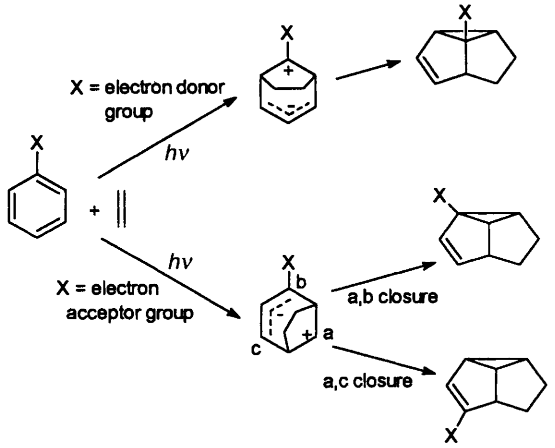
Formation of bicyclo[3.2.1]oct-2-en-8-ones and 1-hydroxydihydrosemibullvalenes from the *meta*-photocycloaddition of cyclopentene to phenols

Andrew Gilbert* and Damian T. Jones

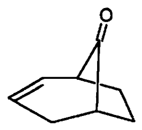
Department of Chemistry, The University of Reading, Whiteknights, PO Box 224, Reading, Berkshire, UK RG6 2AD

Cyano or trifluoromethyl substituents in the 3-position of phenol markedly promote the 2,6-photocycloaddition of cyclopentene. The cyanophenol yields both 2- and 4-cyanobicyclo[3.2.1]oct-2-en-8-ones 13 and 15 with little selectivity. In contrast, the photoreaction of 3-trifluoromethylphenol with cyclopentene gives solely stereoisomeric 1-hydroxy-2-trifluoromethyldihydrosemibullvalenes 23 and 24. The ketones are deduced to arise from a facile 1,5-hydrogen shift in the 1-hydroxydihydrosemibullvalenes. The specificity of the photoaddition to the trifluoromethylphenol and the stability of the resulting 1-hydroxydihydrosemibullvalenes are considered to originate from intramolecular hydrogen bonding between the hydroxy and trifluoromethyl groups.

The mechanism and synthetic scope of the *meta*-photocycloaddition of ethenes to the benzene ring has attracted considerable attention and interest.[1,2] since the first reports of this intriguing process appeared 30 years ago.[3] Both bicyclo[3.2.1]octenyl biradical and zwitterionic intermediates have been postulated in this process.[4] The latter species were favoured as the intermediates for some time since the observed regiochemistry of addition to substituted benzenes could be readily accounted for in terms of substituent stabilisation of charge centres as outlined in Scheme 1.[5] Full bonding between the ethene and the benzene ring may not, however, be a realistic proposal and, indeed, such high regioselectivity as reported for the photoaddition can also be conveniently rationalised by substituent stabilisation of the developing polarity in the S_1 benzene ring on approach of the S_0 ethene.[6] Several attempts have been undertaken to intercept the addition intermediates, particularly the zwitterionic species, but all have failed.[7]



Scheme 1



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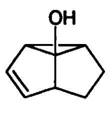

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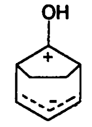

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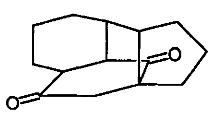

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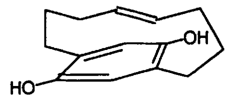

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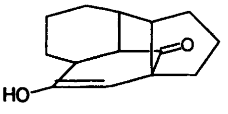

