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2-Cyano-*iso*-propyl Radical Addition to Alkynes

Pier Carlo Montevecchi*, Maria Luisa Navacchia, Piero Spagnolo

Dipartimento di Chimica Organica "A. Mangini", Università di Bologna,
Viale Risorgimento 4. I-40136 Bologna, Italy

Abstract. The thermolysis of azobis*iso*butyronitrile (AIBN) in benzene in the presence of various mono- and di-substituted acetylenes has been investigated in order to ascertain the chemical reactivity of transient 2-cyano-*iso*propyl radical (CPR) towards carbon-carbon triple bonds. Results show that this rather sluggish and bulky carbon centered radical successfully adds in a regioselective fashion to alkynes bearing an electron acceptor phenyl, methoxycarbonyl and trimethylsilyl substituent, but fails with alkylacetylenes and those sterically hindered. The produced vinyl radicals undergo H-abstraction reaction, alkyne addition, aromatic addition and intramolecular cyclization in a relative proportion strongly dependent upon the nature of both 1- and 2-substituent. Two unprecedented examples of 4-*exo* and 6-*exo* vinyl radical cyclization onto the cyano triple bond are reported.

Though azobis*iso*butyronitrile (AIBN)[1] has been widely employed as initiator in radical additions of silyl, stannyl, and sulfanyl radicals to alkynes[2] no data seems to be available about competitive additions of transient 2-cyano-*iso*-propyl radical (CPR) to carbon-carbon triple bonds. However, during a recent study on the AIBN-promoted ethanesulfanyl radical addition to alkynes, we found some evidence for competing attack of CPR to phenylacetylene.[3] Moreover, Tundo, Nanni *et al.* have recently reported a study on the annulation reaction of isonitriles with vinyl radicals generated by 2-cyano-*iso*-propyl radical addition to phenylacetylene.[4]

Actually, the carbon-centered radical additions to alkynes have been scarcely investigated. The available data are mainly confined to those of trichloromethyl[5] and trifluoromethyl[6] radicals as well as to those of various alkyl radicals to electron-poor alkynes.[7] Additionally, alkyl radicals, generated from corresponding alkyl iodides by photolysis[8] or by the triethyl borane method,[9] have been shown to add to alkynes (including EWG-substituted alkynes, phenylacetylene and alkylacetylenes) to give iodoalkenes through iodine abstraction by the ensuing vinyl radicals.

Therefore, we have been prompted to investigate the reaction of AIBN with a number of simple alkynes, including phenylacetylene, phenylpropyne, methyl propiolate, trimethylsilylacetylene, phenyltrimethylsilylacetylene, diphenyl acetylene, 1-hexyne and 3-hexyne. Our aim was to explore the chemical reactivity of CPR towards carbon-carbon triple bonds as well as the fate of possible 2-(2-cyano-*iso*-propyl)vinyl radical adducts. In fact, for several years we have been interested in the chemistry of vinyl radicals, which have been largely studied both from a mechanistic standpoint and as synthetic intermediates in annulation and cyclization reactions.[10]

