# Intramolecular Photocycloaddition of 4-Phenoxybut-1-enes: a Convenient Access to the 4-Oxatricyclo[7.2.0.0³,⁷]undeca-2,10-diene Skeleton

Siham Y. Al-Qaradawi, Kevin B. Cosstick and Andrew Gilbert*
*Chemistry Department, The University of Reading, Whiteknights, PO Box 224, Reading, Berkshire RG6 2AD, UK*

The photochemistry of 4-phenoxybut-1-ene is markedly influenced by the presence and position of electron-withdrawing substituents on the benzene ring. A cyano substituent in the 2'- or 4'-position promotes an efficient intramolecular cycloaddition to give good yields of the 4-oxatricyclo-[7.2.0.0³,⁷]undeca-2,10-dienes, by way of the photolabile 11-oxabicyclo[6.3.0]undeca-1,3,5-triene, the precursor of which is presumed to be a thermally labile intramolecular *ortho* photocycloadduct. The 3'-cyano isomer reacts inefficiently and only the 2'-isomer in the methoxycarbonyl series undergoes the photocycloaddition. The formation of the trienes is efficiently quenched by 1,3-dienes but their intramolecular cyclisation is unaffected by the presence of the triplet quenchers.

Intramolecular arene–ethene *meta* photocycloaddition occurs with high chemical and quantum yields for numerous derivatives of 5-phenylpent-1-ene.[1–3] Such photoreaction of these non-conjugated bichromophores currently attracts considerable interest as a convenient and versatile key step in the synthesis of a variety of polycyclic compounds.[3–5] However, the predominant photoprocess for 4-phenoxybut-1-enes appears to be the formation of much polymeric material:[6,7] the intramolecular cycloaddition is thus inefficient despite appreciable intramolecular quenching of the arene fluorescence by the ethenyl moiety in at least one case,[6] and the ready intermolecular photoaddition of alkenes, cycloalkenes and enol ethers to the 2,6-positions of alkoxybenzenes.[3,8,9]

It has, however, been noted that the photocycloadditions of anisole are markedly influenced both by the presence and position of an electron-withdrawing substituent on the arene and by the electron donor–acceptor characteristics of the ethene addend.[10] Thus, while 3-cyanoanisole undergoes efficient *meta* cycloaddition to (*Z*)-cyclooctene and is comparatively unreactive in the presence of either ethyl vinyl ether or acrylonitrile, the 4-isomer yields a *meta* cycloadduct with the cycloalkene, two *ortho* cycloadducts with ethyl vinyl ether, and with acrylonitrile undergoes [1.2] cycloaddition of the nitrile group to give an azacyclooctatetraene as well as *ortho* cycloaddition. Furthermore, of these ethenes, only the enol ether undergoes addition to any appreciable extent with 2-cyanoanisole. This reaction is, however, efficient and ultimately leads to a facile synthesis of functionalized bicyclo[4.2.0]octa-2,7-dienes.[11] In view of these remarkable differences in the intermolecular photoreactivity of the cyanoanisoles towards ethenes, we studied the influence of electron-withdrawing substituents on the photoprocesses of 4-phenoxybut-1-enes.

During our early work on the photoreactions of these non-conjugated bichromophores, Professor P. J. Wagner kindly

alerted us to his unpublished studies into the photoreactions of valerophenones 1 which had a but-3-enyloxy substituent on the benzene ring. In these systems the Type II reaction of the 2- and 4-isomers is quenched and intramolecular [1,2] photocycloaddition of the ethene onto the benzene ring occurs. Both these results from the phenones[12–14] and our preliminary observations[15] with the corresponding nitriles have been described. In the present paper we give full details of our studies into the intramolecular photoreactions of substituted 4-phenoxybut-1-enes and discuss mechanistic aspects of these highly selective processes.

