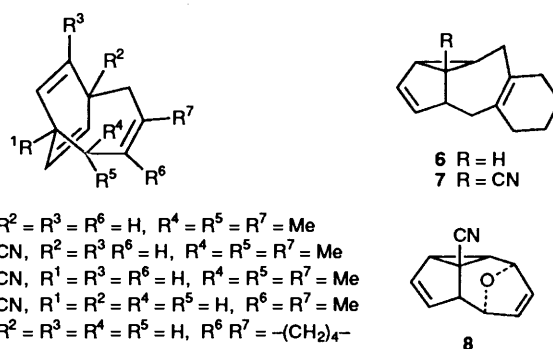# Substituent-directed Regioselectivity in the Photocycloaddition of 2,3-Dimethylbuta-1,3-diene to the Benzene Ring

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The reaction mode selectivity and regiochemistry of the photocycloaddition of 2,3-dimethylbuta-1,3-diene (DMBD) to the benzene ring are markedly dependent on the arene substituent. Mixtures of 1 : 1 adducts and large proportions of diene dimers result from parent benzene and Ph-R for R = Me, OMe, CF$_3$, CO$_2$Me or F, and (2π + 2π) cycloadducts are formed between styrene and phenylacetylene and DMBD. In marked contrast, the (4 + 4) photocycloadduct **4** is essentially the sole product from benzonitrile and the diene. The exceptional directing influence of the cyano group towards 2,5-, 1',4'- attack of the diene is little perturbed by the presence or position of Me, OMe or F substituents on the benzonitrile. The role in these (4 + 4) cycloadditions of polarisation in the S$_1$ arene on approach of the diene is discussed.

The *meta* photocycloaddition of ethenes to the benzene ring was first reported in 1966 and since this time has been the subject of numerous publications dealing with both the mechanistic aspects of this intriguing process, and its exploitation as a key step in complex molecule total synthesis.[1] During the mid-1960s, accounts of the photoreactions between buta-1,3-dienes and benzene also appeared and the formation of 1 : 1 cyclo-adducts arising from (4 + 4) and (2 + 3) processes as well as 2 : 1 and 2 : 2 adducts and 1-phenylbuta-1,3-dienes were described (Scheme 1).[2] The low reaction mode selectivity of these first examples of 1,3-diene–benzene photoadditions apparently discouraged activity in this area. Thus, in marked contrast to the extensive data subsequently published on the ethene–benzene systems and on the photoreactions of both cyclic and acyclic 1,3-dienes with polynuclear arenes,[3] information concerning the photoadditions of 1,3-dienes to the benzene ring is extremely limited. In particular, attempts to determine the factors which could be used to control the reaction mode selectivity have received very little attention. Some years ago, however, Yang and Libman reported from their studies into the photoreactions of benzene with 2,4-dimethylpenta-1,3-diene (DMPD) and 2,3-dimethylbuta-1,3-diene (DMBD) that the ground state conformation of the diene markedly influenced its mode and efficiency of cycloaddition to the arene.[4] This conclusion was based on the formation from the former diene of the (4π + 4π) cycloadduct **1** (37%), a complex mixture of *meta* cycloadducts (21%), but no diene dimers, while irradiation of the latter diene–benzene system gave large amounts of polymer, seven 1 : 1 photoadducts (none in greater yield than 10%), and at

1 R^1 = R^2 = R^3 = R^6 = H, R^4 = R^5 = R^7 = Me
2 R^1 = CN, R^2 = R^3 R^6 = H, R^4 = R^5 = R^7 = Me
3 R^2 = CN, R^1 = R^3 = R^6 = H, R^4 = R^5 = R^7 = Me
4 R^3 = CN, R^1 = R^2 = R^4 = R^5 = H, R^6 = R^7 = Me
5 R^1 = R^2 = R^3 = R^4 = R^5 = H, R^6 R^7 = –(CH$_2$)$_4$–

6 R = H
7 R = CN

8

least three diene dimers. Preliminary studies with substituted benzenes from the same workers[4] suggested that DMPD undergoes (4 + 4) photocycloaddition at the 1,4-positions of benzonitrile to give **2** and **3**, but in an earlier (uncited) account the specific formation of the 2,5-, 1',4'-cycloadduct **4** of benzonitrile and DMBD had been described by Okumura *et al.*[5] We have confirmed that **4** is indeed the sole photoadduct from the latter system.[6] Furthermore, we have shown that greatly improved addition selectivity to the benzene ring occurs with acyclic (but not cyclic) conformationally fixed *cis* 1,3-dienes.[7] Thus, the (4 + 4) and (4 + 3) cycloadducts **5** and **6** respectively are obtained as the sole products from 254 nm irradiation of benzene in the presence of 1,2-dimethylenecyclohexane. The relative efficiencies of these two processes are not,


