05)	0.01 (0.01)
5	0.02 (–0.02)	–0.15 (–0.08)
6	0.03 (0.35)	0.00 (0.00)
7 (N)	–0.39 (–0.65)	0.03 (0.04)

Structure
∡ 3,7,6 178.6°
Length 2–7 2.4 Å
Dihedral ∡ 1,2,3,5 151.8°
Dihedral ∡ 7,3,2,1 73.8°
Total energy (Hartree)
–288.311 37 au

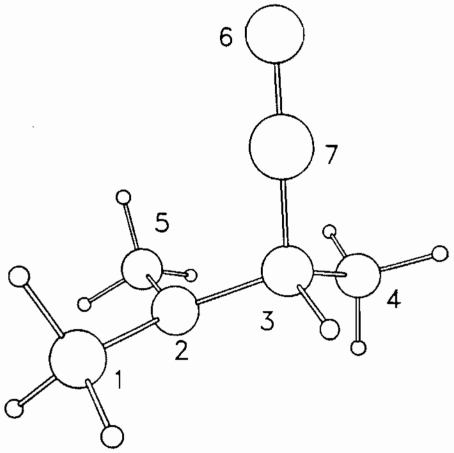
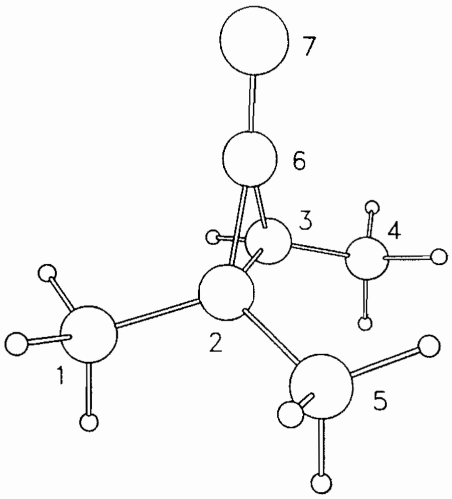


Table 4 (*concluded*).
2-Methyl-2-butene – nitrile radical (bridged)

Atom	Charge	Spin
1	0.05 (0.05)	–0.02 (–0.01)
2	–0.03 (–0.07)	0.23 (0.17)
3	0.00 (–0.01)	0.21 (0.16)
4	0.05 (0.04)	–0.02 (–0.01)
5	0.05 (0.05)	0.01 (–0.01)
6	0.24 (0.15)	–0.77 (–0.60)
7 (N)	–0.38 (–0.20)	1.37 (1.29)

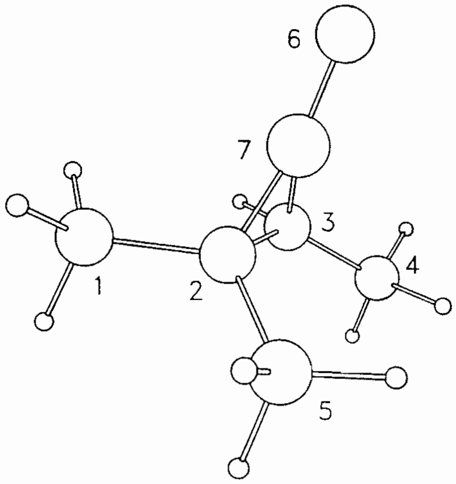
Structure
∡ 2,6,7 149.2°
∡ 3,6,7 148.9°
Length 2–6 1.50 Å
Length 3–6 1.49 Å
Length 2–3 1.53 Å
Length 6–7 1.23 Å
Dihedral ∡ 2,3,6,7 176.7°
Total energy (Hartree)
–288.313 00 au



2-Methyl-2-butene – isonitrile radical (bridged)

Atom	Charge	Spin
1	0.06 (0.04)	–0.01 (0.00)
2	0.15 (0.16)	0.13 (0.11)
3	0.19 (0.21)	0.12 (0.11)
4	0.05 (0.03)	–0.01 (0.00)
5	0.05 (0.04)	–0.01 (0.00)
6	–0.04 (0.18)	1.05 (0.99)
7 (N)	–0.45 (–0.66)	–0.27 (–0.20)

Structure
∡ 2,7,6 148.6°
∡ 3,7,6 148.3°
Length 2–7 1.44 Å
Length 3–7 1.44 Å
Length 2–3 1.51 Å
Length 6–7 1.28 Å
Dihedral ∡ 2,3,7,6 179.2°
Total energy (Hartree)
–288.247 17 au



[a] Values in parentheses are from natural charge and spin population analysis (6*d*).

analysis, for the radical intermediates involved in reactions [5], [8], and [12] are shown in Table 4. Summing the total charge on the substituent indicates the isocyano and methoxy groups are significantly more negative than the cyano group. This order is also evident from the charge on the β-carbon atoms. The carbon atoms directly bonded to the nitrogen of the isocyano group and to the ether oxygen are significantly more positively charged than the corresponding carbon bonded to the carbon of the cyano group. β-Substitution by a cyano, isocyano, or methoxy group has little effect on the spin density distribution of these radicals.

The calculations give an indication of the importance of bridging of the radical with these β-substituents (17). Starting with initially bridged β-cyano and β-isocyano radical structures, the calculations converge to relatively high-energy bridged radicals. Frequency calculations confirm that these bridged radicals are indeed minima. These bridged structures are significantly less stable than conformers that are not bridged, for the nitrile, 96 kJ mol^{-1}, and for the isonitrile 169 kJ mol^{-1}, above the global minimum. Starting with an initially bridged β-methoxy radical, constrained to equal carbon–oxygen bond lengths, the calculations did not converge. The calculations converge to the unbridged structure (**33a**$^{\cdot}$) upon removing the structural constraint.

These calculations also provide a direct comparison of the effect of alkyl substitution on the relative stability of the nitriles, the isonitriles, and the ethers, illustrated with the isodesmic reactions summarized in Table 3 [c] and [f]. The

Table 5. Isodesmic reactions indicating the difference in stability of nitriles and isonitriles.

$NC\text{-}C(CH_3)_3$	$\rightleftarrows$	$CN\text{-}C(CH_3)_3$
ΔH (kJ mol^{-1}) +92.1 (calcd.)^a		
$H_3C\text{-}CH(CH_3)CN$	$\rightleftarrows$	$H_3C\text{-}CH(CH_3)NC$
ΔH (kJ mol^{-1}) +97.6 (calcd.)^a		
$(CH_3)_2CH\text{-}CH_2CN$	$\rightleftarrows$	$(CH_3)_2CH\text{-}CH_2NC$
ΔH (kJ mol^{-1}) +105.3 (calcd.)^a		

stabilizing effect of alkyl substitution on the carbon bearing the cyano group is relatively small; 2,2-dimethylpropanenitrile is 8.4 kJ mol^{-1} more stable than 3-methylbutanenitrile (*tertiary* vs. *primary*, reaction [f]) while 2,2-dimethylbutanenitrile is only 3.5 kJ mol^{-1} more stable than 2,3-dimethylbutanenitrile (*tertiary* vs. *secondary*, reaction [c]). The influence of alkyl substitution is greatest on the isonitrile; 2-isocyano-2-methylpropane is 21.6 kJ mol^{-1} more stable than 1-isocyano-2-methylpropane (*tertiary* vs. *primary*, reaction [f]) while 2-isocyano-2-methylbutane is 9.5 kJ mol^{-1} more stable than 2-isocyano-3-methylbutane (*tertiary* vs. *secondary*, reaction [c]). *tert*-Butyl methyl ether is also significantly (15.3 kJ mol^{-1}) more stable than isobutyl methyl ether (*tertiary* vs. *primary*, reaction [f]) and methyl 2-(2-methylbutyl) ether is more stable (5.0 kJ mol^{-1}) than methyl 2-(3-methylbutyl) ether (*tertiary* vs. *secondary*, reaction [c]) (1*i*).