## Results and Discussion

The influence on the photochemistry of 4-phenoxybut-1-ene of electron-withdrawing substituents on the arene has been investigated with the cyano and methoxycarbonyl substituted bichromophores 2a–f. These non-conjugated bichromophoric compounds were readily synthesised by $S_N2$ reactions of the phenolate anion on 4-bromobut-1-ene. The absorption spectra of the substituted 4-phenoxybut-1-enes exhibited only minor differences in the wavelength maxima and absorptivities from those of the corresponding anisoles thus indicating no significant interaction between the chromophores in the ground state. Furthermore, the absorption characteristics are closely similar within the *ortho*, the *meta* and the *para* series of the substituted bichromophores and anisoles. As discussed by Lui and McGlynn the 2- and 3-cyanoanisoles have similar characteristics but these are markedly different from those of the 4-isomer.[16] The lowest energy transition in the former isomers ($\lambda_{max}$ 295 and 298 nm, respectively) and the much weaker structured tail absorption in this region of 4-cyanoanisole are considered to arise from predominantly $\pi$–$\pi$* ($S_0$–$S_1$) excitation of the arene. At shorter wavelengths, the intense absorption of the 4-isomer ($\lambda_{max}$ 245 nm; $\varepsilon$ 20 000 dm³ mol⁻¹ cm⁻¹) and the corresponding weaker bands of the 2- and 3-isomers ($\lambda_{max} \simeq 230$ nm; $\varepsilon \simeq 7000$ dm³ mol⁻¹ cm⁻¹) are assigned to excitation to a state which is a mixture of the $\pi$–$\pi$* arene (from an $S_0$–$S_2$ transition) and the charge-transfer components of the electron-donor electron-acceptor substituted arene (*i.e.* intramolecular charge-transfer bands). No significant differences in the photochemistries of the bichromophores were observed on changing the wavelength of irradiation. The isomers of the two series did, however, display markedly differing photoreactivities.

Irradiation of 1% w/v solutions of the 3'-cyano isomer 2b in solvents of varying polarity produced trace amounts (<1%
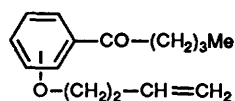


1
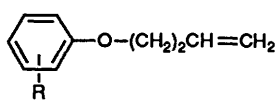
2

a; R = 2'-CN
b; R = 3'-CN
c; R = 4'-CN
d; R = 2'-CO₂Me
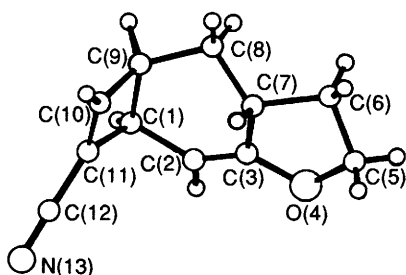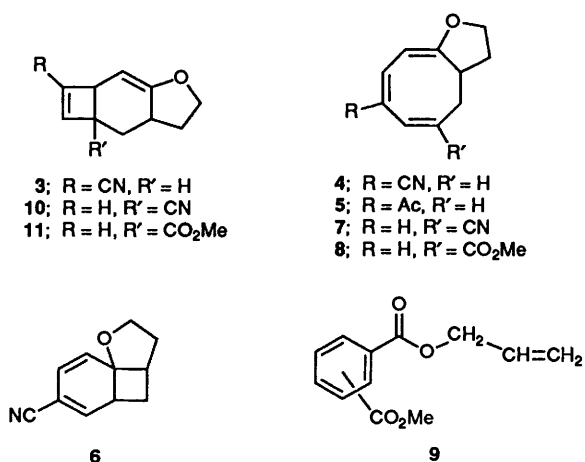e; R = 3'-CO₂Me
f; R = 4'-CO₂Me

**Fig. 1** Molecular structure of 3

conversion after 24 h) of an isomer ($M^+$, 173) and polymeric material: approximately 95% of the bichromophore was then recovered. In contrast, solutions of both the 2'- and 4'-substituted isomers **2a** and **2c** rapidly turned yellow on irradiation and each by GC–MS analysis showed the formation of two isomers. The ratio of the product isomers from both bichromophores was time dependent. Thus the 3:1 ratio (order of elution on non-polar GC columns) at 5% conversion of the 4'-cyano bichromophore became 1:18 respectively at total consumption of the starting material and for the 2'-isomer the ratios of the corresponding isomers were 1:1 at 5% and 1:20 at 50% conversions. In both cases chemical yields of the photostable isomer were of the order of 90%.

The photostable isomer from **2c** was shown by spectroscopic analysis and X-ray crystallographic determination of a single crystal[15] to be 11-cyano-4-oxatricyclo[7.2.0.0³·⁷]undeca-2,10-diene 3 (see Fig. 1). The yellow photolabile isomer was isolated by flash chromatography from solutions irradiated to 50% conversion and was identified as the cycloocta-1,3,5-triene 4 from its spectral data and their comparison with those provided by Wagner and Nahm for the corresponding product 5 from the irradiation of the 4'-acetyl bichromophore.[13] The triene 4 readily polymerised thermally but was quantitatively converted into the stable isomer 3 by 320 nm irradiation (*i.e.* at the $\lambda_{max}$ of the triene absorption) of its cyclohexane solutions. Reversal of this process thermally could be achieved by heating a solution of 3 in anisole at 150 °C but the process was also accompanied by extensive polymer formation.