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The formation of bicyclo[3.2.1]oct-2-en-8-ones **1** rather than 1-hydroxydihydrosemibullvalenes **2**† from the photoaddition of cyclopentene to phenol[8] and (*E*)-1,2-dichloroethene to phenol and the cresols[9] is relevant to the concept of interception of zwitterionic intermediates in the *meta*-photocycloaddition process. Thus a plausible route to **1** would involve attack of the ethene at the 2,6-positions of the phenol and interception of the intermediate **3** (prior to cyclopropane ring closure and formation of **2**) by deprotonation of the hydroxy group and reprotonation at the delocalised allylic anion moiety. Such a proton migration pathway was not, however, considered as the route to the bicyclic ketones from the photoaddition of (*E*)-1,2-dichloroethene to phenol and the cresols.[9] Instead, protonation of the expected 1-hydroxydihydrosemibullvalenes at C-4 was suggested principally because HCl is evolved during the irradiation and the 1-methoxy-*meta*-photoadducts are readily converted to the bicyclic ketones on acid treatment.[8,10] Furthermore, in the only report of intramolecular *meta*-addition to a phenol, although it was suggested that the diketone photoisomer **4** from the (*E*)-2,5-oct-4-enohydroquinone **5** arose from hydrogen migration in a 'biradical' intermediate followed by tautomerism, it was also mentioned that ring closure to the 1-hydroxydihydrosemibullvalene system might precede the formation of the enol **6**.[11] The route for this conversion was not considered by the authors, but could in principle involve a homodienyl 1,5-sigmatropic shift from the 1-hydroxy group on the dihydrosemibullvalene skeleton to the 4-position. It is, however, pertinent to note that 1-hydroxydihydrosemibullvalenes **2** have never been detected in any system

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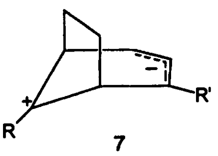
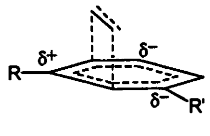
† IUPAC name: tricyclo[5.1.0.0^{4,8}]oct-2-en-8-ol.

and hence their role, if any, in the formation of the bicyclic ketones **1** has not been elucidated.

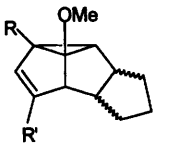
The photocycloaddition of cyclopentene to phenol is very inefficient and non-selective. We have investigated the photochemistry of selected phenols with cyclopentene in order to determine the factors which promote adduct formation and influence the type of photoproduct formed from these systems, and because such additions may provide information on the mechanism of *meta*-photocycloaddition to the benzene ring. The principal objective has been to assess the potential of using substituents on the phenol addend to control and promote the intramolecular cyclisation which gives the cyclopropane ring in the *meta*-cycloadduct precursor, whether this is a discrete bicyclo[3.2.1]octenyl zwitterion **7** or an interaction species **9** between the S_0 ethene and the polarised S_1 benzene. In this paper we describe these studies and discuss mechanistic pathways to the bicyclic ketones involving polarised adduct precursors and 1-hydroxy *meta*-photocycloadducts.



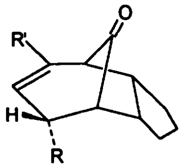
7
8 R = OH, R' = CN



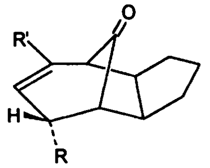
9
10 R = OH, R' = CN



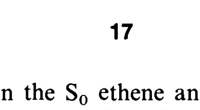
11 R = CN, R' = H
12 R = H, R' = CN



13 R = H, R' = CN
14 R = CN, R' = H



15 R = CN, R' = H
16 R = H, R' = CN



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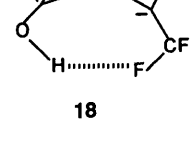

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Results and discussion

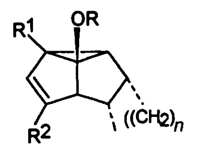
The phenol–cyclopentene systems in this study have addend electron donor and acceptor relationships which favour *meta*- rather than *ortho*-photocycloaddition to the benzene ring.[12] As for all electron donor substituents,[13] the hydroxy group is expected to direct the *meta*-photocycloaddition of an ethene to the 2,6-positions of the benzene ring. This regiochemistry is reflected in the formation of the bicyclic ketones from the photoaddition of cyclopentene to phenol,[8] and of (*E*)-1,2-dichloroethene to phenol and the cresols.[9] Electron withdrawing groups on the benzene ring stabilise the negative end of the polarised intermediate and hence reside on the 2- and/or 4-positions of the *meta*-adduct (Scheme 1). For benzene derivatives having electron donor and acceptor groups at the 1,3-positions, the charge stabilising influences of the substituents, therefore, reinforce one another and regiospecific addition occurs. Generally, however, there is little selectivity in the direction of cyclopropane ring formation (Scheme 1), although there is a marked preference for *endo*-stereochemistry. For example, the 2- and 4-cyano isomers **11** and **12** are formed from the addition of cyclopentene to 3-cyanoanisole in good yield with a respective ratio of 11 : 9, and 85% of the adduct mixture has *endo*-stereochemistry.[14] We examined the analogous reaction with 3-cyanophenol to assess if the charge stabilising influences of the substituent groups acting in concert would promote not only the overall addition, but also the intramolecular cyclisation within the polarised adduct precursor, thus giving the 1-hydroxydihydrosemibullvalene.