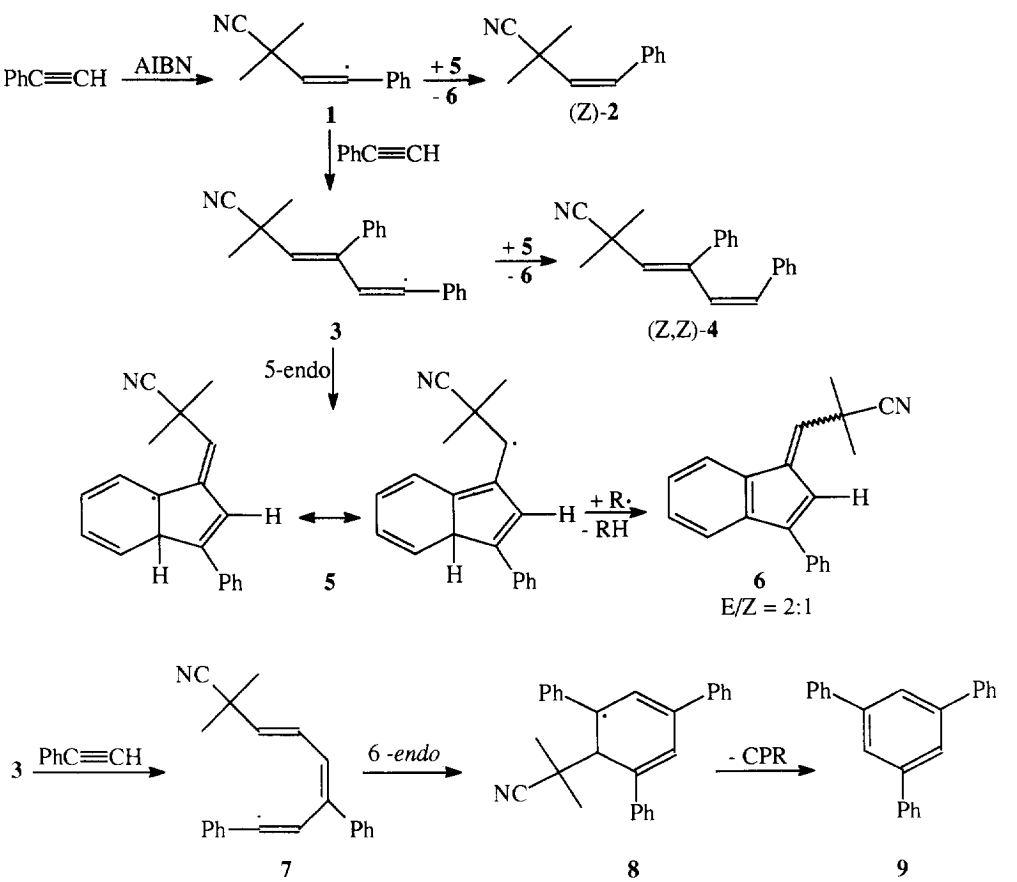
RESULTS AND DISCUSSION

Reactions were normally carried out by treating AIBN with a 2.5-fold excess of the appropriate alkyne in a boiling benzene solution for 4 h. In all cases the reaction mixtures were analyzed by GC-MS and

chromatographed on silica gel column. Reaction products were identified by MS and ^{1}H NMR spectroscopic analysis. Dimerization products of 2-cyano-*iso*-propyl radicals,[1] identified by GC-MS and ^{1}H NMR comparison with authentic specimens obtained from a blank reaction, were not taken into account.

The reaction of AIBN with phenylacetylene gave an inseparable mixture of alkene adduct (Z)-**2** and diene adduct (Z,Z)-**4**, in 60:40 ratio and 24% yield, the indene **6** (22%), as a 2:1 mixture of the (E) and (Z) isomers, along with little amounts (ca. 1%) of triphenylbenzene **9**. The formation of products **2, 4, 6** and **9** is rationalized as depicted in Scheme 1. CPR addition to the alkyne triple bond gives the vinyl radical **1**, which undergoes hydrogen abstraction, to afford the adduct **2**, and addition to a further alkyne molecule leading to vinyl radical **3**. This intermediate **3** in turn exhibits three different reactions: hydrogen abstraction to afford the diene **4**; 5-membered *ortho* cyclization onto the adjacent phenyl ring to give the indene **6**; and addition to another alkyne unit to give the vinyl radical **7**, from which triphenylbenzene **9** would arise through 6-*endo* cyclization and subsequent elimination of CPR from the resulting cyclohexadienyl radical **8**.