**3**; R = CN, R' = H
**10**; R = H, R' = CN
**11**; R = H, R' = CO₂Me

**4**; R = CN, R' = H
**5**; R = Ac, R' = H
**7**; R = H, R' = CN
**8**; R = H, R' = CO₂Me



**6**



**9**

The obvious precursor of the triene 4 is the intramolecular *ortho* photocycloadduct 6 but all attempts to detect this isomer chromatographically or spectroscopically were unsuccessful. Attempts to trap 6 by its reaction with *N*-phenylmaleimide did produce trace amounts of a component in the reaction mixture from refluxing toluene which had a molecular ion of 346 a.m.u.

corresponding to that of the Diels–Alder adduct. However, separation of this product was not achieved and the only evidence for the formation of 6 thus lies in the isolation of its ring-opened product, the triene 4. Nonetheless, we conclude that the primary photoproduct of **2c** is the *ortho* cycloadduct 6: this then undergoes extremely rapid disrotatory thermal ring opening to yield the all-*cis* cycloocta-1,3,5-triene 4 which, as shown by experiment, is photochemically labile and readily cyclises in a disrotatory manner to give the *cis*-fused bicyclo[4.2.0]octa-2,7-diene unit as required in the structure 3.

Similar results were observed from the irradiation of the 2'-cyano- and 2'-methoxycarbonyl bichromophores **2a** and **2d**, respectively. The primary intramolecular *ortho* cycloadducts were again not detected. The respective 6-substituted 11-oxa-bicyclo[6.3.0]undeca-1,3,5-trienes 7 and 8 were detected by their absorption maxima at *ca.* 335 nm: their rates of formation were approximately half that of 4 from **2c**. As noted for the products from the corresponding 2'-acetyl bichromophores,[13] the thermal retro process of the photostable isomer to give the all *cis* cycloocta-1,3,5-triene cannot be a concerted electrocyclic process but could be induced by donor–acceptor conjugation weakening the C–C bridge of the bicyclo[4.2.0]octa-2,7-diene unit. This feature may also assist in the facile ring opening of the primary *ortho* photocycloadduct for the 2'-substituted isomers but is unlikely to be the sole origin of the seemingly equally rapid conversion of 6 into 4 from the 4'-isomer or the thermal retro process of the photostable isomer 3.

The 3'-methoxycarbonyl bichromophore **2e** was essentially unaffected by 254 nm radiation and was recovered almost quantitatively after 14 days exposure. Surprisingly, the 4'-methoxycarbonyl isomer **2f** also did not undergo any detectable intramolecular cycloaddition of the type described above but instead was rapidly converted into polymeric material: this behaviour resembles that of the parent 4-phenoxybut-1-ene.

The intramolecular *ortho* cycloadditions observed for **2a, c** and **d** are unexpected. From the precedent of the intermolecular reactions of cyanoanisoles with alkenes, it may be considered that the 3'- and 4'-substituted 4-phenoxybut-1-ene bichromophores would undergo 2',6'-intramolecular addition to give the 1,6-bridged dihydrosemibullvalene skeleton, while the 2'-isomer may react inefficiently, if at all.[10,17] Furthermore, *ortho* cycloaddition is generally only observed as a major process for addend pairs having clearly defined electron donor–electron acceptor relationships,[18] and intramolecular *ortho* cycloaddition to the benzene has only previously been reported for rather specialised cases such as the Diels–Alder adduct of 1,4-naphthoquinone and cyclopentadiene[19] and 3-(pentafluorophenoxy)propene.[20] Our findings concerning intermolecular additions of the present type will be published in full elsewhere but it is noteworthy here that the formation of the photostable bicyclo[4.2.0]octa-2,7-dienes is only efficient and selective for anisoles having an electron-withdrawing substituent (cyano, acetyl, methoxycarbonyl) at the 2-position and with enol ethers or enol alkanoates as the addends.[21] The present reactions and those reported by Professor Wagner's group[12–14] are thus remarkable.