It is also reassuring to note (Table 5) that there is good agreement between the differences in the calculated (ab initio) total energy and previously reported experimentally determined heats of isomerization for the alkyl isonitriles to nitriles (18).

Summary and conclusions

Cyanide anion can be an effective nucleophile in the photo-NOCAS reaction; yields of the nitrile can be high. Highest yields are obtained when the alkene or diene has an oxidation potential less than 1.5 V (SCE). When the oxidation potential of the alkene or diene is greater than 1.5 V, electron transfer from the cyanide anion to the alkene or diene radical cation competes with the combination.

With alkenes, both nitriles and isonitriles are obtained. Isonitriles were not observed from the dienes. The explanation is based upon the Hard-Soft-Acid-Base (HSAB) principle. The harder alkene radical cation adds to both the hard nitrogen and the soft carbon ends of the ambident cyanide anion. The relatively soft diene radical cation adds preferentially to the soft carbon end of this nucleophile.

The regiochemistry of the adduct, Markovnikov versus *anti*-Markovnikov, is determined during the initial bonding of the cyanide anion with the alkene or diene radical cation. Cyanide anion adds preferentially to the less sterically hindered end of the radical cation, which, on the way to nitrile, yields the more stable β-cyano alkyl radical intermediates. However, bonding of the cyanide anion at the nitrogen, on the way to isonitrile, gives the less stable β-isocyano alkyl radical intermediate.

The difference in regiochemistry of the photo-NOCAS reactions involving methanol and cyanide anion reflects the fact that the initially formed intermediate, upon the addition of methanol to the alkene or diene radical cation, is a distonic radical cation with the possibility of bridging and concomitant equilibration. The addition of cyanide anion to an alkene or diene radical cation leads directly to the β-cyano- or isocyanoalkyl radical, which are not bridged, and with no possibility for equilibration. Therefore, the addition of cyanide anion must be kinetically controlled, the reaction is significantly exothermic, the transition state is early; as with radical addition to alkenes and dienes, steric effects dominate.

The radical cation of allenes can also combine with cyanide anion in the photo-NOCAS reaction. The radical cation $\mathbf{15}^{+\bullet}$ couples with the cyanide anion at the central carbon of the allene and only at the carbon of this ambident anion, as a soft-electrophile.

Experimental

General information

The ^{1}H and ^{13}C nmr spectra were obtained from a Bruker 250 MSL or a Bruker 400 MSL spectrometer. Spectra were recorded in parts per million (ppm) and frequencies are relative to tetramethylsilane. Infrared spectra (ir) were recorded on a Nicolet 205 or 510 FTIR and are reported in wave numbers (cm^{-1}). Elemental analyses were performed by the Canadian Microanalytical Service Ltd., B.C. Exact Mass determinations were obtained using a CEC 21-110 mass spectrometer. Melting points were determined using a Cybron Corporation Thermolyne apparatus with a digital thermocouple and are corrected. Product yields and progress of the reactions were determined using a Hewlett–Packard (HP) 5890 gas chromatograph with a DB-1701 fused silica WCOT column (30 m × 0.25 mm, 0.25-μm film thickness) and a calibrated flame ionization detector (gc/fid) and are based upon 1,4-dicyanobenzene (**1**) as the limiting reagent. An HP 3392A integrator was interfaced with the gc/fid to obtain peak areas. An HP 5890 gas chromatograph with a 5% phenyl methyl silicone fused silica WCOT column (25 m × 0.20 mm, 0.33-μm film thickness) interfaced with an HP 5970 mass selective detector (gc/ms) was also used for product analyses. Mass spectra are reported as *m/z* (relative intensity). Separation of product mixtures was generally carried out using preparative medium-pressure liquid chromatography (mplc) (1*d*). The mplc consists of a 2.5 cm × 1 m column packed with thin-layer chromatography (tlc) grade silica gel (without binder) (Rose Scientific Ltd., Cat. 81632) at a pressure of 19 psi using helium (1 psi = 6.9 kPa). Connected to the mplc was a uv spectrophotometer – fraction collector that collects ca. 10-mL fractions. Dry column flash chromatography (dc/fc) was also used (19). The column was packed with thin-layer chromatography grade silica gel (without binder) (Rose Scientific Ltd., Cat. 81632). Fraction sizes were ca. 5 mL.

Materials

Acetonitrile (Fisher ACS grade) 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 (under nitrogen), and stored over molecular sieves (3 Å) (20). Methanol was distilled and then stored over molecular sieves (4 Å). 1,4-Dicyanobenzene (**1**) (Aldrich) was purified by treatment with Norite in methylene chloride, followed by recrystallization from 95% ethanol. Tetraethylammonium perchlorate (TEAP) (Aldrich) was recrystallized three times from water and then dried in a vacuum oven for 15 h, 70°C, 0.25 Torr (1 Torr = 133.3 Pa). 2,3-Dimethyl-2-butene, 98% (**2**), 2-methyl-2-butene, 99+% (**10**), 2-methyl-1,3-butadiene, 99% (**11**), 2,3-dimethyl-1,3-butadiene, 98% (**12**), 2,4-dimethyl-1,3-pentadiene, 98+% (**14**), 2,4-dimethyl-2,3-pentadiene, 97% (**15**), and 18-crown-6, 99% were obtained from the Aldrich Chemical Co. 2-Methylpropene (**9**) was obtained from Matheson and was of a minimum 99.0% purity. 4-Methyl-1,3-pentadiene, ≥98% (**13**) was obtained from Fluka Chemika-BioChemika. Biphenyl (**8**) (Eastman Kodak Co.) was recrystallized from methanol. Potassium cyanide was obtained from BDH, Inc.

Irradiations

Irradiations were generally carried out on acetonitrile solutions of the alkene or diene, 1,4-dicyanobenzene (**1**), biphenyl (**8**), potassium cyanide, and 18-crown-6 ether. Solutions were irradiated in either 2 cm i.d. Pyrex tubes or 5 mm Pyrex nmr tubes, which were degassed by nitrogen ebullition. These samples were irradiated at 10°C using a CGE 1-kW medium-pressure mercury vapour lamp contained in a water-cooled Pyrex immersion well.