Scheme 1

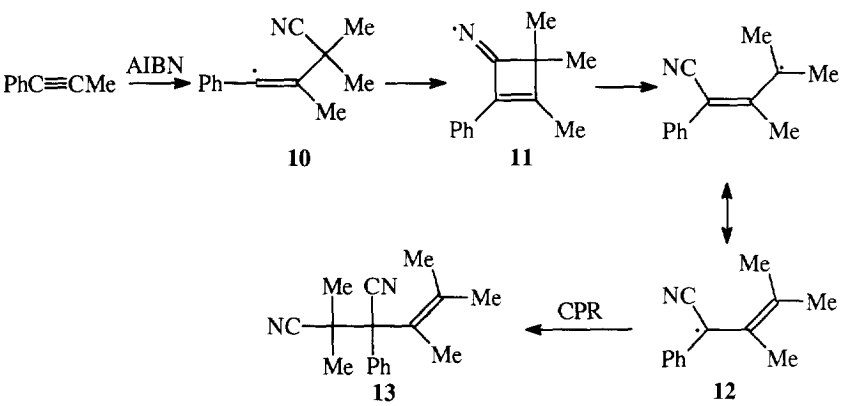


In line with previous evidence[10,11] that the linear sp-hybridized 1-phenylvinyl radicals are preferentially intercepted by radical scavengers on the less hindered side, the intermediates **1** and **3** underwent highly stereoselective trapping by alkyne and/or H-donor to give exclusively the adducts Z-**2** and (Z,Z)-**4**. Moreover,

consistent with earlier data that 5-membered *ortho* cyclization is stereoelectronically feasible for 1-phenylvinyl radicals, [3,11] the radical **3** displayed intramolecular attack onto the adjacent phenyl group to give the cyclized radical **5** and thence indene **6** upon subsequent aromatization. As mentioned above, the radical **3** was seemingly involved also in the observed minute formation of triphenylbenzene **9**. However, we have no explanation of the reason why **3** would afford the triphenylbenzene radical precursor **7** in the required (Z,E) configuration rather than in the (expected) (Z,Z) one.

Upon reaction with phenylpropyne AIBN only furnished the alkene adduct **13** in rather small isolated yield (12%). As shown in Scheme 2, compound **13** was probably produced through initial 4-*exo* attack of transient vinyl radical **10** onto the cyano moiety forming the iminyl radical **11**. Subsequent ring opening of **11** with β-scission of the C-CMe_2 bond would afford the resonance-stabilized species **12** and thence **13** by eventual trapping by CPR. In sharp contrast with the vinyl radical **1**, the homologue **10** provided no evidence for any intermolecular reaction. This fact is in line with our previous observation[3] that replacement of β-hydrogen with β-methyl group greatly enhances the intramolecular reactivity of 2-substituted 1-phenylvinyl radicals. The postulated mechanistic route to **13** is noteworthy since it could provide an unprecedented instance of intramolecular vinyl radical cyclization onto a cyano group[12] that would occur in unusual 4-*exo* mode[13,14] and result in novel radical 1,3-migration.