From orbital symmetry correlation anslysis of modes of cycloaddition of ethenes to benzene, it is deduced that the *ortho* addition is forbidden as a concerted process from the $S_1$ arene and $S_0$ ethene unless mixing of charge-transfer states occurs:[22] it is, however, allowed as a concerted homopolar reaction between the $S_0$ ethene and benzene of $B_{1u}$ symmetry (the $S_2$ or $T_1$ state). In agreement with the requirement for polar intermediates in the reaction pathway, it has been concluded that the intramolecular cycloaddition of the 2'- and 4'-acetyl substituted 4-phenoxybut-1-enes involve charge-transfer interaction between the ethene (donor) and the arene (acceptor).[14] Furthermore, the photoreaction of these bichromophores must

proceed by way of the triplet $\pi,\pi^*$ state of the arene moiety. For the present bichromophores **2a, c, d,** the involvement of polar intermediates is supported, as with other reported arene–ethene *ortho* photocycloadditions,[23] by the marked increase in the rates of product (*i.e.* the octa-1,3,5-trienes) formation on increase in the polarity of the solvent (*e.g.* four-fold increase on changing from cyclohexane to acetonitrile). However, unlike the intramolecular addition of the alkenyloxy aryl ketones, the corresponding process for the nitrile and methoxycarbonyl bichromophores **2** does not necessarily arise from the triplet $\pi,\pi^*$ state of the arene. Comparison of the fluorescence spectral intensities of the cyano-substituted bichromophores **2a, b** and **c** with the analogues having a saturated side chain showed that intramolecular interaction does occur between the $S_1$ arene and the $S_0$ ethene. However, the fluorescence quenching is only approximately 50% in all three cases and this is appreciably less than in other arene–ethene bichromophores[6] which are assumed to undergo the cycloadditions from the singlet $\pi,\pi^*$ arene. We have observed by GC monitoring that the photoreactions of **2a** and **2c** are quenched in the presence of low concentrations of 2,5-dimethylhexa-2,4-diene or 2,3-dimethylbuta-1,3-diene.

Reproducibility of the numerical data was, however, unsatisfactory, probably as a result of the unpredictable thermal lability of the cycloocta-1,3,5-trienes under the conditions of their estimation, and the formation of traces of light-absorbing by-products. The use of absorption spectroscopy to monitor the cycloocta-1,3,5-triene formation proved more reliable and, furthermore, this procedure provided evidence for the formation of this isomer from **2b**. The 1,3-dienes (0.50 mol dm$^{-3}$) quenched the rate of formation of the trienes ($\lambda_{max}$ of 340, 333 and 320 nm from **2a, 2b** and **2c,** respectively) by approximately 50% in cyclohexane solution. The rapid photocyclisation of the trienes from **2a** and **2c** induced by irradiation at 340 and 320 nm, respectively was unaffected by the presence of the 1,3-dienes and this reaction is thus deduced to be a singlet process. In contrast, the 333 nm absorption produced on irradiation of the 3'-isomer **2b** at 290 nm disappeared very slowly photochemically in the absence or presence of the quencher, but did decay thermally at approximately three times the rate of the corresponding absorptions from **2a** and **2c**. A detailed study of the photophysical properties of these bichromophores is to be undertaken but from the present findings it is evident that the primary photoreaction of intramolecular *ortho* cycloaddition of the ethene moiety to the benzene ring involves the $^3\pi,\pi^*$ state of the arene and the subsequent cyclisation of the cycloocta-1,3,5-triene arises from the singlet state. It is interesting to note that while the absorption and fluorescence spectral data of the cyanoanisoles differ markedly, the effects of substituent position on the triplet state are much less pronounced and, in particular, for all three isomers there is appreciably less intramolecular charge-transfer character mixed into the arene $^3\pi,\pi^*$ state than in the corresponding $S_1$ state.[16]

The photoreactions of **2a, 2c** and **2d,** and those reported for the 2'- and 4'-acetyl derivatives are the first examples of cycloaddition of an ethene to the $^3\pi,\pi^*$ state of the benzene ring. Furthermore, they provide a convenient, efficient, and high-yielding access to the 4-oxatricyclo[7.2.0.0$^{3,7}$]undeca-2,10-diene skeleton. However, the scope of the process does not extend to the isomeric bichromophores in which the alkenyl side chain is attached to the carbonyl or methoxycarbonyl function since no intramolecular photocycloaddition from either 1-(2'-methoxyphenyl)pent-4-en-1-one or the allyl methoxybenzoates has been observed.[24]

The photostability in these examples may result from a conformation, as in **9,** in which the intervening unit inhibits interaction between the arene and ethene chromophores.