3-Cyanophenol–cyclopentene

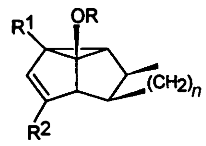
Irradiation (254 nm) of solutions of 3-cyanophenol and cyclopentene in acetonitrile, methanol or dioxane gave, as the major photoproducts, four adducts (respective relative retention times 1.0 : 1.1 : 1.2 : 1.3; GC–MS, M^+ 187 mu) in relative yields which varied appreciably from experiment to experiment in all solvents. However, the two shorter retention time adducts were always in the greater proportion. On prolonged irradiation, a secondary photoproduct (relative retention time 0.9, M^+ 159 mu) became the dominant component of the reaction mixture at the expense of the major adduct with the longer retention time. Treatment of the initial reaction mixture with HCl under a variety of conditions induced no change in the chromatogram, indicating either that no 1-hydroxy *meta*-adducts were present or that they were not susceptible to acidolysis. The former possibility was substantiated by the lack of reaction of any components of the mixture with phenyl isocyanate and the presence of carbonyl but no –O–H stretching absorptions in the infrared spectrum following removal of residual cyanophenol.

The components of the mixture proved extremely difficult to resolve on a preparative scale but following repeated flash chromatography of the reaction mixture from prolonged irradiation, samples of the photoproducts of relative GC retention times of 0.9, 1.0, and 1.3 were isolated with the necessary purity (one spot TLC and one component by GC). From spectral data, the two 1 : 1 adducts were deduced to have the *endo*- and *exo*-tricyclo[5.3.1.$0^{2,6}$]undec-8-en-11-one structures **13** and **15**, respectively, and the shortest retention time product was identified as the 3-cyanotricyclo[5.3.0.$0^{2,6}$]dec-4-ene **17**. Evidently, **17** arises from photodecarbonylation of a tricyclo[5.3.1.$0^{2,6}$]undec-8-en-11-one. The absence of the *endo*-isomer **14** in this mixture would be consistent with this adduct being the photochemical precursor of **17**, and in support of this proposal, of the possible photoproducts from this system, only **17** and isomers **13** and **14** would have the observed seven C–H coupled carbons in the ^{13}C DEPT-90 analysis. Furthermore, at short exposure times the adduct isomer of relative retention time 1.1 was the major reaction product, and the ^{1}H NMR spectrum of the crude mixture had the most intense signals in the ethenyl proton region as doublets of doublets at 5.94 and 5.68 ppm. The appearance of these unassigned signals is closely similar to that of the corresponding ones in the *exo*-isomer **15** and thus they are considered to arise from the major adduct which is deduced to be the *endo*-isomer **14**. The fourth (minor) photoadduct could not be isolated with sufficient purity for unambiguous analysis but from ^{1}H NMR spectral data of an 85% enriched mixture, it is tentatively deduced to be the 'missing' *exo*-isomer **16**.[15] Thus all the major products are deduced to be derivatives of bicyclo[3.2.1]oct-2-en-8-one and, in particular, no spectroscopic evidence was obtained from irradiation of 3-cyanophenol and cyclopentene in any solvent for the presence of 1-hydroxy *meta*-photocycloadducts in the reaction product mixture. The influence of the 3-cyano substituent in promoting the efficiency and selectivity of the photoaddition of cyclopentene to phenol was emphasised by the low yield of multicomponent mixtures from the corresponding experiments with 2- and 4-cyanophenols.