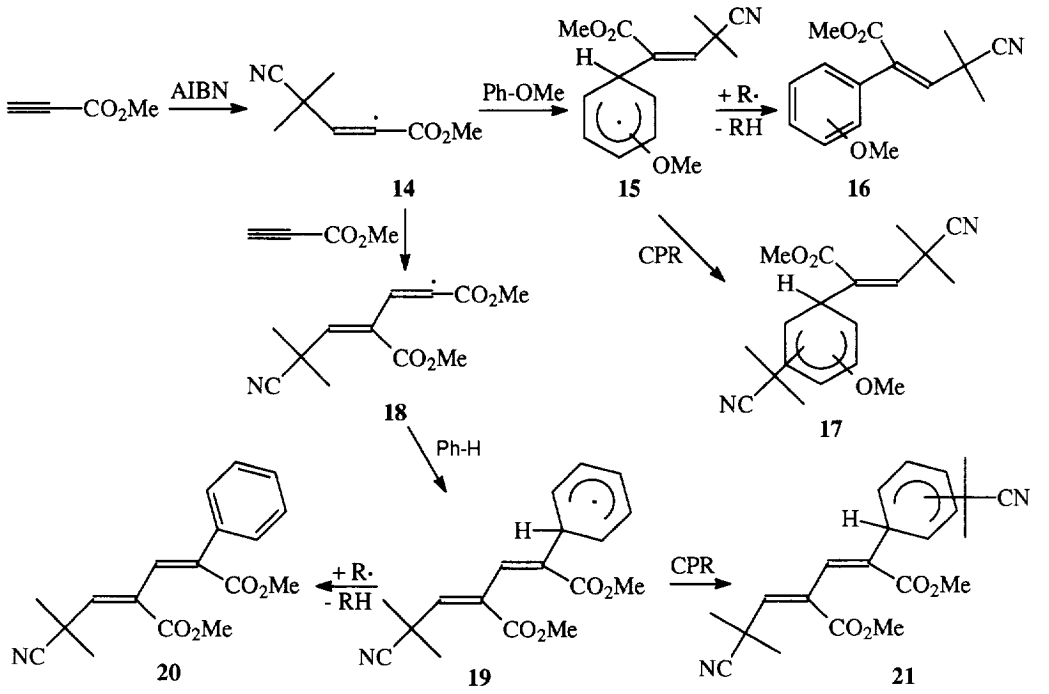
Scheme 2



In the presence of methyl propiolate AIBN led to a complex product mixture, from which chromatography separated little amounts (4%) of the phenyl-substituted (Z,Z)-diene **20** along with major amounts (10%) of an inseparable mixture of undetermined cyclohexadiene adducts **21** (Scheme 3). In such case the intially-formed 2-H-substituted 1-methoxycarbonylvinylic radical **14** was evidently capable to undergo intermolecular addition to its alkyne precursor. The derived radical **18** instead preferred to display homolytic addition on the benzene solvent forming the cyclohexadienyl intermediate **19** and then the final products **20** and **21** through subsequent aromatization and competing interception by CPR (Scheme 3). Interestingly, when the same reaction was performed in activated anisole solvent, the original radical **14** similarly added to the aromatic solvent leading, through resulting cyclohexadienyl intermediates **15**, to *ortho*-, *meta*- and *para*-methoxy-substituted (Z)-styrenes **16** (in ca. 70:5:25 ratio respectively and 10% overall yield) accompanied to a major extent (30%) by a complex mixture of possible cyclohexadiene compounds **17** (Scheme 3). Structural and (Z)-configurational assignment to the *ortho*-isomer, *ortho*-**16**, could be established through MS and ^{1}H NMR analysis (including n.O.e experiments) of a pure sample which was successfully obtained upon chromatographic separation. Structural assignment to the *meta* and *para* isomers, *meta*- and *para*-**16**, was essentially based upon the ^{1}H NMR spectral evidence displayed in the aromatic and vinylic region by an

unresolved mixture containing the three isomeric components. The above findings, while showing that the postulated 1-methoxycarbonyl radicals **14** and **18** tend to react in a strictly stereoselective fashion, like their congener **1**, also uncovered a fair tendency of such vinylic radicals to perform intermolecular addition to an aromatic substrate, a process hardly reported in the literature[15]. Presumably the chemical behaviour displayed by radicals **14** and **18** resulted from significant electrophilic power conferred to the radical centre by the strongly electron-attracting methoxycarbonyl substituent.