Cyclic voltammetric measurements

Cyclic voltammetry was used to obtain the oxidation potential of the alkenes/ dienes. The apparatus has been described (21). The working electrode was a platinum sphere (1 mm diameter) and the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE), which was connected to the solution (TEAP 0.1 M, acetonitrile) through a Luggin capillary. The alkene/ diene concentration was ca. 0.005 M in acetonitrile. Since the anodic wave was irreversible, the half-wave potential was taken as 0.028 V before the anodic peak potential (8).

Formation of the cyanide anion, 2,3-dimethyl-2-butene (2), 1,4-dicyanobenzene (1) photo-NOCAS adducts 3 and 16: reaction [4]

A solution of 2,3-dimethyl-2-butene (**2**) (0.9 mL, 0.6 g, 0.0076 mol), 1,4-dicyanobenzene (**1**) (0.6 g, 0.0047 mol), biphenyl (**8**) (0.4 g, 0.0026 mol), potassium cyanide (0.3 g, 0.0046 mol), and 18-crown-6 (0.3 g, 0.0011 mol) in acetonitrile (40 mL) was degassed by nitrogen ebullition and irradiated for 43 h using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was partially separated by repetitive chromatography (mplc) using a linear solvent gradient (hexanes – 10% diethyl ether, 90% hexanes). Two 1:1:1 adducts were detected (gc/ms) and were eluted (mplc) in the order **16** followed by **3**. Purification of **16** required preparative thin-layer chromatography on silica gel, eluting repeatedly with 5% diethyl ether, 95% hexanes.

*3-(4-Cyanophenyl)-2,3-dimethylbutanenitrile (**3**)*

The yield of **3** was 15%. The gc/ms of this compound was identical to that reported (1*a*).

*3-(4-Cyanophenyl)-2,3-dimethyl-2-isocyanobutane (**16**)*

The yield of **16** was 5%; infrared (Nicolet 205) ν: 2989(s), 2951(m), 2923(s), 2852(m), 2229(s), 2131(s), 1682(m), 1607 (m), 1507(m), 1461(m), 1404(m), 1384(m), 1150(m), 1093(m), 1019(m), 843(m); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.34 (st, 6H, $^3J_{1-N}$ = 1.8 Hz, 2 CH_3's (1-H)), 1.52 (s, 6H, 2 CH_3's), 7.58 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.64 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 24.07 (q), 26.14 (q), 43.92 (s, quaternary carbon, aryl-substituted), 63.78 (st, quaternary carbon, isocyano substituted), 111.10 (s, quaternary aryl carbon, cyano substituted), 118.87 (s, CN), 129.13 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 131.67 (d, aromatic CH adjacent to cyano-substituted carbon), 149.40 (s, quaternary aryl carbon, alkyl substituted), 155.95 (st, $R\text{-}N\equiv C$); ms *m/z*: 51(7), 69(69), 76(5), 77(8), 89(10), 101(6), 102(6), 103(5), 104(17), 116(88), 117(10), 128(8), 130(7), 142(5), 144(100), 145(12), 170(6), 212(4). Exact Mass calcd. for $C_{14}H_{16}N_2$: 212.1313; found: 212.1326.

Irradiation of an acetonitrile solution of potassium cyanide, 2-methylpropene (9), 1,4-dicyanobenzene (1), and biphenyl (8)

A solution of 2-methylpropene (**9**) (0.054 g, 9.6 × 10^{-4} mol), 1,4-dicyanobenzene (**1**) (0.062 g, 4.8 × 10^{-4} mol), biphenyl (**8**) (0.040 g, 2.6 × 10^{-4} mol), potassium cyanide (0.030 g, 4.6 × 10^{-4} mol), and 18-crown-6 (0.025 g, 9.5 × 10^{-5} mol) in acetonitrile (4 mL) was degassed by nitrogen ebullition and irradiated for 16 h using a 1-kW lamp at 10°C. No photo-NOCAS products were detected (gc/ms, selective ion monitoring).

Formation of the cyanide anion, 2-methyl-2-butene (10), 1,4-dicyanobenzene (1) photo-NOCAS adducts 17, 18, 19, and 20: reaction [5]

A solution of 2-methyl-2-butene (**10**) (4.1 mL, 2.7 g, 0.038 mol), 1,4-dicyanobenzene (**1**) (2.5 g, 0.020 mol), biphenyl (**8**) (1.6 g, 0.010 mol), potassium cyanide (1.2 g, 0.018 mol), and 18-crown-6 (1.1 g, 0.0042 mol) in acetonitrile (160 mL) was degassed by nitrogen ebullition and irradiated for 24 h using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was separated by repetitive chromatography (mplc) using a linear solvent gradient (hexanes – 10% diethyl ether, 90% hexanes). Four 1:1:1 adducts were detected (gc/ms) and these products were eluted (mplc) in the order **20**, **19**, **18** followed by **17**. Purification of **20** required preparative thin-layer chromatography on silica gel, eluting repeatedly with 5% diethyl ether, 95% hexanes.

*3-(4-Cyanophenyl)-2,3-dimethylbutanenitrile (**17**)*

The yield of **17** was 9%: the melting point was 70–71°C; infrared (Nicolet 205) ν: 2979(s), 2947(m), 2885(w), 2228(s), 1608(m), 1507(m), 1468(m), 1459(m), 1454(m), 1406(m), 1383(m), 1087(m), 1018(w), 915(m), 840(s), 734(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.10 (d, 3H, $^3J_{1-2}$ = 7.3 Hz, CH_3 (1-H)), 1.52 (s, 6H, 2 CH_3's), 2.97 (q, 1H, $^3J_{1-2}$ = 7.3 Hz, H of methine group (2-H)), 7.52 (d, 2H, $^3J_{2'-3'}$ = 8.9 Hz, $^3J_{5'-6'}$ = 8.9 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.66 (d, 2H, $^3J_{2'-3'}$ = 8.9 Hz, $^3J_{5'-6'}$ = 8.9 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 13.69 (q), 23.78 (q), 27.29 (q), 37.61 (d, CH, cyano substituted), 40.27 (s, quaternary carbon, aryl substituted), 110.75 (s, quaternary aryl carbon, cyano substituted), 118.62 (s, CN), 121.38 (s, CN), 127.07 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.31 (d, aromatic CH adjacent to cyano-substituted carbon), 150.46 (s, quaternary aryl carbon, alkyl substituted); ms *m/z*: 51(7), 75(6), 77(7), 89(8), 101(5), 102(5), 104(13), 116(70), 117(7), 128(6), 144(100), 145(11). Anal. calcd. for $C_{13}H_{14}N_2$: C 78.75, H 7.12, N 14.13; found: C 78.77, H 7.06, N 14.01.