Scheme 1
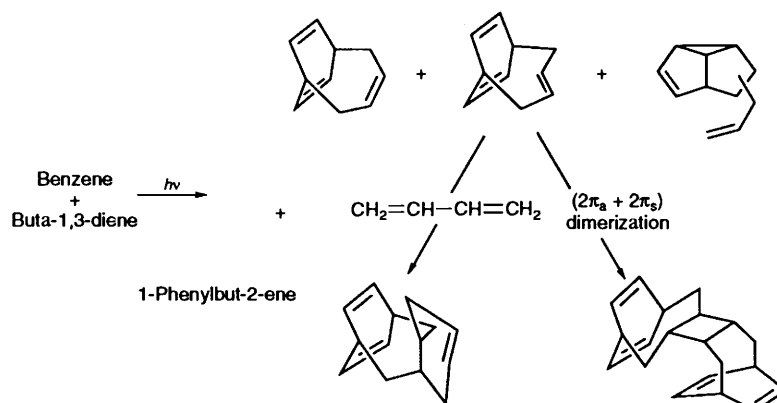
however, significantly influenced by a cyano directing group on the benzene ring,[6] and hence, unlike the photocycloadditions of ethenes to the benzene ring, there is no apparent correlation between the ease of electron transfer and the mode of photocycloaddition.[8] The formation of 7[6] as the sole isomer from the (4 + 3) addition of 1,2-dimethylenecyclohexane to benzonitrile is, however, wholly consistent with a mechanism in which the orientation of the addends is controlled by substituent stabilisation of the developing charges which arise from polarisation of the S_1 arene on approach of the 1,3-diene.[9] The direction of polarisation on approach of the 1,3-diene is the reverse of that deduced to occur during *meta* photocycloaddition of ethenes to the benzene ring.[10] In order to induce greater reaction mode selectivity towards the (4 + 3) process, a second directing influence is apparently necessary and, as we have reported, the addition of furan to benzonitrile is a regio- and stereo-specific process giving the *exo* 2,6-, 2',5'-addition product **8**.[6]

The lack of widespread interest in benzene–1,3-diene photoreactions is somewhat surprising in view of the potential of the (4 + 4) and (4 + 3) photocycloadditions of these addends to provide a convenient access to bicyclo[4.2.2]- and bicyclo-[5.3.0]-decanes, respectively, from readily available starting materials. Furthermore, the complexity of the reaction mixture from DMBD and benzene[4] and the specificity for the 1,4-, 2',5'-addition of this 1,3-diene to benzonitrile[5] emphasise the importance of substituent influences in directing the (4 + 4) process. In order to assess the scope of these processes and the features which control reaction mode selectivity and the regiochemistry of the (4 + 4) and (4 + 3) cycloadditions, we have investigated the photoreactions of DMBD and of furan with a range of mono-and di-substituted benzenes. In this paper we describe the results from the former series and discuss the mechanistic features which may operate and influence the (4 + 4) addition process.

Results and Discussion

In order to determine if selectivity could be induced into the (4 + 4) cycloaddition process by substituent stabilisation of the developing polarity in the S_1 benzene ring on approach of the 1,3-diene, we examined the photoreactions of DMBD with benzenes monosubstituted with groups which do not perturb the π,π^* character of the lowest excited state of the arene. Both electron donor and acceptor substituents on the benzene ring are well known to exert powerful directing effects on the regiochemistries of the addition of ethenes as a result of their abilities to stabilise the developing charges in the singlet excited C_6 ring.[1] In marked contrast, however, the photoreactions of DMBD with toluene, anisole, α,α,α-trifluorotoluene and fluorobenzene all produced multicomponent mixtures comprising 1:1 adducts and diene dimers. Only in the anisole system was one of the 1:1 adducts a significant component (*ca.* 12%) of the reaction mixture and this proved impractical to isolate free from isomers and the dimers. Thus, the (4 + 4) cycloaddition of 1,3-dienes to the benzene ring is not seemingly susceptible to the same directing influences as the photocycloaddition of ethenes.
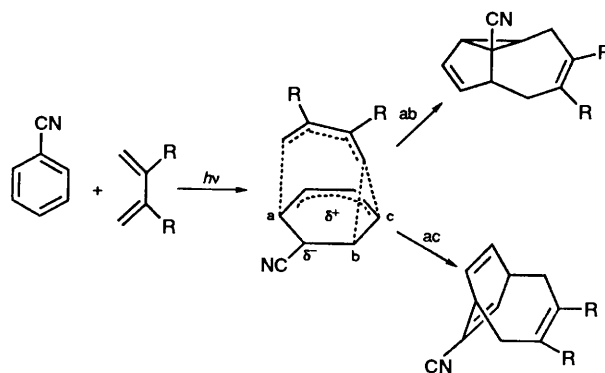
The photocycloaddition of furan to the benzene ring can be directed to a (4 + 3) process by an ethenyl and an ethynyl as well as a cyano group on the arene,[6] and so the photoreactions of styrene and of phenylacetylene with DMBD were examined. From both systems although 1:1 adducts were formed, unlike the addition of furan, the reaction with DMBD did not involve the benzene ring and the major products were the two stereoisomers (*e.g.* **9** and **10** from styrene) from (2π + 2π) head-to-head cycloaddition of the addends. It becomes apparent, therefore, that the cyano group is exceptional in its specific direction not only of the addition mode of DMBD to the
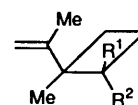
9 R[1] = Ph, R[2] = H
10 R[1] = H, R[2] = Ph

benzene ring to give bicyclo[4.2.2]deca-3,7,9-trienes but also of the regiochemistry of this (4 + 4) process. The importance of this feature in controlling the addition and its scope in accessing functionalised systems were assessed by studying the photoreactions of DMBD with the toluonitriles, the cyanoanisoles and the fluorobenzonitriles: these results are summarised in Table 1.
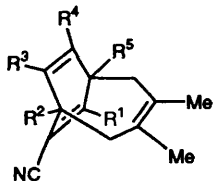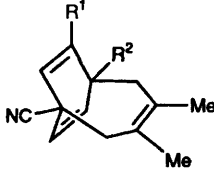
From the analysis of these results and their comparison with the data reported for arene–ethene systems[1] and those given in references 4, 6 and 7, it becomes evident that the features which influence the mode of photocycloaddition of 1,3-dienes to the benzene ring are not so clearly defined as those that have been deduced to delineate between the *ortho* and *meta* processes of ethenes, and to control the regiochemistries of these (2 + 2) and (2 + 3) reactions. Neither the efficiency nor the selectivity of the cycloadditions of DMBD described here were influenced by change in solvent polarity. Furthermore, as shown by the data in Table 2, unlike the ethene additions,[8] there is no correlation between the mode of photocycloaddition of 1,3-dienes and the free energy change (ΔG°) of electron transfer between the addends. It thus appears that in the diene systems the reaction selectivity is controlled by structural features of the addends. The marked directing influence of the cyano group towards (4 + 4) cycloaddition of DMBD is maintained for the present series of disubstituted benzenes, and, in particular, no evidence is obtained from any system for the formation of (4 + 3) cycloadducts. The ability of the cyano group to induce selectivity towards either of these processes is, however, remarkable and may indicate, as illustrated in Scheme 2, that the two additions have a common type of polarised intermediate involving the S_1 arene and S_0 1,3-diene, which is similar