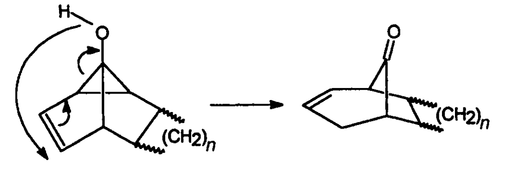
Under the non-acidic conditions of the photoaddition of cyclopentene to 3-cyanophenol [contrast photoadditions of (*E*)-dichloroethene to phenols],[9] the involvement of protonation of 1-hydroxy *meta*-cycloadducts at the 4-position in the formation of the bicyclic ketones is discounted. However, the fact that only one of the two 5-cyano stereoisomers of both the *endo*- and *exo*-tricyclo[5.3.1.0^{2,6}]undec-8-en-11-ones (*i.e.* **14** and **15**) was formed suggests a more sterically discriminating mechanism operates in their formation than would be expected from a deprotonation–protonation sequence in a polar intermediate. While such a proton migration mechanism in **8** and/or **10** cannot be totally discounted on this evidence, it is far more likely that the selective *endo*-stereochemistry of the 5-hydrogen results from a thermal suprafacial 1,5-hydrogen shift in the respective 1-hydroxy-4-cyanodihydrosemibullvalenes **19** and **20**: the 3-cyano tricyclic ketones **14** and **16** would similarly arise from the 1-hydroxy-2-cyanodihydrosemibullvalenes **21** and **22**. This 1,5-shift route to the bicyclic ketone has not been previously discussed[2] and remains speculative until the 1-hydroxydihydrosemibullvalenes are isolated and their stability assessed.



19 R = R^1 = H, R^2 = CN, *n* = 3
21 R = R^2 = H, R^1 = CN, *n* = 3
23 R = R^2 = H, R^1 = CF$_3$, *n* = 3
25 R = Me, R^1 = CF$_3$, R^2 = H, *n* = 3
27 R = CONHC$_6$H$_5$, R^1 = CF$_3$, R^2 = H, *n* = 3
29 R = R^2 = H, R^1 = CF$_3$, *n* = 6



20 R = R^1 = H, R^2 = CN, *n* = 3
22 R = R^2 = H, R^1 = CN, *n* = 3
24 R = R^2 = H, R^1 = CF$_3$, *n* = 3
26 R = Me, R^1 = CF$_3$, R^2 = H, *n* = 3
28 R = CONHC$_6$H$_5$, R^1 = CF$_3$, R^2 = H, *n* = 3
30 R = R^2 = H, R^1 = CF$_3$, *n* = 6



31

We investigated the possibility of using intramolecular hydrogen bonding between the hydroxy group of the phenol and a fluorine atom, both to inhibit any proton migration in an intermediate polar species thereby promoting intramolecular cyclisation and to stabilise the resulting *meta*-photocycloadduct. The first system examined was 2-fluorophenol with cyclopentene, but this only gave minor amounts of solvent dependent product mixtures. The potential of the trifluoromethyl substituent to produce the required control for the photocycloaddition of an ethene to a phenol was then examined.

3-Trifluoromethylphenol–cyclopentene

The trifluoromethyl group stabilises a negative charge by the inductive effect of the fluorine atoms and hence its placement at the 3-position on a benzene ring, relative to an electron donor substituent, allows the directing influences of the two groups on *meta*-photocycloaddition to reinforce one another. Furthermore, if there is a degree of negative charge localisation induced by the –CF$_3$ group, then formation of the cyclopropane ring between the 1,3-positions would be promoted and the 2-trifluoromethyl-substituted dihydrosemibullvalene may be formed selectively. But in the addition of cyclopentene to 3-trifluoromethylanisole there is little sign of such selectivity, and the 2- and 4-substituted 1-methoxydihydrosemibullvalenes are formed in proportions of 52:48, respectively.[7b] There is, however, a secondary substituent effect possible in 3-trifluoromethylphenol which requires consideration. Molecular models suggest that as the benzene ring distorts from planarity during the addition of the ethene, the hydroxy hydrogen and the fluorine atoms may achieve a sufficiently close approach to favour hydrogen bonding. This feature may be expected not only to inhibit proton migration and to stabilise the final adduct, but also to induce an asymmetric distortion of the C$_6$ ring as depicted in **18** for the zwitterionic species. Thus the 1,3-positions increase in proximity and thereby cyclopropane ring formation would be promoted between these carbons in preference to a 1,5-closure. If this reasoning is valid, selectivity of addition would be observed for the phenol but would not be expected for the corresponding anisole.