*3-(4-Cyanophenyl)-2,2-dimethylbutanenitrile (**18**)*

The yield of **18** was 2%; infrared (Nicolet 205) ν: 2980(s), 2928(m), 2894(w), 2879(w), 2230(s), 1607(m), 1505(m), 1461(s), 1417(m), 1383(m), 1053(w), 841(s) ; ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.18 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.50 (d, 3H, $^3J_{3-4}$ = 7.3 Hz, CH_3 (4-H)), 2.77 (q, 1H, $^3J_{3-4}$ = 7.3 Hz, H of methine group (3-H)), 7.43 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.64 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to cyano substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 16.89 (q), 25.55 (q), 26.08 (q), 37.06 (s, quaternary carbon, cyano substituted), 48.15 (d, CH, aryl-substituted), 111.42 (s, quaternary aryl carbon, cyano-substituted), 118.64 (s, CN), 123.69 (s, CN), 129.23 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.25 (d, aromatic CH adjacent to cyano-substituted carbon), 147.05 (s, quaternary aryl carbon, alkyl substituted); ms *m/z*: 51(7), 69(8), 77(12), 103(21), 104(8), 130(100), 131(11). Exact Mass calcd. for $C_{13}H_{14}N_2$: 198.1157; found: 198.1167.

*3-(4-Cyanophenyl)-3-methyl-2-isocyanobutane (**19**)*

The yield of **19** was 4%; infrared (Nicolet 205) ν: 2981(s), 2943(m), 2229(s), 2138(s), 1608(m), 1508 (m), 1473(m), 1467(m), 1453(m), 1405(m), 1380(m), 1112(w), 1094(m), 1064(w), 1031(w), 1018(w), 840(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.17 (dt, 3H, $^3J_{1-2}$ = 6.7 Hz, $^3J_{1-N}$ = 2.4 Hz, CH_3 (1-H)), 1.45 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 3.84 (qt, 1H, $^3J_{1-2}$ = 6.7 Hz, $^2J_{2-N}$ = 1.8 Hz, H of methine group (2-H)), 7.48 (d, 2H, $^3J_{2'-3'}$ = 9.2 Hz, $^3J_{5'-6'}$ = 9.2 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.66 (d, 2H, $^3J_{2'-3'}$ = 9.2 Hz, $^3J_{5'-6'}$ = 9.2 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 17.06 (q), 22.65 (q), 25.38 (q), 41.46 (s, quaternary carbon, aryl substituted), 59.65 (dt, CH, isocyano substituted), 110.84 (s, quaternary aryl carbon, cyano substituted), 118.59 (s, CN), 127.20 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.23 (d, aromatic CH adjacent to cyano-substituted carbon), 150.00 (s, quaternary aryl carbon, alkyl substituted), 156.48 (st, $R-N\equiv C$); ms *m/z*: 51(9), 52(4), 54(4), 55(18), 63(5), 75(6), 76(5), 77(8), 89(9), 101(5), 102(5), 103(4), 104(15), 116(77), 117(8), 128(6), 144(100), 145(11), 198(4). Exact Mass calcd. for $C_{13}H_{14}N_2$: 198.1157; found: 198.1152.

*3-(4-Cyanophenyl)-2-methyl-2-isocyanobutane (**20**)*

The yield of **20** was < 1%; infrared (Nicolet 205) ν: 2981(s), 2927(s), 2229(s), 2131(s), 1608(m), 1505(m), 1461(s), 1416(m), 1208(m), 1185(w), 1162(m), 1091(m), 1075(m), 1055(m), 1020(w), 856(w), 839(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.27 (t, 3H, $^3J_{1-N}$ = 1.8 Hz, CH_3 (1-H)), 1.46 (d, 3H, $^3J_{3-4}$ = 6.7 Hz, CH_3 (4-H)), 1.47 (t, 3H, $^3J_{1-N}$ = 1.8 Hz, CH_3 (1-H)), 2.84 (qt, 1H, $^3J_{3-4}$ = 6.7 Hz, $^3J_{3-N}$ = 2.4 Hz, H of methine group (3-H)), 7.41 (d, 2H, $^3J_{2'-3'}$ = 8.2 Hz, $^3J_{5'-6'}$ = 8.2 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.64 (d, 2H, $^3J_{2'-3'}$ = 8.2 Hz, $^3J_{5'-6'}$ = 8.2 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 15.97 (q), 28.19 (q), 28.45 (q), 48.90 (d, CH, aryl substituted), 60.49 (st, quaternary carbon, isocyano substituted), 111.64 (s, quaternary aryl carbon, cyano substituted), 118.85 (s, CN), 129.75 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.29 (d, aromatic CH adjacent to cyano-substituted carbon), 146.85 (s, quaternary aryl carbon, alkyl substituted); ms *m/z*: 51(10), 69(35), 77(19), 103(31), 104(12), 130(100), 131(16), 142(13), 183(13), 198(11). Exact Mass calcd. for $C_{13}H_{14}N_2$: 198.1157; found: 198.1155.

Formation of the cyanide anion, 2-methyl-1,3-butadiene (11), 1,4-dicyanobenzene (1) photo-NOCAS adducts 21 and 22: reaction [6]

A solution of 2-methyl-1,3-butadiene (**11**) (5.0 mL, 3.4 g, 0.050 mol), 1,4-dicyanobenzene (**1**) (3.1 g, 0.024 mol), biphenyl (**8**) (2.0 g, 0.013 mol), potassium cyanide (1.5 g, 0.023 mol), and 18-crown-6 (1.2 g, 0.0047 mol) in acetonitrile (200 mL) was degassed by nitrogen ebullition and irradiated for 7 days using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was separated by repetitive chromatography (mplc) using a linear solvent gradient (hexanes – 10% diethyl ether, 90% hexanes). Two 1:1:1 adducts were detected (gc/ms) and were eluted (mplc) in the order **21** followed by **22**.

*3-(4-Cyanophenyl)-3-methyl-4-pentenenitrile (**21**)*

The yield of **21** was 2%; infrared (Nicolet 205) ν: 3089(w), 2977(s), 2939(m), 2229(s), 1638(m), 1607(s), 1505(s), 1459(m), 1415(s), 1379(m), 1075(m), 1018(m), 1000(m), 929(s), 838(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.61 (s, 3H, CH_3), 2.77 (s, 2H, CH_2CN), 5.19 (d, 1H, $^3J_{4\text{-}5trans}$ = 17.4 Hz, vinyl H (5*trans*-H)), 5.34 (d, 1H, $^3J_{4\text{-}5cis}$ = 10.7 Hz, vinyl H (5*cis*-H)), 6.02 (dd, 1H, $^3J_{4\text{-}5trans}$ = 17.4 Hz, $^3J_{4\text{-}5cis}$ = 10.7 Hz, vinyl H (4-H)), 7.46 (d, 2H, $^3J_{2'-3'}$ = 8.6 Hz, $^3J_{5'-6'}$ = 8.6 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.66 (d, 2H, $^3J_{2'-3'}$ = 8.6 Hz, $^3J_{5'-6'}$ = 8.6 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 25.45 (q), 29.82 (t, CH_2, cyano substituted), 43.58 (s, quaternary carbon, aryl substituted), 111.04 (s, quaternary aryl carbon, cyano substituted), 115.34 (t, alkene CH_2), 117.18 (s, CN), 118.44 (s, CN), 127.20 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.52 (d, aromatic CH adjacent to cyano-substituted carbon), 141.93 (d, alkene CH), 148.94 (s, quaternary aryl carbon, alkyl substituted); ms *m/z*: 51(13), 52(4), 53(5), 62(3), 63(8), 64(4), 65(2), 74(3), 75(8), 76(8), 77(8), 78(2), 87(2), 88(2), 89(7), 90(2), 100(2), 101(6), 102(5), 103(3), 113(4), 114(4), 115(7), 116(25), 127(14), 128(14), 129(32), 130(4), 140(13), 141(7), 153(3), 154(12), 156(100), 157(11), 196(2). Exact Mass calcd. for $C_{13}H_{12}N_2$: 196.1000; found: 196.1023.