Scheme 3

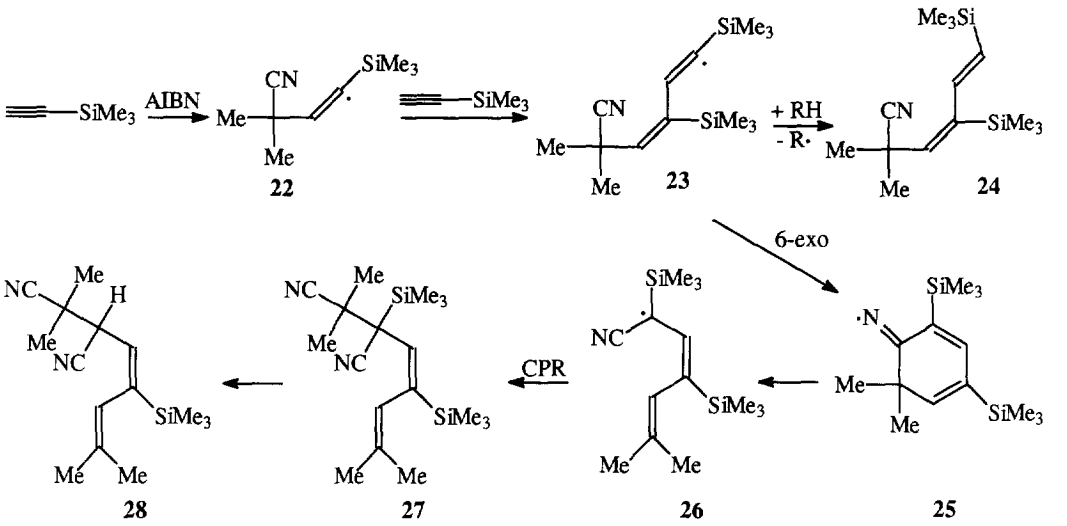


The reaction of AIBN with trimethylsilylacetylene also furnished convincing evidence for production of corresponding vinyl radical **22**. This reaction, in fact, led to the silylated diene compound **28**, in ca. 8% isolated yield, along with small amounts of an unresolved mixture of three components, one of which possibly being the diene adduct **24** as suggested by the ^{1}H NMR spectrum.

The observed diene **28** probably arose from regioselective desilylation of the bis-silylated analogue **27** upon chromatographic separation. The diene **27** in turn is ascribable to the primary intervention of radical **23** which would result from addition of initial 1-trimethylsilylvinyl radical **22** to the alkyne. 6-*Exo*-cyclization of **23** onto the cyano moiety would afford the iminyl radical **25** and thence **27** through subsequent β-cleavage of the C-CMe_2 bond, forming the resonance-stabilized intermediate **26**, and final trapping of **26** by CPR (Scheme 4). Such a possible route could uncover another novel instance of intramolecular vinyl radical cyclization, that could result in formal 1,5-cyano migration. The postulated intervention of the (E)- radical **23** would imply approach of alkyne scavenger from the more hindered side (*cis* to CMe_2CN) of the linear radical **22**, which is opposite to that encountered with the 1-phenyl and 1-methoxycarbonyl congeners. On the basis of our present evidence, along with our previous findings of thiol[17] and tributyltin hydride[18] additions to alkynes, it can be

confidently assumed that the stereochemical outcome of vinylic radical reactions is normally governed by easy approach of the radical scavenger, unless bulky α- and/or β-substituents are present, in which cases the stereochemical course can be preferentially governed by steric repulsion between the α and β vinylic substituents in the transition state.

Scheme 4



In the presence of diphenylacetylene or phenyltrimethylsilylacetylene AIBN instead furnished no vinilyc radical product. It is possible that addition of bulky CPR to these two alkynes was essentially discouraged by (high) steric hindrance of their substituents.

Finally, attempted reactions of AIBN with 1-hexyne and 3-hexyne similarly provided no evidence for any addition of 2-cyano-*iso*-propyl radical to either alkyl-substituted alkyne. These observations lead to suggest that the addition of this radical to the carbon-carbon triple bond is largely encouraged by the presence an electron-acceptor substituent that can confer stabilization to the ensuing vinyl radical through delocalization of the unpaired electron.[19]