Monitoring the irradiation of the 3-trifluorophenol–cyclopentene system by GC–MS indicated the formation of numerous products, some of which were 1:1 adducts and others were adducts which had lost the elements of HF; furthermore, no distinct components could be resolved by silica or alumina TLC. The ^{1}H NMR spectrum of the crude reaction product at either low or high conversion of the phenol was, however, unexpectedly simple and clearly showed that only two photoproducts, in an approximate ratio of 2.5:1, had been formed. The clarity of the spectrum at total consumption of the arene suggested a near quantitative yield of adduct formation and allowed structural assignments to be made. In particular, the four ethenyl proton coupled signals between 5.90 and 5.50 ppm are wholly consistent with a 2.5:1 mixture of the *endo*- and *exo*-1-hydroxy-2-trifluoromethyldihydrosemibullvalenes **23** and **24**, respectively: it is expected that the major isomer would have *endo*-stereochemistry as a result of secondary orbital interactions.[16] These resonances were an identical pair of double doublets and the couplings between the doublet at 5.68 ppm (J = 5.9 Hz) and the double doublet at 5.87 ppm and between the identical signals at 5.55 and 5.73 ppm, respectively, were confirmed by COSY analysis. All the ^{1}H NMR spectral data closely resembled those of the *endo*- and *exo*-isomers of the corresponding 1-methoxy *meta*-cycloadducts **25** and **26** respectively as reported in ref. 7*b*. No singlet for the hydroxy proton was evident but this signal would be expected to be appreciably broadened by hydrogen bonding and probably hidden by the other resonances. The presence of this functionality was, however, confirmed by a broad intense absorption in the infrared spectrum at 3390 cm^{-1}. Despite the brown appearance of the crude product, the ^{1}H NMR spectrum indicated that the adducts had been formed in high purity, but attempts to remove coloured material by high vacuum distillation gave a complex mixture with intense absorptions in the carbonyl region of the infrared spectrum. Even storage of the reaction product at 0 °C did not prevent a slow conversion of the two adducts into the multicomponent mixture. The appearance of carbonyl absorption (1760 cm^{-1}) and an ethenyl proton resonance (6.10 ppm, br m) on heating the mixture of **23** and **24** at 100 °C under neutral conditions (toluene), does, however, strongly suggest that the 1-hydroxy *meta*-photoadducts are the precursors of the bicyclic ketones. Acid conditions are not required for this conversion and indeed, did not accelerate the process. Hence, it is proposed that the 1-hydroxydihydrosemibullvalenes from the *meta*-photocycloaddition of ethenes to phenols are the precursors of the bicyclic ketones, and that the conversion involves a 1,5-hydrogen shift from the hydroxy group to the 4-position as depicted in **31**.

Numerous methods were investigated to stabilise **23** and **24** by derivatisation of the hydroxy functionality and hence allow their separation. Eventually the crude adducts were converted, albeit inefficiently, into the urethanes by reaction with phenyl isocyanate in refluxing hexane for 5 h. The isomeric urethanes were separated by flash chromatography on alumina and their spectroscopic data allowed the assignment of the *endo*- and *exo*-structures **27** and **28** to the major and minor isomers, respectively. Thus the original adduct structures are confirmed as **23** and **24**.

Irradiation of 3-trifluoromethylphenol in the presence of (*Z*)-cyclooctene to low or complete consumption of the arene gave only two products as evidenced by ^{1}H NMR spectroscopy. Again GC–MS indicated several adduct isomers ($M^+ = 272$ mu) and adducts with loss of HF, and TLC analysis under a variety of conditions gave diffuse streaks rather than distinct spots. Attempts to separate the isomers once more resulted in multicomponent mixtures and the *endo*- and *exo*-structures for the major and minor products were assigned as **29** and **30** from extracted ^{1}H NMR spectral data and their comparison with those from the cyclopentene system.