*3-(4-Cyanophenyl)-4-methyl-4-pentenenitrile (**22**)*

The yield of **23** was 1%; infrared (Nicolet 205) ν: 3088(w), 2971(s), 2925(s), 2855(w), 2229(s), 1720(m), 1650(m), 1608(s), 1505(s), 1430(m), 1414(s), 1378(m), 1291(w), 1279(w), 905(s), 835(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.61 (s, 3H, CH_3), 2.72 (dd, 1H, $^2J_{2-2'}$ = 16.7 Hz, $^3J_{2-3}$ = 7.0

Hz, H of methylene group (2-H)), 2.85 (dd, 1H, $^2J_{2-2'}$ = 16.7 Hz, $^3J_{2'-3}$ = 7.0 Hz, H of methylene group (2′-H)), 3.66 (dd, 1H, $^3J_{2-3}$ = 7.0 Hz, $^3J_{2'-3}$ = 8.2 Hz, H of methine group (3-H)), 4.99 (s, 1H, terminal vinyl H), 5.11 (s, 1H, terminal vinyl H), 7.36 (d, 2H, $^3J_{2'-3'}$ = 7.0 Hz, $^3J_{5'-6'}$ = 8.2 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.65 (d, 2H, $^3J_{2'-3'}$ = 8.2 Hz, $^3J_{5'-6'}$ = 8.2 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 21.59 (q), 22.43 (t, CH_2, cyano substituted), 48.55 (d, CH, aryl substituted), 112.10 (s, quaternary aryl carbon, cyano substituted), 113.21 (t, alkene CH_2), 117.83 (s, CN), 118.95 (s, CN), 128.49 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.76 (d, aromatic CH adjacent to cyano-substituted carbon), 143.18 (s), 145.06 (s); ms *m/z*: 51(16), 52(7), 53(7), 62(6), 63(15), 64(7), 74(5), 75(14), 76(12), 77(12), 88(4), 89(12), 101(12), 102(12), 103(6), 113(6), 114(7), 115(7), 116(31), 127(18), 128(26), 129(60), 130(8), 140(16), 141(12), 153(8), 154(23), 155(29), 156(100), 157(12), 169(8), 179(8), 196(4). Exact Mass calcd. for $C_{13}H_{12}N_2$: 196.1000; found: 196.0998.

Formation of the cyanide anion, 2,3-dimethyl-1,3-butadiene (12), 1,4-dicyanobenzene (1) photo-NOCAS adducts 23 and 24: reaction [7]

A solution of 2,3-dimethyl-1,3-butadiene (**12**) (6.0 mL, 4.4 g, 0.053 mol), 1,4-dicyanobenzene (**1**) (3.1 g, 0.024 mol), biphenyl (**8**) (2.0 g, 0.013 mol), potassium cyanide (2.0 g, 0.031 mol), and 18-crown-6 (1.2 g, 0.0047 mol) in acetonitrile (200 mL) was degassed by nitrogen ebullition and irradiated for 7 days using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was separated by repetitive chromatography (mplc) using a linear solvent gradient (hexanes – 10% diethyl ether, 90% hexanes). Two 1:1:1 adducts were detected (gc/ms) and these products eluted (mplc) in the order **23** followed by **24**.

3-(4-Cyanophenyl)-3,4-dimethyl-4-pentenenitrile (23)

The yield of **23** was 7%; infrared (Nicolet 205) *ν*: 3092(w), 2976(s), 2952(m), 2926(m), 2887(w), 2229(s), 1642(m), 1607(s), 1505(s), 1451(m), 1431(m), 1406(m), 1382(m), 1072(w), 1019(w), 909(s), 842(s), 734(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.55 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 2.84 (AB apparent singlet, 2H, CH_2CN), 5.07 (s, 1H, terminal vinyl H), 5.15 (s, 1H, terminal vinyl H), 7.43 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.66 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 19.98 (q), 24.79 (q), 29.83 (t, CH_2, cyano substituted), 46.35 (s, quaternary carbon, aryl substituted), 111.25 (s, quaternary aryl carbon, cyano substituted), 113.06 (t, alkene CH_2), 117.49 (s, CN), 118.52 (s, CN), 127.11 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.54 (d, aromatic CH adjacent to cyano-substituted carbon), 147.00 (s), 148.84 (s); ms *m/z*: 51(24), 75(18), 77(19), 115(26), 116(39), 127(22), 128(29), 140(23), 142(71), 143(35), 153(24), 154(35), 155(21), 167(21), 168(33), 169(69), 170(100). Exact Mass calcd. for $C_{14}H_{14}N_2$: 210.1157; found: 210.1155.

(E)-5-(4-Cyanophenyl)-3,4-dimethyl-2-pentenenitrile (24)

The yield of **24** was 2%; infrared (Nicolet 205) *ν*: 2971(m), 2933(m), 2876(w), 2253(w), 2228(s), 2219(s), 1627(m), 1608(m), 1505(m), 1459(m), 1440(m), 1415(m), 1380(m), 913(s), 846(m), 822(m), 734(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.08 (d, 3H, $^3J_{4-7}$ = 6.7 Hz, CH_3 (7-H)), 2.06 (s, 3H, CH_3), 2.62 (m, 1H, $^3J_{4-7}$ = 6.7 Hz, $^3J_{4-5}$ = 6.1 Hz, $^3J_{4-5'}$ = 6.1 Hz, H of methine group (4-H)), 2.69 (m, 1H, $^2J_{5-5'}$ = 12.9 Hz, $^3J_{4-5}$ = 6.1 Hz, H of methylene group, aryl substituted (5-H)), 2.82 (m, 1H, $^2J_{5-5'}$ = 12.9 Hz, $^3J_{4-5'}$ = 6.1 Hz, H of methylene group, aryl substituted (5′-H)), 5.05 (s, 1H, vinyl H), 7.22 (d, 2H, $^3J_{2'-3'}$ = 8.6 Hz, $^3J_{5'-6'}$ = 8.6 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.60 (d, 2H, $^3J_{2'-3'}$ = 8.6 Hz, $^3J_{5'-6'}$ = 8.6 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)). The nOe experiment (400 MHz): the methyl group bonded to the alkene was irradiated; a small enhancement was observed for the methine and methylene H's (ABC splitting pattern) and the *ortho*-aryl H's were enhanced. The irradiation of the vinyl H showed a large methine and methylene H (ABC splitting pattern) enhancement and the *ortho*- and *meta*-aryl H's were enhanced; ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 18.34 (q), 18.47 (q), 41.21 (t, CH_2, aryl substituted), 43.67 (d), 95.89 (d, alkene CH), 110.58 (s, quaternary aryl carbon, cyano substituted), 116.84 (s, CN), 118.74 (s, CN), 129.61 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.34 (d, aromatic CH adjacent to cyano-substituted carbon), 144.71 (s, quaternary aryl carbon, alkyl substituted), 167.39 (s, alkene quaternary carbon); ms *m/z*: 51(5), 63(8), 65(5), 67(11), 89(22), 90(7), 94(13), 116(100), 117(36), 210(10). Exact Mass calcd. for $C_{14}H_{14}N_2$: 210.1157; found: 210.1150.