Scheme 2

to, but of opposite polarity from, the species proposed in the *meta* photocycloaddition of ethenes to the benzene ring.[9,10] For the present addition, the flexibility of the acyclic diene favours a 2,6- rather than the 2,5-attack observed with furan as the addend.[6] However, if this type of polarised intermediate is involved in the additions of 1,3-dienes, it is then surprising that the presence of an electron donating group on the arene has no apparent effect on the regiochemistry of the reaction since in the *meta* photocycloaddition of ethenes to the benzene ring it is the methoxy not the cyano group which is the more powerful directing substituent: this, as well as the polarity in the intermediate, is apparently reversed in diene additions. Thus,

Table 1 (4 + 4) Photocycloaddition of DMBD to substituted benzonitriles

Arene		
2-Toluonitrile[a]	11 R^1 = Me, R^2 = R^3 = R^4 = R^5 = H	
	12 R^2 = Me, R^1 = R^3 = R^4 = R^5 = H	
	Ratio 11:12 3:1	
3-Toluonitrile[a]	13 R^3 = Me, R^1 = R^2 = R^4 = R^5 = H	15 R^1 = Me, R^2 = H
	14 R^5 = Me, R^1 = R^2 = R^3 = R^4 = H	
	Ratio 13:14:15 6:3:1	
4-Toluonitrile[a]	16 R^4 = Me, R^1 = R^2 = R^3 = R^5 = H	17 R^1 = H, R^2 = Me
	Ratio 16:17 6:1	
2-Cyanoanisole[b]	18 R^1 = OMe, R^2 = R^3 = R^4 = R^5 = H	
	(sole adduct in minor amounts)	
3-Cyanoanisole[a]	19 R^3 = OMe, R^1 = R^2 = R^4 = R^5 = H	
	Minor unidentified isomer X[c]	
	Ratio 19:X 3:1	
4-Cyanoanisole[a]	20 R^4 = OMe, R^1 = R^2 = R^3 = R^5 = H	
2-Fluorobenzonitrile[a]	21 R^1 = F, R^2 = R^3 = R^4 = R^5 = H	
	22 R^2 = F, R^1 = R^3 = R^4 = R^5 = H	
	Ratio 21:22 5:1	
3-Fluorobenzonitrile[a]	23 R^3 = F, R^1 = R^2 = R^4 = R^5 = H	
	24 R^5 = F, R^1 = R^2 = R^3 = R^4 = H	
	Ratio 23:24 2:1	
4-Fluorobenzonitrile[a]	25 R^4 = F, R^1 = R^2 = R^3 = R^5 = H	

[a] Minor amounts of photodimers of DMBD. [b] Major amounts of photodimers of DMBD. [c] The high thermal lability and acid sensitivity of this isomer prevented its isolation with reasonable purity.

Table 2 $\Delta G°$ Values and modes of reaction for benzene and benzonitrile with 1,3-dienes

1,3-Diene	$E_{\frac{1}{2}}^{ox}$/eV	Benzene		Benzonitrile	
		$\Delta G°$/eV	Reaction mode	$\Delta G°$/eV	Reaction mode
Buta-1,3-diene[14]	2.03	1.96	unselective	1.10	low selectivity (4 + 4)
DMBD	1.84	1.72	unselective	0.92	(4 + 4)
1,2-Dimethylenecyclohexane	2.00 (1.90)[14]	1.93 (1.83)	(4 + 4):(4 + 3) 2:1	1.08 (0.98)	(4 + 4):(4 + 3) 2.5:1
Furan	1.98 (1.87)[14]	1.91 (1.80)	unselective	1.06 (0.96)	(4 + 3)

with the exception of the minor products from the 3- and 4-toluonitriles, the regiochemistry of the (4 + 4) diene addition is controlled by the cyano group with attack preferentially occurring at the 2,5-positions except where this results in substitution at the bridgehead of the bicyclo[4.2.2]deca-3,7,9-triene and then the 3,6-mode is favoured.

Using the frontier molecular orbital method which Houk has described to analyse the photocycloadditions to the benzene ring,[11] we deduce that both the *meta* and *para* approach of a 1,3-diene to the arene are more favoured (possibly equally) than an approach of the diene to the *ortho* positions: significantly, the formation of bicyclo[4.4.0]deca-2,4,8-trienes has not been reported from 1,3-diene–benzene systems. From orbital symmetry analysis of the photoadditions of s-*cis* 1,3-dienes to the benzene ring, it is deduced that the *meta*-1,4-reaction is allowed as a concerted process from the S_1 arene and S_0 diene whereas the corresponding *para* reaction requires the S_2 or T_1 (B_{1u} state) benzene.[12] The fluorescence of all the arenes studied here was quenched by DMBD with rate coefficients of the order of 10^9 l mol^{-1} s^{-1}, but our attempts to determine the multiplicity of the excited state involved in these additions were thwarted by the considerable difficulties in obtaining meaningful data for

product quenching and sensitisation. It was, however, evident from selective wavelength radiation that the arene, not the 1,3-diene, is the initially excited species leading to the (4 + 4) cycloadducts. We have been unable to determine with certainty if the *cis* geometry of the but-2-ene bridge arises from a concerted addition of the s-*cis* conformer of the diene or a non-concerted addition of the s-*trans* isomer. However, no evidence was obtained in the present study to account for this geometry by initial formation and isomerisation of the adduct with a *trans* butene bridge as is observed with the benzene–buta-1,3-diene system.