In conclusion, the overall results indicate that the rather sluggish (and bulky) 2-cyano-*iso*-propyl radical can add in a regioselective fashion to acetylenes bearing an electron-acceptor phenyl, methoxycarbonyl or trimethylsilyl substituent, but it is unreactive towards simple alkylacetylenes and those sterically hindered. The chemical behaviour of the produced 2-(2-cyano-*iso*-propyl)vinylic radicals is strongly affected by the nature of both 1- and additional 2-substituent. The 1-phenyl- and 1-methoxycarbonyl-vinyl radicals bearing a vicinal hydrogen can undergo intermolecular H-abstraction reaction and/or alkyne addition on the less hindered side (ie. *trans* to CMe_2CN), whereas the corresponding 1-trimethylsilyl radical seems to react on the more hindered side (ie. *cis* to CMe_2CN) to avoid steric repulsion between the two bulky vicinal substituents. The 2-methyl-substituted 1-phenyl radical instead undergoes no intermolecular reaction but exhibits unprecedented 4-*exo* cyclization onto the adjacent cyano group eventually leading to radical 1,3-cyano migration. Moreover, the 1-methoxycarbonyl radicals can display a peculiar reactivity in that they show a tendency to add to an aromatic substrate.

EXPERIMENTAL SECTION

Phenylacetylene, phenylpropyne, methyl propiolate, trimethylsilyl-acetylene, diphenyl acetylene, 1-hexyne and 3-hexyne are commercially available. Phenyltrimethylsilylacetylene[20] was prepared as described in the literature.

Structural assignment of reaction products was generally based on ^{1}H NMR, GC-MS and MS spectral data in addition to elemental analysis or HRMS. Compounds **24** and **28** which were contaminated by unidentified product(s) could not be fully characterized. Triphenylbenzene **9** was identified by GC-MS comparison with a commercial specimen.

Column chromatography was performed on Merck silica gel (0.040-0.063 particle size) by gradual elution with light petroleum (b.p. 40-70 °C)-diethyl ether. ^{1}H NMR spectra were recorded at 300 MHz using Me_4Si as internal standard. Mass spectra were determined by the elctron impact method.

Reaction of AIBN with Alkynes. General Procedure. A benzene solution (40 mL) of AIBN (4 mmol., 656 mg.) and the appropriate alkyne (10 mmol.) was refluxed for 4 h. The solvent was removed and the residue analyzed by GC-MS and then chromatographed. The reaction of AIBN with methyl propiolate in anisole was similarly performed in a sealed tube at 85 °C. TLC and/or GC-MS analyses of the crude reaction mixtures obtained with 1-hexyne, 3-hexyne, diphenylacetylene and phenyltrimethylsilylacetylene detected no product ascribable to addition of 2-cyano-*iso*-propyl radical to these alkynes.

Reaction with Phenylacetylene. Column chromatography gave a mixture of (Z)-*3-cyano-3-methyl-1-phenylbut-1-ene* (Z)-**2** and (Z,Z)-*5-cyano-5-methyl-1,3-diphenylhexa-1,3-diene* (Z,Z)-**4** in 60:40 ratio as determined by ^{1}H NMR and GC-MS analysis (402 mg, 24% overall yield). Repeated chromatography gave small amounts of almost pure samples of compounds (Z)-**2** [^{1}H NMR δ 1.40 (6H, s), 5.42 (1H, d, J=11 Hz), 6.6 (1H, d, J=11 Hz), 7.25 (5H, m); MS m/z (rel. intensity) 171 (M^+, 40), 156 (60), 129 (100), 128 (40); HRMS calcd for $C_{12}H_{13}N$ 171.10480; found 171.1046.] and (Z,Z)-**4** [^{1}H NMR δ 1.15 (6H, s), 5.34 (1H, d, J=1.5 Hz), 6.06 (1H, dd, J_1=11 Hz, J_2=1.5 Hz), 6.44 (1H, d, J=11 Hz), 7.25 (5H, m); irradiation at δ 7.25 caused a 3% increase in the intensity of the signal at δ 6.06 and a 4% increase of the signal at δ 6.44; MS m/z (rel. intensity) 273 (M^+, 20), 258 (10), 243 (20), 231 (10), 205 (100), 180 (50). HRMS calcd for $C_{20}H_{19}N$ 273.15175; found 273.1515.]; *1-(2-cyano-2-methyl-1-propylidene)-3-phenylindene* **6** *(2:1 E/Z mixture)* (474 mg, 22%) [^{1}H NMR $\delta_{(E\text{-isomer})}$ 1.75 (6H, s), 6.31 (1H, d, J=1Hz, collapsing to a singlet upon irradiation at δ 7.30), 7.2-7.7 (10H, m); irradiation at δ 1.75 caused 20% enhancement at δ 6.09 and 10% enhancement at δ 7.30; $\delta_{(Z\text{-isomer})}$ 1.80 (6H, s), 6.09 (1H, s), 6.41 (1H, s), 7.2-7.7 (9H, m); irradiation at δ 1.80 caused 20% enhancement at δ 6.09; MS m/z (rel. intensity) 271 (M^+, 60), 256(100), 229(30). Anal. Calcd. for $C_{20}H_{17}N$: C, 88.52; H, 6.32; N, 5.16. Found: C, 88.9; H, 6.25; N, 5.10]