## Experimental

*Bichromophores.*—The bichromophores **2a–f** were synthesised by the common method of reaction of 4-bromobut-1-ene with the appproriate phenolate anion. The synthesis of **2a** is given to illustrate the procedure. 4-Bromobut-1-ene (8.9 g, 0.066 mol) was added over 20 min to a vigorously stirred mixture of 2-cyanophenol (7.9 g, 0.066 mol) and anhydrous potassium carbonate (45 g) in refluxing butan-2-one (100 ml). Refluxing was continued for a further 6 h, by which time complete consumption of the phenol was evident by TLC. The cooled mixture was filtered and the solvent removed from the filtrate by rotary evaporation. The residue was taken up in diethyl ether (50 cm$^3$) and this solution was washed twice with 2 mol dm$^{-3}$ aqueous sodium hydroxide (30 cm$^3$), twice with water (30 cm$^3$) and dried (MgSO$_4$). Removal of the diethyl ether and vacuum distillation of the resulting yellow residue (0.1 mmHg/110–115 °C) gave **2a** (9.1 g) as a colourless liquid (80%).

4-(2'-*Cyanophenoxy*)*but-1-ene* **2a.** $\delta_H$(CD$_3$CN), 7.6 (overlapping m's, 3'-H, 5'-H), 7.1 (overlapping m's, 4'-H, 6'-H), 5.9 (q of t, $J_{2,1(trans)}$ 17, $J_{2,1(cis)}$ 12.5, $J_{2,3}$ 8, 2-H), 5.3–5.1 (m, $J_{gem}$ 2, $J_{1(cis),3}$ 1.5, $J_{1(trans),3}$ 1.75, 1-H$_2$), 4.2 (t, $J_{4,3}$ 8.5, 4-H$_2$) and 2.5 (ddd, t, 3-H$_2$); $\nu_{max}$/cm$^{-1}$ 2230m and 1647w; $\lambda_{max}$/nm (ethanol) 293 and 232, $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 2100 and 7000, respectively (Found: [M + NH$_4$]$^+$ 191.1181. Calc. for C$_{11}$H$_{15}$N$_2$O: *M,* 191.1184).

4-(3'-*Cyanophenoxy*)*but-1-ene* **2b.** $\delta_H$(CD$_3$CN), 7.5–7.2 (overlapping m's aromatic H$_4$), 6.2 (q, of t, $J_{2,1(trans)}$ 16.5, $J_{2,1(cis)}$ 12, $J_{2,3}$ 8, 2-H), 5.25 (m, $J_{gem}$ 2, $J_{1(cis),3}$ 1.25, $J_{1(trans),3}$ 1.75, 1-H$_2$), 4.2 (t, $J_{4,3}$ 8.5, 4-H$_2$) and 2.5 (ddd, t, 3-H$_2$); $\nu_{max}$/cm$^{-1}$ 2230m and 1645; $\lambda_{max}$/nm (ethanol) 291 and 230, $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 3000 and 7000, respectively (Found: [M + NH$_4$]$^+$ 191.1182. Calc. for C$_{11}$H$_{15}$N$_2$O: *M,* 191.1184).

4-(4'-Cyanophenoxy)but-1-ene **2c**. $\delta_H$ 7.5 (dd, $J_{ortho}$ 8.5, $J_{para}$ 2, 2'-H, 6'-H), 6.8 (dd, 3'-H, 5'-H), 5.8 (q of t, $J_{2,1(trans)}$ 17, $J_{2,1(cis)}$ 12.5, $J_{2,3}$ 8, 2-H), 5.3–4.9 (m, $J_{gem}$ 2, $J_{1(cis),3}$ 2, $J_{1(trans),3}$ 1.75, 1-H$_2$), 4.0 (t, $J_{4,4}$ 8.5, 4-H$_2$) and 2.5 (ddd, t, 3-H$_2$); $\lambda_{max}$/cm$^{-1}$ 2231m and 1648w; $\lambda_{max}$/nm (ethanol) 245, $\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ 22 000 (Found: [M + NH$_4$]$^+$ 191.1183. Calc. for C$_{11}$-H$_{15}$N$_2$O: $M$, 191.1184).