The (4 + 4) cycloadducts from irradiation of the DMBD-disubstituted benzene systems have no observable tendency to undergo a [3.3]sigmatropic rearrangement or yield caged isomers on direct or sensitised irradiation in contrast to the benzene–furan (4 + 4) adducts.[13] Structures of the present (4 + 4) cycloadducts have been unambiguously assigned from NMR spectral data but in order to understand this lack of reactivity between the 3- and 9-ethenes moieties and the equal coupling between each of the methylene protons with the doubly allylic methine proton, single crystal X-ray analysis of the adducts was undertaken. The computer derived structure for 23 from 3-
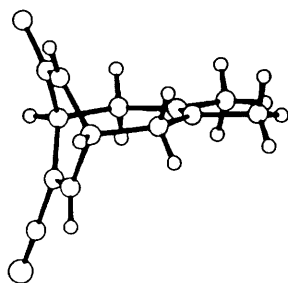
Fig. 1

fluorobenzonitrile and DMBD is given in Fig. 1 and shows that the cis but-2-ene bridge lies essentially perpendicular to the cyclohexa-1,4-diene unit. This conformation accounts for both the absence of interaction between the ethenes and the NMR spectral detail.

To summarise, we have shown that the remarkable selectivity of (4 + 4) photocycloaddition of DMBD to benzonitrile also occurs for a range of disubstituted benzenes and that this process is not influenced by electron donating groups. Unlike the ethene additions to the aromatic ring, for 1,3-dienes there is no electronic direction of the process and ease of electron transfer between the addends has no discernible controlling influence on reaction mode selectivity. The reaction does, however, provide an excellent route to functionalised bicyclo[4.2.2]deca-3,7,9-trienes, particularly since for the majority of adducts, they can be readily isolated and purified by simple crystallisation of the adduct mixtures at $-25\,^\circ$C from pentane solution.

Experimental

Photochemical and Analytical Methods.—No attempts were made to optimise product formation but with the exception of 2-cyanoanisole, all disubstituted arene–DMBD systems yielded the 1:1 adducts with similar efficiencies. In a typical experiment, 254 nm irradiation (circular array of 6 × 18 W low-pressure mercury arc lamps) of arene (1.0 mol dm^{-3}) and diene (1.5 mol dm^{-3}) in dioxane solution (100 cm^3) for 36 h gave approximately 1.0 g of the 1:1 adducts. When corrected for unchanged arene, the yields were in the 55–65% range except for **18** which was obtained in *ca.* 20% yield. Periodic cleaning of the quartz tubes greatly increased the chemical yields within specified times. The irradiations were monitored by GC using a Hewlett Packard 5790A instrument fitted with a flame ionisation detector and a 12 m BP1 (SGE OV1 equivalent) bonded phase capillary column. Analysis of product mixtures by TLC used Camlab Polygram G/UV precoated sheets and varying proportions of light petroleum (b.p. 30–40 °C) and diethyl ether as the eluent. Isolation of the crystalline adducts was achieved by dissolving the vacuum distilled product mixture in pentane and cooling the solution overnight at $-25\,^\circ$C: the filtered product was recrystallised from the same solvent. In other cases, separation and purification of the photoisomers were achieved either by flash chromatography on ICN silica 32–63 (Park Scientific Ltd) or by preparative GC using a Perkin-Elmer F21 instrument fitted with 6.4 mm i.d. × 1 m columns packed with 15% w/w OV101 on 80–100 Chromosorb P. NMR spectra were recorded on a Bruker WM250 or a Bruker WH400 (SERC Spectrometer Service Warwick) instrument with tetramethylsilane as an internal standard and in CDCl$_3$ solution unless otherwise stated: all coupling constants are given in Hz. IR spectra of liquid films and CCl$_4$ solutions were obtained using a Perkin-Elmer 881 spectrometer. Accurate mass data were provided by the SERC Mass

Spectrometer Service Centre, Swansea, after chromatographic purity assurance.

Photoproducts.—cis-1-*Methyl*-2-*phenyl*-1-(*prop*-2'-*enyl*)-*cyclobutane* **9.** Separated and purified by preparative GC. δ_H 7.30–7.22 (m, Ph), 4.76 (m, $J_{1'cis,2'}$ 1.0 $J_{1'cis,Me}$ 0.6, *cis* 1'-H), 4.73 (overlapping dq, $J_{1'trans,Me}$ 1.4, *trans* 1'-H), 3.23 (overlapping dd, $J_{2exo,3exo}$, $J_{2exo,3endo}$ 7.5, *exo* 2-H), 2.54–2.40 (m, *endo* 4-H), 2.37–2.26 (m, *exo* 3-H), 2.13–1.99 (m, *endo* 3-H), 1.91–1.80 (m, *exo* 4-H), 1.42 (dd, CH$_3$) and 1.11 (s, 3'-CH$_3$); δ_C 128.1 (Ph), 125.8 (C-2'), 109.9 (C-1'), 51.10 (C-2), 44.44 (C-1), 30.24 (C-4), 28.93 (3'-CH$_3$), 21.90 (C-3) and 19.38 (CH$_3$); ν_{max}/cm^{-1} 1619w and 1602w (Found: M$^+$, 186.1410. Calc. for C$_{14}$H$_{18}$, *M*, 186.1409).