Reaction with 1-Phenylpropyne. Chromatography gave *4,5-dicyano-2,3,5-trimethyl-4-phenylhex-2-ene* **13** (120 mg., 12%) [^{1}H NMR δ 1.44 (3H, s), 1.56 (3H, br s, collapsing to singlet upon irradiation at δ 2.28), 1.74 (3H, br s; collapsing to singlet upon irradiation at δ 2.28), 1.80 (3H, s), 2.28 (3H, br s), 7.2-7.5 (5H, m); IR 2240 cm^{-1}(CN); MS m/z (rel. intensity) 252 (M^+, 4), 184 (100), 170 (60), 143 (40), 115 (90). Anal. Calcd. for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.95; H, 8.0; N, 11.2]

Reaction with Methyl Propiolate in Benzene Chromatography gave *1,3-bis(methoxycarbonyl)-5-cyano-5-methyl-1-phenylhexa-1,3-diene* **20** (98 mg, 4%) [^{1}H NMR δ 1.55 (6H, s), 3.72 (3H, s), 3.76 (3H, s), 6.53 (1H, d, J=2.0 Hz), 7.09 (1H, d, J=2.0 Hz; collapsing to singlet upon irradiation at δ 6.53), 7.3-7.4 (3H, m), 7.48-7.57 (2H, m); MS m/z (rel. intensity) 313 (M^+, 2), 245 (100), 236 (30), 169 (30), 143 (25). Anal. Calcd. for $C_{18}H_{19}NO_4$: C, 69.00; H, 6.11; N, 4.47; O, 20.42. Found: C, 69.35; H, 6.15; N, 4.43.] and *1,3-bis(methoxycarbonyl)-5-cyano-5-methyl-1-[(2-cyano-iso-propyl)cyclohexadienyl]hexa-1,3-diene* **21** (150 mg, 10%) [^{1}H NMR δ 1.3-1.5 (singlets, 12H), 3.70 (br s, 6H), 5.8-6.5 (multiplets); MS m/z (rel. intensity) 382

(M^+, 2), 351 (10), 350 (5), 314 (25), 282 (100), 254 (70), 237 (10), 236 (15). Anal. Calcd. for $C_{22}H_{26}N_2O_4$: C, 69.09; H, 6.85; N, 7.32; O, 16.73. Found: C, 69.40; H, 6.88; N, 7.29.].