4-(2'-Methoxycarbonylphenoxy)but-1-ene **2d**. $\delta_H$ 7.2 (overlapping m's, 3'-H, 5'-H), 6.7 (overlapping m's, 4'-H, 6'-H), 5.7 (q of t, $J_{2,1(trans)}$ 16, $J_{2,1(cis)}$ 12.5, $J_{2,3}$ 8, 2-H), 5.1–4.7 (m, $J_{gem}$ 2, $J_{1(cis),3}$ 1.5, $J_{1(trans),3}$ 1.75, 1-H$_2$), 3.8 (t, $J_{4,3}$ 8.5, 4-H$_2$), 3.5 (s, –CH$_3$) and 2.3 (ddd, t, 3-H$_2$); $\nu_{max}$/cm$^{-1}$ 1710s and 1602m; $\lambda_{max}$/nm (ethanol) 293 and 230, $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 2500 and 6800, respectively (Found: M$^+$, 206.0943. Calc. for C$_{12}$H$_{14}$O$_3$: $M$, 206.0943).

4-(3'-Methoxycarbonylphenoxy)but-1-ene **2e**. $\delta_H$(CCl$_4$), 7.6–6.8 (overlapping m's, aromatic-H$_4$), 5.9 (q of t, $J_{2,1(trans)}$ 17, $J_{2,1(cis)}$ 12, $J_{2,3}$ 8.5, 2-H), 5.3–4.9 (m, $J_{gem}$ 2, $J_{2(cis),3}$ 1.5, $J_{1(trans),3}$ 1.75, 1-H$_2$), 4.0 (t, $J_{4,3}$ 8.5, 4-H$_2$), 3.8 (s, –CH$_3$) and 2.5 (ddd, t, 3-H$_2$); $\nu_{max}$/cm$^{-1}$ 1728s and 1645w; $\lambda_{max}$/nm (ethanol) 295 and 231, $\varepsilon$/cm$^3$ mol$^{-1}$ cm$^{-1}$ 2500 and 6900, respectively (Found: M$^+$, 206.0945. Calc. for C$_{12}$H$_{14}$O$_3$: $M$, 206.0943).

4-(4'-Methoxycarbonylphenoxy)but-1-ene **2f**. $\delta_H$ 7.9 (dd, $J_{ortho}$ 8.5, $J_{para}$ 2, 2'-H, 6'-H), 6.9 (dd, 3'-H, 5'-H), 6.0 (q, of t, $J_{2,1(trans)}$ 17, $J_{2,1(cis)}$ 12, $J_{2,3}$ 8.5, 2-H), 5.3–4.9 (m, $J_{gem}$ 2.5, $J_{1(cis),3}$ 1.5, $J_{1(trans),3}$ 1.75, 1-H$_2$), 4.0 (t, $J_{4,3}$ 8.5, 4-H$_2$), 3.9 (s, –CH$_3$) and 2.5 (ddd, t, 3-H$_2$); $\nu_{max}$/cm$^{-1}$ 1718s and 1609m; $\lambda_{max}$/nm (ethanol) 256, $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 24 000 (Found: M$^+$, 206.0946. Calc. for C$_{12}$H$_{14}$O$_3$: $M$, 206.0943).

*Photoproducts.*—11-*Cyano-4-oxatricyclo*[7.2.0.0$^{3,7}$]*undeca-2,10-diene* **3**. M.p. 78–79 °C (methanol); $\delta_H$(C$_6$D$_6$) 6.00 (br d, $J_{10,9}$ 1.1, $J_{10,2}$ 0.5, 10-H), 4.89 (br dd, $J_{2,1}$ 5, $J_{2,7}$ 2.5, $J_{2,6}$ 1, 2-H) 3.78 (overlapping dds, $J_{gem}$ 9, $J_{5exo,6exo}$ 9, $J_{5exo,6endo}$ 1, $J_{5exo,7}$ 0.5, 5-H$_{exo}$), 3.50 (m, 8 lines, $J_{5endo,6endo}$ 12, $J_{5endo,6exo}$ 5.5, 5-H$_{endo}$), 3.2 (d of dd, $J_{1,9}$ 4, $J_{1,7}$ 1, 1-H), 2.56 (m, 10 lines, $J_{9,8exo}$ 6, $J_{9,8endo}$ 2, 9-H), 1.76 (m, $J_{7,8exo}$ 11.5, $J_{7,8endo}$ 5.5, 7-H), 1.5 (m, $J_{6gem}$ 20, $J_{8gem}$ 13, 6-H$_{exo}$, 8-H$_{endo}$), 1.08 (m, 6-H$_{endo}$) and 0.64 (m, 8 lines, 8-H$_{exo}$); $\delta_C$(22.49 MHz, C$_6$D$_6$) 161.94 (C-3), 150.10 (C-10), 128.27 (C-2), 121.40 (CN), 113.90 (C-11), 87.69 (C-7), 69.10 (H-5), 44.16 (C-1), 42.90 (C-9), 33.67 (C-6) and 31.13 (C-3); $\nu_{max}$/cm$^{-1}$ (Nujol mull) 2220w (Found: M$^+$, 173.0839. Calc. for C$_{11}$H$_{11}$NO: $M$, 173.0841).