trans-1-*Methyl*-2-*phenyl*-1-(*prop*-2'-*enyl*)*cyclobutane* **10.** Separated and purified by preparative GC. δ_H 7.25 (m, Ph), 4.83 (m, $J_{1'cis,2'}$ 0.9, $J_{1'cis,Me}$ 0.5, *cis* 1'-H), 4.77 (overlapping dq, $J_{1'trans,Me}$ 1.2 *trans* 1'-H), 3.68 (overlapping dd, $J_{2exo,3endo}$, $J_{2exo,3exo}$ 7.5, *exo* 2-H), 2.28 (m, *exo* 4-H), 2.32–2.18 (m, *endo* 4-H, *exo* 3-H, *endo* 3-H), 1.75 (d, CH$_3$) and 0.99 (s, CH$_3$); ν_{max}/cm^{-1} 1640m and 1604m (Found: M$^+$, 186.1410. Calc. for C$_{14}$H$_{18}$, *M*, 186.1409).

7-*Cyano*-3,4,8-*trimethylbicyclo*[4.2.2]*deca*-3,7,9-*triene* **11.** M.p. 84.5–85.5 °C; δ_H(C$_6$D$_6$) 5.70 (ddd, $J_{10,9}$ 8.5, $J_{10,6}$ 4.7, $J_{10,1}$ 1.5, 10-H), 5.66 (ddd, $J_{9,1}$ 4.7, $J_{9,6}$ 1.5, 9-H), 2.81 (br q, $J_{1,2}$, $J_{1,2'}$ 4.4, 1-H), 2.50 (d of m, $J_{5,5'}$ 17.5, $J_{5,6}$ 4.4, 5-H), 2.33 (br q, $J_{6,5'}$ 4.4, 6-H), 2.18 (br s, 2-H, 2'-H), 2.15 (d of m, 5'-H), 1.71 (s, CH$_3$), 1.38 (m, CH$_3$) and 1.35 (m, CH$_3$); δ_C 130.1 (C-10), 129.9 (C-9), 123.3 (C-4), 122.6 (C-3), 118.4 (C-7), 110.4 (C-8), 46.01 (C-2), 45.47 (C-5), 42.20 (C-1), 38.26 (C-6), 24.34 (CH$_3$) and 21.04 (CH$_3$); ν_{max}/cm^{-1} (CCl$_4$ solution): 2209s, 1681w and 1649m (Found: C, 84.2; H, 8.7; N, 7.0. C$_{14}$H$_{17}$N requires C, 84.37; H, 8.60; N, 7.03%).

7-*Cyano*-3,4,6-*trimethylbicyclo*[4.2.2]*deca*-3,7,9-*triene* **12.** Separated and purified by preparative GC. δ_H 7.01 (d, $J_{7,6}$ 5.3, 7-H), 6.07 (dd, $J_{10,9}$ 8.8, $J_{10,1}$ 5.3, 10-H), 5.88 (d, 9-H), 3.16 (q, $J_{6,5}$, $J_{6,5'}$ 4.4, 6-H), 2.65 (br s, 5-H, 5'-H), 2.70–2.55 (m, 2-H, 2'-H), 2.28 (s, 2 CH$_3$) and 1.68 (s, CH$_3$); ν_{max}/cm^{-1} 2214m and 1634m (Found: M$^+$, 199.1362. Calc. for C$_{14}$H$_{17}$N, *M*, 199.1361).

7-*Cyano*-3,4,10-*trimethylbicyclo*[4.2.2]*deca*-3,7,9-*triene* **13.** Separated and purified by flash chromatography using 0–10% diethyl ether in n-pentane as the eluent. M.p. 82–83 °C; δ_H 6.94 (d of overlapping dd, $J_{8,1}$ 6.0, $J_{8,6}$, $J_{8,9}$ 1.0, 8-H), 5.65 (d of m, $J_{9,1}$ 6.0, $J_{9,Me}$ 1.5, 9-H), 3.07 (m, $J_{6,5}$, $J_{6,5'}$ 4.4, $J_{6,Me}$ 0.5, 6-H), 2.92 (overlapping dd, $J_{1,2}$, $J_{1,2'}$ 4.3, 1-H), 2.70 (br s, 5-H), 5'-H), 2.55 (br s, H-2, H-2'), 1.83 (dd, CH$_3$), 1.54 (m, CH$_3$) and 1.57 (m, CH$_3$); δ_C 148.4 (C-8), 137.5 (C-10), 123.6 (C-9), 123.1 (C-4), 122.6 (C-3), 118.6 (C-7), 116.8 (CN), 45.99 (C-5), 44.81 (C-2), 43.03 (C-6), 36.75 (C-1), 24.35 (CH$_3$) and 20.83 (2 CH$_3$); ν_{max}/cm^{-1} (CCl$_4$) 2213m and 1647m (Found: C, 84.3; H, 8.55; N, 7.0. C$_{14}$H$_{17}$N requires C, 84.37; H, 8.60; N, 7.03%).

Isomers **14** and **15** were separated and purified by preparative GC of the oil from flash chromatography.