Formation of the cyanide anion, 4-methyl-1,3-pentadiene (13), 1,4-dicyanobenzene (1) photo-NOCAS adducts 25 and 26: reaction [8]

A solution of 4-methyl-1,3-pentadiene (**13**) (1.1 mL, 0.79 g, 0.0096 mol), 1,4-dicyanobenzene (**1**) (1.2 g, 0.0094 mol), biphenyl (**8**) (0.8 g, 0.0052 mol), potassium cyanide (0.6 g, 0.0092 mol), and 18-crown-6 (0.5 g, 0.0019 mol) in acetonitrile (80 mL) was degassed by nitrogen ebullition and irradiated for 21 h using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was separated by repetitive chromatography (mplc) using a linear solvent gradient (hexanes – 20% diethyl ether, 80% hexanes). Two 1:1:1 adducts were detected (gc/ms) and these products eluted (mplc) in the order **25** followed by **26**.

3-(4-Cyanophenyl)-5-methyl-4-hexenenitrile (25)

The yield of **25** was 14%; infrared (Nicolet 510) *ν*: 2974(s), 2926(s), 2863(m), 2230(s), 1676(m), 1614(s), 1504(s), 1451(m), 1428(s), 1380(m), 840(s), 734(m); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.69 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 2.66 (dd, 1H, $^2J_{2-2'}$ = 16.7 Hz, $^3J_{2-3}$ = 7.1 Hz, H of methylene group, cyano substituted (2-H)), 2.70 (dd, 1H, $^2J_{2-2'}$ = 16.7 Hz, $^3J_{2'-3}$ = 6.9 Hz, H of methylene group, cyano substituted (2′-H)), 3.97 (m, 1H, $^3J_{3-4}$ = 9.3 Hz, $^3J_{2-3}$ = 7.1 Hz, $^3J_{2'-3}$ = 6.9 Hz, H of methine group, aryl substituted (3-H)), 5.35 (d, 1H, $^3J_{3-4}$ = 9.3 Hz, vinyl H (4-H)), 7.38 (d, 2H, $^3J_{2'-3'}$ = 8.3 Hz, $^3J_{5'-6'}$ = 8.3 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.63 (d, 2H, $^3J_{2'-3'}$ = 8.3 Hz, $^3J_{5'-6'}$ = 8.3 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 18.36 (q), 24.90 (t, CH_2, cyano substituted), 25.82 (q), 40.56 (d, CH, aryl substituted), 111.10 (s, quaternary aryl carbon, cyano substituted), 117.92 (s, CN), 118.64 (s, CN), 123.08 (d, alkene CH), 128.00 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.72 (d, aromatic CH adjacent to cyano-substituted carbon), 136.94 (s, alkene quaternary carbon), 147.40 (s, aromatic quaternary carbon); ms *m/z*: 51(9), 63(5), 75(5), 76(4), 77(5), 89(6), 101(5), 102(4), 115(9), 116(17), 127(11), 128(11), 129(5), 130(5), 140(9), 141(4), 142(36), 143(11), 153(11), 154(11), 155(9), 168(9), 170(100), 171(14). Anal. calcd. for $C_{14}H_{14}N_2$: C 79.96, H 6.71, N 13.32; found: C 80.23, H 6.83, N 13.17.

*(E)-5-(4-Cyanophenyl)-2,2-dimethyl-3-pentenenitrile (**26**)*
The yield of **26** was 1%; infrared (Nicolet 205) ν: 2978(m), 2919(s), 2850(m), 2227(s), 1605(s), 1504(m), 1467(m), 1413(m), 1392(m), 1371(m), 1177(m), 973(s), 856(m), 808(m); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.41 (s, 6H, 2 CH_3's), 2.47 (d, 2H, $^3J_{4-5}$ = 6.7 Hz, CH_2, aryl substituted (5-H)), 6.40 (dt, 1H, $^3J_{3-4}$ = 15.9 Hz, $^3J_{4-5}$ = 6.7 Hz, vinyl H (4-H)), 6.55 (d, 1H, $^3J_{3-4}$ = 15.9 Hz, vinyl H (3-H)), 7.47 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.61 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 26.46 (q, 2 CH_3's), 32.65 (s, quaternary carbon, cyano-substituted), 44.32 (t, CH_2, aryl substituted), 111.00 (s, quaternary aryl carbon, cyano substituted), 118.91 (s, CN), 124.44 (s, CN), 126.87 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 127.87 (d, alkene CH), 132.48 (d, aromatic CH adjacent to cyano-substituted carbon), 133.31 (d, alkene CH), 141.04 (s, aromatic quaternary carbon); ms *m/z*: 51(4), 52(3), 63(5), 75(3), 76(3), 89(8), 113(3), 114(4), 115(31), 116(18), 140(15), 142(100), 143(11), 210(5). Exact Mass calcd. for $C_{14}H_{14}N_2$: 210.1157; found: 210.1153.

Formation of the cyanide anion, 2,4-dimethyl-1,3-pentadiene (14), 1,4-dicyanobenzene (1) photo-NOCAS adducts 27, 28, and 29: reaction [9]

A solution of 2,4-dimethyl-1,3-pentadiene (**14**) (3.0 mL, 2.2 g, 0.023 mol), 1,4-dicyanobenzene (**1**) (1.9 g, 0.015 mol), biphenyl (**8**) (1.2 g, 0.0078 mol), potassium cyanide (0.9 g, 0.014 mol), and 18-crown-6 (0.8 g, 0.0030 mol) in acetonitrile (120 mL) was degassed by nitrogen ebullition and irradiated for 55 h using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was separated by repetitive chromatography (mplc) using a linear solvent gradient (hexanes – 10% diethyl ether, 90% hexanes). Three 1:1:1 adducts were detected (gc/ms) and these products eluted (mplc) in the order **28**, **29**, then **27**.