The formation of **23**, **24**, **29** and **30** represent the first reported examples of *meta*-photocycloaddition of an ethene to a phenol in which the hydroxy function remains intact in the product. The arguments outlined above for the use of the 3-trifluoromethyl group on the arene therefore appear to be valid, and are reinforced by the observation that product formation from the irradiation of 4-trifluoromethylphenol in the presence of cyclopentene is inefficient and non-selective. The hydrogen bonding feature thus successfully inhibits any proton migration in the reaction intermediate and specifically controls the direction of cyclopropane ring formation. The stability of the adduct is also increased by this feature and isolation of the 1-hydroxydihydrosemibullvalenes, albeit as a stereoisomeric mixture, is facilitated. However, the thermal conversion of these adducts to the bicyclic ketones is not a selective process and other pathways, including decomposition by the loss of HF, compete to give mixtures. In the absence of the hydrogen bond, the 1-hydroxydihydrosemibullvalenes appear to be very labile and as with those from 3-cyanophenol, seemingly undergo the 1,5-hydrogen at ambient temperature and with high selectivity, as only minor amounts of other products are formed. The lack of detection of the 1-hydroxy *meta*-photocycloadducts from 3-cyanophenol–cyclopentene and other systems[8,9] may, therefore, now be accounted for by the thermal lability of such adducts. There may still, however, be a contribution to the formation of the bicyclic ketones from prototropy in a polarised intermediate, but if this was significant, then detectable amounts of stereoisomers of **14** and **15** would be expected. The present study has thus indicated that the previously unconsidered route of a 1,5-hydrogen shift in the 1-hydroxy photoadduct may well be the major, if not the sole route to the carbonyl compounds. The possibility of polar intermediates in the *meta*-photocycloaddition of ethenes.to the benzene ring, however, remains, but if such species are formed during the 2,6-addition to phenols, they apparently undergo intramolecular cyclisation to give the cyclopropane ring in preference to proton migration.

Experimental

Photochemical and analytical methods

Solutions of the phenol (0.3 mol dm^{-3}) and the cycloalkene (1.0 mol dm^{-3}) in acetonitrile, methanol or dioxane were irradiated under air in 50 × 1.25 cm (id) quartz tubes in a reactor fitted with six 18 W low pressure mercury arc lamps. Reactions were monitored by capillary gas chromatography (Hewlett-Packard 5790A, OV101, 12m, 80–150 °C), TLC (Camlab Polygram G/UV precoated alumina or silica sheets using varying proportions of 30–40 °C light petroleum and diethyl ether as eluent) and NMR spectroscopy (JEOL EX400 and Bruker WM250 spectrometers). Separation of the products from the irradiation of the 3-cyanophenol–cyclopentene system and the urethanes of the 1-hydroxy *meta*-photocycloadducts from 3-trifluoromethylphenol and cyclopentene involved flash chromatography on ICN silica 32–63 (Park Scientific Ltd.). This procedure gave **13**, **15**, **17**, **27** and **28** with high purity as shown by ^{1}H NMR spectroscopy, one spot on TLC and one peak by GC for the former three compounds. However, all compounds underwent some deterioration on standing at room temperature and combustion analyses gave variable results. In-house accurate mass spectral measurements were, therefore, recorded on samples soon after their separation and purity assurance.

NMR spectra of isolated photoadducts and their derivatives were recorded on the above instrumentation using tetramethylsilane as an internal standard and in $CDCl_3$ solution: all coupling constants are given in Hz. Mass spectral data were obtained from a Fisons VG Autospec instrument operating in EI and CI (NH_3) modes. IR spectra of liquid films and Nujol mulls were recorded on a Perkin-Elmer 881 spectrometer.

Photoproducts from 3-cyanophenol–cyclopentene

Irradiation of the addends in methanol solution gave a mixture of **13**, **15** and **17** in an approximate ratio of 0.5:0.5:1.0, respectively, in a combined yield (GC) of *ca.* 65%, based on the 50% of the phenol consumed.

***endo*-8-Cyanotricyclo[5.3.1.$0^{2,6}$]undec-8-en-11-one 13.** Colourless oil from flash chromatography; δ_H 6.48 (1 H, overlapping dd, $J_{9.10}$ 3.3, $J_{9.10'}$ 3.7, 9-H), 2.83 (1 H, overlapping ddd, $J_{10.10'}$ 20.2, $J_{10'.1}$ 4.0, 10′-H), 2.69 (1 H, ddd, $J_{10.1}$ 1.8, 10-H), 2.67 (1 H, hidden d, 7-H), 2.66 (1 H, m, 6-H), 2.50 (1 H, m, 2-H), 2.45 (1 H, m, 1-H), and 1.20–1.90 (6 H overlapping ms propane bridge); δ_C 210.83 (C-11), 144.06 (C-9), 117.29 (CN), 114.43 (C-8), 49.48, 44.96, 44.85, 39.95 (C-1, C-2, C-6, C-7), 34.77 (C-10), 27.95, 27.64, and 26.43; ν_{max}(liquid film)/cm^{-1} 2212w, 1763vs and 1627w (Found: M$^+$, 187.0999. Calc. for $C_{12}H_{13}NO$: *M*, 187.0997).