7-*Cyano*-1,3,4-*trimethylbicyclo*[4.2.2]*deca*-3,7,9-*triene* **14.** δ_H 6.65 (br s, $J_{8,Me}$ 1.1, 8-H), 5.95 (dd, $J_{10,9}$ 8.0, $J_{10,6}$ 5.1, 10-H), 5.73 (dd, $J_{9,6}$ 1.1, 9-H), 3.12 (overlapping dd, $J_{6,5}$, $J_{6,5'}$ 4.0, 6-H), 2.90–2.50 (m, 2-H, 2'-H), 2.48 (br s, 5-H, 5'-H), 1.25 (s, CH$_3$) and 1.58 (s, 2 CH$_3$); δ_C 152.4 (C-8), 134.7 (C-10), 128.2 (C-9), 123.3 (C-4), 122.9 (C-3), 121.0 (C-7), 115.4 (CN), 55.92 (C-5), 44.98 (C-2), 39.97 (C-6), 37.46 (C-1), 29.27 (CH$_3$), 24.48 (CH$_3$) and 24.43 (CH$_3$); ν_{max}/cm^{-1} 2214m; *m/z* 199 (M$^+$).

1-*Cyano*-3,4,7-*trimethylbicyclo*[4.2.2]*deca*-3,7,9-*triene* **15.** δ_H 6.15 (dd, $J_{10,9}$ 8.0, $J_{10,6}$ 5.1, 10-H), 6.02 (dd, $J_{9,6}$ 1.1, 9-H), 5.75 (br s, $J_{8,6}$ 1.0, $J_{8,Me}$ 1.1, 8-H), 2.75 (overlapping dd, $J_{6,5}$, $J_{6,5'}$ 4.1, 6-H), 2.90–2.50 (m, 2-H, 2'-H, 5-H, 5'-H), 1.85 (d, CH$_3$) and 1.53 (s, 2 CH$_3$); δ_C 148.4 (C-7), 140.5 (C-9), 132.9 (C-8), 127.1 (C-10),

123.6 (C-3), 123.3 (C-4), 118.4 (CN), 53.71 (C-2), 44.44 (C-5), 38.82 (C-6), 29.61 (C-1), 24.27 (CH_3), 24.05 (CH_3) and 20.79 (CH_3); v_{max}/cm^{-1} 2213m; m/z 199 (M$^+$).

Product from 2,3-dimethylbuta-1,3-diene and 4-toluonitrile. Pure by GC and TLC (R_f = 0.34, 5% diethyl ether in n-pentane); v_{max}/cm^{-1} 2214m (Found: C, 84.05; H, 8.6; N, 6.9. $C_{13}H_{17}N$ requires C, 84.37; H, 8.60; N, 7.03%). M.p. 89.5–100 °C suggested a mixture of adducts, and analysis by ^1H NMR spectroscopic techniques revealed that the crystals comprised two components in a 6:1 ratio. Structures 17 and 18 were assigned respectively from the extracted data given below.

7-Cyano-3,4,9-trimethylbicyclo[4.2.2]*deca-3,7,9-triene* 16. δ_H 6.90 (d, $J_{8,1}$ 6.5, 8-H), 5.67 (d of overlapping dd, $J_{10,6}$ 6.2, $J_{10,1}$, $J_{10,Me}$ 1.1, 10-H), 3.07 (m, $J_{6,5}$, $J_{6,5'}$ 4.2, 6-H), 2.87 (m, $J_{1,2}$, $J_{1,2'}$ 4.2, 1-H), 2.72 (br s, 5-H), 2.67 (br s, 5'-H), 2.54 (br s, 2-H), 2.51 (br s, 2'-H), 1.78 (d, CH_3) and 1.54 (s, 2 CH_3); δ_C 148.2 (C-8), 137.4 (C-10), 123.3 (C-9), 122.9 (C-4), 122.5 (C-3), 118.6 (C-7), 116.7 (CN), 45.98 (C-5), 44.61 (C-2), 41.56 (C-6), 38.02 (C-1), 24.24 (CH_3) and 20.62 (2 CH_3).

1-Cyano-3,4,6-trimethylbicyclo[4.2.2]*deca-3,7,9-triene* 17. δ_H 5.97 (d, $J_{8,7}$, $J_{9,10}$ 9.0, 8-H, 9-H), 5.86 (d, 7-H, 10-H), 2.82 (br s, 2-H, 2'-H), 2.39 (br s, 5-H, 5'-H), 1.52 (s, CH_3) and 1.17 (s, 2 CH_3); δ_C 137.4 (C-7, C-10), 125.5 (C-8, C-9), 124.7 (C-3), 123.1 (C-4), 120.7 (CN), 55.18 (C-2), 51.08 (C-5), 37.76 (C-1), 36.80 (C-6), 28.27 (CH_3) and 24.19 (2 CN_3).

7-Cyano-8-methoxy-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 18. Separated and purified by flash chromatography using 5% diethyl ether in pentane as the eluent. M.p. 114–115 °C. δ_H 6.06 (ddd, $J_{10,9}$ 8.0, $J_{10,6}$ 6.0, $J_{10,1}$ 0.5, 10-H), 5.92 (ddd, $J_{9,1}$ 6.0, $J_{9,6}$ 0.5, 9-H), 4.12 (s, OCH$_3$), 3.13 (m, $J_{6,5}$, $J_{6,5'}$ 4.8, 6-H), 2.94 (m, $J_{1,2}$, $J_{1,2'}$ 4.8, 1-H), 2.70 (br d, $J_{5,5'}$ 18, 5-H), 2.65 (br s, 2-H), 2.58 (br s, 2'-H), 2.51 (br d, 5'-H), 1.60 (m, CH_3) and 1.58 (m, CH_3); δ_C 130.9 (C-10), 128.9 (C-9), 123.5 (C-4), 122.7 (C-3), 119.5 (CN), 113.3 (C-7), 107.6 (C-8), 57.90 (OCH$_3$), 45.91 (C-5), 45.46 (C-2), 40.63 (C-6), 39.17 (C-1), 24.34 (CH_3) and 24.21 (CH_3) (Found: C, 78.0; H, 8.0; N, 6.5. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.51%).