*3-(4-Cyanophenyl)-3,5-dimethyl-4-hexenenitrile (**27**)*
The yield of **27** was 17%; infrared (Nicolet 205) ν: 2972(s), 2934(m), 2917(m), 2880(m), 2228(s), 1607(m), 1503(m), 1449(m), 1424(m), 1409(m), 1385(m), 1067(m), 839(s), 813(m), 737(m); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.14 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.68 (AB apparent singlet, 2H, CH_2CN), 5.54 (br s, 1H, vinyl H), 7.52 (d, 2H, $^3J_{2'-3'}$ = 8.6 Hz, $^3J_{5'-6'}$ = 8.6 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.64 (d, 2H, $^3J_{2'-3'}$ = 8.6 Hz, $^3J_{5'-6'}$ = 8.6 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 19.62 (q), 26.79 (q), 27.08 (q), 33.44 (t, CH_2, cyano substituted), 41.90 (s, quaternary carbon, aryl substituted), 110.60 (s, quaternary aryl carbon, cyano substituted), 117.63 (s, CN), 118.71 (s, CN), 127.31 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 129.15 (d, alkene CH), 132.42 (d, aromatic CH adjacent to cyano-substituted carbon), 137.27 (s, alkene quaternary carbon), 151.53 (s, aromatic quaternary carbon); ms *m/z*: 51(7), 77(7), 115(8), 116(11), 127(8), 130(9), 140(9), 142(100), 143(12), 153(7), 154(10), 156(8), 168(11), 184(57), 185(8). Exact Mass calcd. for $C_{15}H_{16}N_2$: 224.1313; found: 224.1308.

*4-(4-Cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile (**28**)*
The yield of **28** was 2%; infrared (Nicolet 205) ν: 2975(s), 2934(m), 2929(m), 2922(m), 2229(s), 2206(s), 1608(s), 1504(s), 1467(m), 1444(m), 1405(m), 1381(m), 1375(m), 1100(m), 1058(m), 1019(m), 840(s); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.31 (s, 3H, CH_3), 1.58 (s, 6H, 2 CH_3's), 2.11 (s, 3H, CH_3), 7.41 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.61 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 22.26 (q), 26.40 (q), 30.66 (q, 2 CH_3's), 41.08 (s, quaternary carbon, aryl substituted), 110.14 (s, quaternary aryl carbon, cyano substituted), 118.26 (s), 118.32 (s), 118.71 (s), 126.43 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.55 (d, aromatic CH adjacent to cyano-substituted carbon), 154.57 (s), 155.69 (s); ms *m/z*: 51(15), 53(12), 77(15), 89(10), 104(10), 116(51), 140(14), 144(61), 154(15), 166(10), 167(15), 168(19), 169(12), 182(43), 183(11), 194(11), 209(100), 210(15), 223(11), 224(21). X-ray data: see footnote 3.

*(Z)-5-(4-Cyanophenyl)-3,5-dimethyl-2-hexenenitrile (**29**)*
The yield of **29** was 2%; melting point 105–106°C; infrared (Nicolet 205) ν: 3045(w), 2973(s), 2942(m), 2881(m), 2223(s), 2212(s), 1618(s), 1502(s), 1470(m), 1440(s), 1404(m), 1372(m), 1316(m), 1230(m), 1184(m), 1096(m), 1016(m), 835(s), 815(m); ^{1}H nmr (250.13 MHz, $CDCl_3$) δ_{TMS}: 1.39 (s, 3H, CH_3), 1.46 (s, 6H, 2 CH_3's), 2.79 (s, 2H, CH_2), 5.17 (br s, 1H, vinyl H), 7.52 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to alkyl-substituted aryl carbon (2′-H, 6′-H)), 7.64 (d, 2H, $^3J_{2'-3'}$ = 8.5 Hz, $^3J_{5'-6'}$ = 8.5 Hz, H's adjacent to cyano-substituted aryl carbon (3′-H, 5′-H)); ^{13}C nmr (62.90 MHz, $CDCl_3$) δ: 24.76 (q), 28.88 (q, 2 CH_3's), 39.48 (s, quaternary carbon, aryl substituted), 50.19 (t), 99.24 (d, alkene CH), 110.18 (s, quaternary aryl carbon, cyano substituted), 117.21 (s, CN), 118.79 (s, CN), 126.81 (d, aromatic CH adjacent to alkyl-substituted aryl carbon), 132.20 (d, aromatic CH adjacent to cyano-substituted carbon), 153.76 (s, quaternary aryl carbon, alkyl substituted), 162.15 (s, alkene quaternary carbon); ms *m/z*: 51(6), 52(3), 53(9), 63(3), 75(4), 76(4), 77(7), 81(3), 89(7), 101(4), 102(4), 104(13), 116(66), 117(7), 128(4), 144(100), 145(11). X-ray data: see footnote 3.

Formation of the cyanide anion, 2,4-dimethyl-2,3-pentadiene (15), 1,4-dicyanobenzene (1) photo-NOCAS adduct 28: reaction [10]

A solution of 2,4-dimethyl-2,3-pentadiene (**15**) (1.0 mL, 0.7 g, 0.0073 mol), 1,4-dicyanobenzene (**1**) (0.6 g, 0.0048 mol), biphenyl (**8**) (0.4 g, 0.0026 mol), potassium cyanide (0.3 g, 0.0046 mol), and 18-crown-6 (0.3 g, 0.0011 mol) in acetonitrile (40 mL) was degassed by nitrogen ebullition and irradiated for 48 h using a 1-kW lamp at 10°C. The solvent was removed to yield a crude photolysate. The crude photolysate was separated by repetitive chromatography (dc/fc) using a linear solvent gradient (hexanes – 20% diethyl ether, 80% hexanes). One 1:1:1 adduct, 4-(4-cyanophenyl)-2,4-dimethyl-2-pentene-3-nitrile (**28**), was detected (gc/ms); the yield was 22%. The retention time and gc/ms of this compound were identical to the product obtained from **14** (reaction [9]).