Reaction with Methyl Propiolate in Anisole Chromatography gave *(Z)-3-cyano-3-methyl-1-methoxycarbonyl-1-(o-anisyl)-but-1-ene ortho*-**16** (68 mg, 4.5 %) [^{1}H NMR δ 1.68 (6H, s), 3.80 (3H, s), 3.85 (3H, s), 5.77 (1H, s), 6.80 (1H, d, J=8.5 Hz), 6.90 (1H, dt, J_d= 1.0 Hz, J_t= 8.0 Hz), 7.15 (1H, dd, J_1= 8.0 Hz, J_2= 1.0 Hz, collapsing to br s upon irradiation at δ 6.90), 7.26 (1H, br dd, J_1=8.0 Hz, J_2=8.5 Hz); irradiation at δ 5.77 caused 2.5% enhancement at δ 1.6 and 13% enhancement at δ 7.15 (*ortho* proton of the aromatic ring); MS m/z (rel. intensity) 259 (M^+, 100), 191 (40), 173 (50), 159 (40), 131 (55). Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40; O, 18.50. Found: C, 69.65; H, 6.65; N, 5.45]; isomeric mixture of *(Z)-3-cyano-3-methyl-1-methoxycarbonyl-1-(o, m, and p-anisyl)-but-1-ene ortho, meta* and *para*-**16** (82 mg, 5.5%) [^{1}H NMR $\delta_{(para\ isomer)}$ 1.62 (6H, s), 3.81 (3H, s), 3.90 (3H, s), 5.65 (1H, s), 6.88 (2H, d, J= 8.5 Hz), 7.27 (2H, d, J=8.5 Hz); the ^{1}H NMR spectrum showed, in addition to signals due to the *ortho* and *para* isomers, a vinylic proton at δ 5.73 ascribable to the *meta* isomer. The ratio of the vinylic protons at δ 5.65 (*para* isomer), 5.73 (*meta* isomer) and 5.77 (*ortho* isomer) was found to be ca. 5:1:5. Anal. Calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40; O, 18.50. Found: C, 69.8; H, 6.65; N, 5.35]; isomeric mixture of *1-methoxycarbonyl-1-[(2-cyano-iso-propyl)methoxycyclohexadienyl]-3-cyano-3-methylbut-1-ene* **17** (394 mg, 30%) [^{1}H NMR δ 1.2-1.3 (6H, m), 1.43 (3H, s), 1.47 (3H, s), 3.45-3.50 (3H, two singlets), 3.70-3.80 (3H, m), 5.4-5.8 (ca. 4H, m); MS m/z (rel. intensity) 328 (M^+, 10), 260 (90), 228 (70), 200 (100), 173 (85). Anal. Calcd. for $C_{19}H_{24}N_2O_3$: C, 69.49; H, 7.37; N, 8.53; O, 14.62. Found: C, 69.3; H, 7.40; N, 8.58].

Reaction with Trimethylsilylacetylene. Chromatography gave *2,7-dimethyl-6,7-dicyano-4-trimethylsilyl octa-2,4-diene* **28** (80 mg, 8%) contaminated to some extent by an unknown product [^{1}H NMR δ 0.1 (9H, s), 1.2 (3H, s), 1.35 (3H, s), 1.55 (3H, d, J=1.0 Hz; collapsing to singlet upon irradiation at δ 5.58), 1.82 (3H, d, J=1.0 Hz; collapsing to singlet upon irradiation at δ 5.58), 3.60 (1H, d, J=9.0 Hz), 5.58 (1H, m), 5.73 (1H, dd, J_1=9.0 Hz, J_2=2.0 Hz; collapsing to doublet, J=2.0 Hz, upon irradiation at δ 3.6; collapsing to doublet, J=9.0 Hz, upon irradiation at δ 5.58). MS m/z (rel. intensity) 260 (M^+, 10), 219 (25), 192 (15), 166 (45), 73 (100). HRMS calcd for $C_{15}H_{24}N_2Si$ 260.17088; found 260.1711.] and a fraction of three compounds (50 mg.), one of which possibly was *2-cyano-2-methyl-4,6-bis(trimethylsilyl)hexa-3,5-diene* **24** [^{1}H NMR δ 0.08 (9H, s), 0.10 (9H, s), 1.25 (3H, s), 1.35 (3H, s), 5.51 (1H, d, J=19.0 Hz, collapsing to singlet upon irradiation at δ 6.82), 5.80 (1H, d, J=1.0 Hz, collapsing to singlet upon irradiation at δ 6.82) and 6.82 (1H, dd, J_1=19.0 Hz, J_2=1.0 Hz).

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