7-Cyano-10-methoxy-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 19. M.p. 110–111 °C; δ_H 6.94 (d of overlapping dd, $J_{8,1}$ 6.5, $J_{8,6}$, $J_{8,9}$ 0.5, 8-H), 4.77 (dd, $J_{9,1}$ 6.5, $J_{9,6}$ 1.3, 9-H), 3.58 (s, OCH$_3$), 3.19 (ddd, $J_{1,2}$, $J_{1,2'}$ 4.2, 1-H), 3.02 (overlapping dd with fine coupling, $J_{6,5}$, $J_{6,5'}$ 4.1, 6-H), 2.75 (br d, $J_{5,5'}$ 16, 5-H, 5'-H), 2.58 (br s, 2-H, 2'-H), 1.57 (m, CH_3) and 1.55 (m, CH_3); δ_C 158.2 (C-8), 149.4 (C-10), 123.1 (C-4), 122.6 (C-3), 118.2 (C-7), 115.7 (CN), 93.49 (C-9), 55.09 (OCH$_3$), 46.78 (C-5), 45.05 (C-2), 41.53 (C-6), 35.82 (C-1), 24.44 (CH_3) and 24.23 (CH_3); v_{max}/cm^{-1} (CCl$_4$) 2215m (Found: C, 77.9; H, 8.0; N, 6.6. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.51%).

7-Cyano-9-methoxy-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 20. M.p. 147–148 °C; δ_H 6.85 (dd, $J_{8,1}$ 6.5, $J_{8,6}$ 0.8, 8-H), 4.82 (dd, $J_{10,6}$ 6.7, $J_{10,1}$ 1.5, 10-H), 3.56 (s, CH$_3$O), 3.20 (dddd, $J_{6,5}$, $J_{6,5'}$ 4.2, 6-H), 2.98 (dddd, $J_{1,2}$, $J_{1,2'}$ 4.2, 1-H), 2.75 (m, $J_{2',2}$ 15.0, $J_{2',5'}$ 3.0, $J_{2',5}$ 4.2, $J_{5',2}$ 4.4, $J_{5',5}$ 14.2, 2'-H, 5'-H), 2.55 (m, $J_{2,5}$ 2.5, 2-H, 5-H) and 1.58 (s, 2 CH_3); δ_C 158.4 (C-10), 146.8 (C-7), 123.0 (C-3), 122.6 (C-4), 118.5 (C-8), 117.9 (CN), 93.61 (C-9), 55.09 (OCH$_3$), 46.99 (C-2), 45.02 (C-5), 40.49 (C-6), 37.49 (C-1), 24.44 (CH_3) and 24.21 (CH_3); v_{max}/cm^{-1} 2216m and 1688m (Found: C, 78.0; H, 8.0; N, 6.55. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96; N, 6.51%).

7-Cyano-8-fluoro-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 21. Separated and purified by flash chromatography using 0–10% diethyl ether in pentane as the eluent. M.p. 71–72 °C; δ_H 6.03 (ddd, $J_{9,10}$ 8.9, $J_{9,1}$ 5.8, $J_{9,6}$ 1.1, 9-H), 5.96 (ddd, $J_{10,6}$ 5.6, $J_{10,1}$ 1.0, 10-H), 3.20 (m, $J_{1,2}$, $J_{1,2'}$ 4.6, 1-H), 3.11 (m, $J_{6,F}$ 12, $J_{6,5}$, $J_{6,5'}$ 5.0, 6-H), 2.95–2.55 (m, $J_{2,2'}$ 15, $J_{5,5'}$ 18, 2-H, 2'-H, 5-H, 5'-H) and 1.58 (s, 2 CH_3); δ_C 173.6 (C-8, $J_{C,F}$ 291), 130.1 (C-10), 128.4 (C-9, $J_{C,F}$ 6), 123.2 (C-4), 122.3 (C-3), 114.2 (CN), 105.6 (C-7),

46.06 (C-5), 44.85 (C-2, $J_{C,F}$ 3), 38.21 (C-1, $J_{C,F}$ 21), 37.23 (C-6), 24.52 (CH_3) and 24.28 (CH_3); δ_F 75.5, relative to CFCl$_3$; v_{max}/cm^{-1} (CCl$_4$) 2222m and 1681m (Found: C, 76.3; H, 7.0; N, 6.6; F, 10.2. $C_{13}H_{14}NF$ requires C, 76.82; H, 6.91; F, 9.35; N, 6.89%).

7-Cyano-6-fluoro-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 22. Separated and purified by flash chromatography using 0–10% diethyl ether in pentane as the eluent. M.p. 90.5–91.5 °C; δ_H 6.98 (ddd, $J_{8,1}$ 6.5, $J_{8,F}$ 4.5, $J_{8,9}$ 1.0, 8-H), 6.21–6.05 (m, $J_{9,10}$ 9.5, $J_{9,F}$ 3.5, $J_{9,1}$ 5.0, $J_{10,F}$ 12, 9-H, 10-H), 3.25–3.15 (m, $J_{1,2}$, $J_{1,2'}$ 4.5, 1-H), 3.02–2.75 (m, $J_{5,5'}$ 17.7, $J_{5,F}$, $J_{5',F}$ 9.0, 5-H, 5'-H), 2.58 (br s, 2-H, 2'-H), 1.59 (s, CH_3) and 1.54 (s, CH_3); δ_C 146.5 (C-8, $J_{C,F}$ 6), 130.3 (C-10, $J_{C,F}$ 27), 128.6 (C-9, $J_{C,F}$ 12), 123.6 (C-3), 120.9 (C-4, $J_{C,F}$ 14), 117.8 (C-7, $J_{C,F}$ 21), 114.9 (CN), 88.91 (C-6, $J_{C,F}$ 172), 52.08 (C-5, $J_{C,F}$ 30), 43.11 (C-2, $J_{C,F}$ 4), 36.65 (C-1), 26.61 (CH_3) and 24.03 (CH_3); δ_F +5.92 relative to CFCl$_3$; v_{max}/cm^{-1} 2226m and 1675w (Found: C, 75.55; H, 6.9; F, 10.2; N, 6.8. $C_{13}H_{14}FN$ requires C, 76.82; H, 6.94; F, 9.35; N, 6.89%; Found: M$^+$, 203.1110. Calc. for $C_{13}H_{14}FN$, M, 203.1110).