4-*Cyano-11-oxabicyclo*[6.3.0]*undeca-1,3,5-triene* **4**. $\delta_H$ 7.3 (d, $J_{2,3}$ 6.5, 2-H), 6.2 (d, $J_{5,6}$ 12.5, 5-H), 5.7 (m, $J_{6,7}$ 7, 6-H), 5.4 (d, 3-H), 4.4–4.0 (m's, $J_{gem}$ 7, 10-H$_2$) and 2.0–1.7 (m's, 9-H$_2$); $\nu_{max}$/cm$^{-1}$ 2224m, 1626w and 1610w; $\lambda_{max}$/nm (cyclohexane) 320, $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ 10 000 (Found: M$^+$, 173.0843. Calc. for C$_{11}$H$_{11}$NO: $M$, 173.0841).

9-*Cyano-4-oxatricyclo*[7.2.0.0$^{3,7}$]*undeca-2,10-diene* **10**. $\delta_H$-(CD$_3$CN) 5.67 (d, $J_{11,10}$ 3, 11-H), 5.59 (d, 10-H), 4.75 (dd, $J_{2,1}$ 6.5, $J_{2,7}$ 2.5, 2-H), 4.18 (dd, $J_{gem}$ 8, $J_{5exo,6exo}$ 8.2, $J_{5exo,6endo}$ 1, 5-H$_{exo}$), 3.93 (m, 8 lines, $J_{5endo,6exo}$ 10.5, $J_{5endo,6endo}$ 4.8, 5-H$_{endo}$), 3.71 (d, 1-H), 2.6 (m, $J_{7,8exo}$ 11.5, $J_{7,8endo}$ 5, 7-H), 1.9 (m, 6-H$_{endo}$, 8-H$_{endo}$), 1.74 (m, $J_{gem}$ 19, 6-H$_{exo}$) and 1.41 (m, $J_{gem}$ 12.5, 8-H$_{exo}$); $\nu_{max}$/cm$^{-1}$ 2224m and 1646w (Found: M$^+$, 173.0840. Calc. for C$_{11}$H$_{11}$NO: $M$, 173.0841).

9-*Methoxycarbonyl-4-oxatricyclo*[7.2.0.0$^{3,7}$]*undeca-2,10-diene* **11**. $\delta_H$(CDCl$_3$) 6.06 (s, 11-H, 10-H), 4.90 (dd, $J_{2,1}$ 6.5, $J_{2,7}$ 2.5, 2-H), 4.24 (overlapping dd, $J_{gem}$ 8.5, $J_{5exo,6exo}$ 8.4, $J_{5exo,6endo}$ 1, 5-H$_{exo}$), 3.99 (m, 8 lines, $J_{5endo,6exo}$ 11.5, $J_{5endo,6endo}$ 5.5, 5-H$_{endo}$), 3.70 (s, CH$_3$), 3.61 (br d, $J_{1,7}$ 1.2, 1-H), 2.52 (m, $J_{7,8exo}$ 11.7, $J_{7,8endo}$ 5.2, 7-H), 2.34 (dd, $J_{gem}$ 12.5, 8-H$_{endo}$), 2.23 (m, $J_{gem}$ 20, 6-H$_{endo}$), 1.77 (m, 6-H$_{exo}$) and 1.57 (m, 8-H$_{exo}$); $\nu_{max}$/cm$^{-1}$ 1729s (Found: M$^+$, 206.0942. Calc. for C$_{12}$H$_{14}$O$_3$: $M$, 206.0943).

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