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References

1. (*a*) R.M. Borg, D.R. Arnold, and T.S. Cameron. Can. J. Chem. **62**, 1785 (1984); (*b*) K.A. McManus and D.R. Arnold. Can. J. Chem. **72**, 2291 (1994); (*c*) A.J. Maroulis, Y. Shigemitsu, and D.R. Arnold. J. Am. Chem. Soc. **100**, 535 (1978); (*d*) D.R. Arnold and M.S. Snow. Can. J. Chem. **66**, 3012 (1988); (*e*) K.A. McManus and D.R. Arnold. Can. J. Chem. **73**, 2158 (1995); (*f*) D.R. Arnold, X. Du, and H.J.P. de Lijser. Can. J. Chem. **73**, 522 (1995); (*g*) D.A. Connor, D.R. Arnold, P.K. Bakshi, and T.S. Cameron. Can. J. Chem. **73**, 762 (1995); (*h*) D.R. Arnold, D.A. Connor, K.A. McManus, P.K. Bakshi, and T.S. Cameron. Can. J. Chem. **74**, 602 (1996); (*i*) D.R. Arnold, M.S.W. Chan, and K.A. McManus. Can. J. Chem. **74**, 2143 (1996); (*j*) D.R. Arnold, P.C. Wong, A.J. Maroulis, and T.S. Cameron. Pure Appl. Chem. **52**, 2609 (1980).
2. (*a*) D.R. Arnold and A.J. Maroulis. J. Am. Chem. Soc. **98**, 5931 (1976); (*b*) A.L. Perrott and D.R. Arnold. Can. J. Chem. **70**, 272 (1992); (*c*) D.R. Arnold, X. Du, and J. Chen. Can. J. Chem. **73**, 307 (1995); (*d*) H.J.P. de Lijser and D.R. Arnold. J. Phys. Chem. **100**, 3996 (1996).
3. (*a*) L.J. Johnston and N.P. Schepp. J. Am. Chem. Soc. **115**, 6564 (1993); (*b*) Pure Appl. Chem. **67**, 71 (1995).
4. (*a*) R.G. Pearson and J. Songstad. J. Am. Chem. Soc. **89**, 1827 (1967); (*b*) R.G. Pearson, H. Sobel, and J. Songstad. J. Am. Chem. Soc. **90**, 319 (1968); (*c*) P.L. Bock and G.M. Whitesides. J. Am. Chem. Soc. **96**, 2826 (1974); (*d*) T.-L. Ho. Chem. Rev. **75**, 1 (1975).
5. M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzales, R.L. Martin, D.J. Fox, D.J. Defrees, J. Baker, J.J.P. Stewart, and J.A. Pople. Gaussian 92/DFT, Revision F.2. Gaussian, Inc., Pittsburgh, Pa. 1993.
6. (*a*) C. Møller and M.S. Plesset. Phys. Rev. **46**, 618 (1934); (*b*) W.J. Hehre, L. Radom, P.v.R. Schelyer, and J.A. Pople. *Ab initio* molecular orbital theory. Wiley–Interscience, New York, 1987; (*c*) R.S. Mulliken. J. Chem. Phys. **23**, 1983 (1955); (*d*) A.E. Reed, R.B. Weinstock, and F. Weinhold. J. Chem. Phys. **83**, 735 (1985).
7. R.M. Silverstein, G.C. Bassler, and T.C. Morrill. Spectrometric identification of organic compounds. 5th ed. John Wiley & Sons, Inc., Toronto. 1991.
8. (*a*) R.S. Nicholson and I. Shain. Anal. Chem. **36**, 706 (1964); (*b*) Anal. Chem. **37**, 178 (1965).
9. (*a*) S. Andreades and E.W. Zahnow. J. Am. Chem. Soc. **91**, 4181 (1969); (*b*) J.F. Evans and H.N. Blount. J. Am. Chem. Soc. **100**, 4191 (1978); (*c*) R.G. Pearson. J. Am. Chem. Soc. **108**, 6109 (1986); (*d*) J.-M. Savéant. J. Phys. Chem. **98**, 3716 (1994).
10. (*a*) K. Yoshida and T. Fueno. J. Org. Chem. **36**, 1523 (1971); (*b*) K. Yoshida. J. Am. Chem. Soc. **101**, 2116 (1979); (*c*) K. Yoshida, T. Kanbe, and T. Fueno. J. Org. Chem. **42**, 2313 (1977); (*d*) K. Yoshida and S. Nagase. J. Am. Chem. Soc. **101**, 4268 (1979); (*e*) K. Koyama, T. Susuki, and S. Tsutsumi. Tetrahedron, **23**, 2675 (1967); (*f*) V.D. Parker and B.E. Burgert. Tetrahedron Lett. 4065 (1965).
11. (*a*) L. Herbert, I.W.M. Smith, and R.D. Spencer-Smith. Int. J. Chem. Kinet. **24**, 791 (1992); (*b*) D.L. Yang, T. Yu, N.S. Wang, and M.C. Lin. Chem. Phys. **160**, 317 (1992); (*c*) G.E. Bullock and R. Cooper. Trans. Faraday Soc. **67**, 3258 (1971).
12. (*a*) J.M. Tedder. Angew. Chem. Int. Ed. Engl. **21**, 401 (1982); (*b*) B. Giese. Angew. Chem. Int. Ed. Engl. **22**, 753 (1983); (*c*) K.N. Houk, M.N. Paddon-Row, D.C. Spellmeyer, N.G. Rondan, and S. Nagase. J. Org. Chem. **51**, 2874 (1986).
13. (*a*) M.W. Klett and R.P. Johnson. Tetrahedron Lett. 1107 (1983); (*b*) K. Somekawa, K. Haddaway, P.S. Mariano, and J.A. Tossell. J. Am. Chem. Soc. **106**, 3060 (1984).
14. (*a*) X.-Z. Qin and A.D. Trifunac. J. Phys. Chem. **95**, 6466 (1991); (*b*) Y. Kubozono, H. Ujita, M. Okada, M. Ata, Y. Matsuda, and Y. Gondo. Bull. Chem. Soc. Jpn. **65**, 2442 (1992).
15. (*a*) S.W. Benson. Thermochemical kinetics. 2nd ed. Wiley-Interscience, New York 1976; (*b*) H.E. O'Neal and S.W. Benson. Thermochemistry of free radicals. *In* Free radicals. Vol. II. *Edited by* J.K. Kochi. Wiley–Interscience, New York. 1973. Chap.17; (*c*) N. Cohen and S.W. Benson. Chem. Rev. **93**, 2419 (1993); (*d*) T. Ni, R.A. Caldwell, and L.A. Melton. J. Am. Chem. Soc. **111**, 457 (1989).
16. D.R. Lide (*Editor*). Handbook of chemistry and physics. 76th ed. (1995–1996). CRC Press, Inc., New York. 1995.
17. (*a*) D.D. Tanner, H. Yabuuchi, and E.V. Blackburn. J. Am. Chem. Soc. **93**, 4802 (1971); (*b*) P.S. Skell and K.J. Shea. *In* Free radicals. Vol. II. *Edited by* J.K. Kochi. Wiley–Interscience, New York. 1973. Chap. 26; (*c*) H.L. Goering, P.I. Abell, and B.F. Aycock. J. Am. Chem. Soc. **74**, 3588 (1952); (*d*) P.J. Krusic and J.K. Kochi. J. Am. Chem. Soc. **93**, 846 (1971); (*e*) D.A. Lindsay, J. Lusztyk, and K.U. Ingold. J. Am. Chem. Soc. **106**, 7087 (1984); (*f*) J.J. Russell, H.S. Rzepa, and D.A. Widdowson. J. Chem. Soc. Chem Commun. 625 (1983).
18. M. Meier, B. Dogan, H.-D. Beckhaus, and C. Rüchardt. New J. Chem. **11**, 1 (1987).
19. L.M. Harwood. Aldrichimica Acta, **18**, 25 (1985).
20. A. Okamoto, M.S. Snow, and D.R. Arnold. Tetrahedron, **42**, 6175 (1986).
21. D.R. Arnold and D.D.M. Wayner. Can. J. Chem. **64**, 100 (1986).