7-Cyano-10-fluoro-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 23. M.p. 122–123 °C; δ_H 6.89 (dd, $J_{8,1}$ 6.4, $J_{8,6}$ 2.1, 8-H), 5.39 (ddd, $J_{9,F}$ 10, $J_{9,1}$ 6.7, $J_{9,6}$ 1.3, 9-H), 3.16 (m, 1-H, 6-H), 2.88 (br d, $J_{5,5'}$ 17, 5-H), 2.73 (br d, H-5'), 2.60 (br s, H-2, H-2'), 1.61 (s, CH_3) and 1.57 (s, CH_3); δ_C 160.6 (C-10), $J_{C,F}$ 264), 148.2 (C-8), 123.0 (C-4), 122.2 (C-3), 117.3 (CN), 115.3 (C-7, $J_{C,F}$ 8), 102.6 (C-9, $J_{C,F}$ 13), 46.16 (C-2), 44.37 (C-5, $J_{C,F}$ 3), 39.47 (C-6, $J_{C,F}$ 29), 35.33 (C-1), $J_{C,F}$ 8), 24.47 (CH_3) and 24.26 (CH_3); δ_F − 75.9 relative to CFCl$_3$; v_{max}/cm^{-1} (CCl$_4$) 2219m and 1655w (Found: C, 76.6; H, 7.0; F, 9.5; N, 6.94. $C_{13}H_{14}FN$ requires C, 76.82; H, 6.94; F, 9.35; N, 6.89%).

7-Cyano-1-fluoro-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 24. Separated and purified by preparative GC. δ_H 6.92 (dd, $J_{8,F}$ 11, $J_{8,1}$ 1.5, 8-H), 6.10 (m, $J_{9,F}$ 11.5, $J_{9,10}$ 8.9, $J_{9,6}$ 0.7, 9-H), 6.06 (m, $J_{10,6}$ 5.4, 10-H), 3.17 (m, $J_{6,5}$, $J_{6,5'}$ 4.5, 6-H), 2.79 (br d, 2-H, 2'-H), 2.68 (br dd, $J_{5,F}$ 18, 5-H), 2.55 (br dd, $J_{5',F}$ 18, 5'-H), 1.56 (s, CH_3) and 1.53 (s, CH_3); δ_C 147.0 (C-8, $J_{C,F}$ 29), 130.2 (C-9, $J_{C,F}$ 27), 128.2 (C-10, $J_{C,F}$ 12), 123.5 (C-4), 123.4 (C-3), 120.7 (C-7, $J_{C,F}$ 14), 116.9 (CN), 52.15 (C-2, $J_{C,F}$ 30), 46.56 (C-1, $J_{C,F}$ 186), 43.01 (C-5, $J_{C,F}$ 4.5), 38.16 (C-6), 24.41 (CH_3) and 23.86 (CH_3); δ_F − 138.7 relative to CFCl$_3$; v_{max}/cm^{-1} (CCl$_4$) 2229m and 1644m (Found: M$^+$, 203.1111. Calc. for $C_{13}H_{14}FN$; M, 203.1110).

7-Cyano-9-fluoro-3,4-dimethylbicyclo[4.2.2]*deca-3,7,9-triene* 25. M.p. 95–96 °C; δ_H 6.83 (ddd, $J_{8,1}$ 6.5, $J_{8,F}$ 3.7, $J_{8,6}$ 1.0, 8-H), 5.43 (ddd, $J_{10,F}$ 9.9, $J_{10,6}$ 6.9, $J_{10,1}$ 1.7, 10-H), 3.20 (m, 6-H), 3.12 (m, 1-H), 2.90 (br d, $J_{5,5'}$ 17, 5-H), 2.80 (m, $J_{2,2'}$ 17, 2'-H), 2.60 (br d, 2-H, 5'-H) and 1.60 (s, 2 CH_3); δ_C 161.1 (C-9, $J_{C,F}$ 265), 145.7 (C-8, $J_{C,F}$ 7), 122.9 (C-4), 122.2 (C-3), 117.8 (CN), 117.3 (C-7), 102.6 (C-10, $J_{C,F}$ 14), 46.4 (C-5), 44.3 (C-2, $J_{C,F}$ 3), 38.3 (C-1, $J_{C,F}$ 28), 37.08 (C-6, $J_{C,F}$ 8), 24.48 (CH_3) and 24.27 (CH_3); δ_F(C$_6$D$_6$) − 39.0 relative to CFCl$_3$; v_{max}/cm^{-1} (CCl$_4$) 2221m (Found: C, 76.6; H, 7.0; F, 9.4; N, 6.9. $C_{13}H_{14}FN$ requires C, 76.82; H, 6.94; F, 9.35; N, 6.89%).

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