***exo*-8-Cyanotricyclo[5.3.1.$0^{2,6}$]undec-8-en-11-one 15.** Colourless oil from flash chromatography; δ_H 6.07 (1 H, ddd, $J_{10.9}$ 9.2, $J_{10.1}$ 7.3, $J_{10.8}$ 2.6, 10-H), 5.40 (1 H, ddd, $J_{9.1}$ 2.6, $J_{9.8}$ 1.5, 9-H), 3.96 (1 H, overlapping ddd, $J_{8.7}$ 4.4, 8-H), 2.84 (1 H, dt, $J_{2.6}$ 17.2, $J_{2.3}$ 8.4, $J_{2.1}$ 1.2, 2-H), 2.74 (1 H, dd, $J_{6.5}$ 8.4, 6-H), 2.39 (1 H, d, 1-H), 2.27 (1 H, d, 7-H), and 1.09–2.06 (6 H, overlapping ms propane bridge); δ_C 211.16 (C-11), 136.35 (C-10), 119.65 (C-9), 117.71 (CN), 51.98 (C-7), 50.61 (C-1), 48.73 (C-6), 40.74 (C-2), 40.33 (C-8), 33.91, 32.58, and 26.32; ν_{max}(liquid film)/cm^{-1} 2241w, 1758vs, and 1635w (Found: M$^+$, 187.1026. Calc. for $C_{12}H_{13}NO$: *M*, 187.0997).

***endo*-3-Cyanotricyclo[5.3.0.$0^{2,6}$]dec-4-ene 17.** Colourless oil from flash chromatography; δ_H 5.81 (1 H, ddd, $J_{5.4}$ 9.9, $J_{5.6}$ 5.5, $J_{5.7}$ 2.6, 5-H), 5.16 (1 H, dd, $J_{4.3}$ 1.8, 4-H), 2.43 (1 H, collapsed ddd, $J_{1.10}$ 9.2, $J_{1.2}$ 8.4, $J_{1.7}$ 8.4, 1-H), 2.22 (1 H, collapsed dddd, $J_{7.8}$ 10.6, $J_{7.6}$ 8.4, $J_{7.5}$ 2.6, 7-H), 1.83 (1 H, hidden dd, $J_{3.2}$ 4.4, 3-H), 1.83 (1 H, collapsed ddd, $J_{6.2}$ 8.4, 6-H), 1.30–1.86 (6 H overlapping ms, propane bridge,) and 1.25 (1 H, dt, 2-H); δ_C 130.69 (C-4), 122.71 (C-5), 119.96 (CN), 35.86 (C-7), 34.51 (C-1), 33.06, 30.87 (C-8, C-10), 25.11 (C-3), 23.66 (C-9), 18.56 (C-6) and 11.14 (C-2); ν_{max}(liquid film)/cm^{-1} 2233m and 1642w (Found: M$^+$, 159.1039. Calc. for $C_{11}H_{13}N$: *M*, 159.1048).

Photoproducts from 3-trifluoromethylphenol–cyclopentene

Irradiation of the addends in acetonitrile until the phenol had been totally consumed gave a mixture of the adducts **23** and **24** in an approximate respective ratio of 2.5:1 and in essentially quantitative yield, as judged by ^{1}H NMR spectroscopy of the crude photoproduct after removal of the solvent and excess cyclopentene. It is considered that yields of the 4-

trifluoromethyldihydrosemibullvalene isomers of the order of 5% would have been readily detected.

***endo*-1-Hydroxy-11-trifluoromethyltetraacyclo-[6.3.0.0$^{2.11}$.0$^{3.7}$]undec-9-ene 23.** δ_H 5.87 (1 H, dd, $J_{9.10}$ 5.9, $J_{9.8}$ 2.9, 9-H), 5.68 (1 H, d, 10-H), 3.39 (1 H, m, 7-H), 3.15 (1 H, d, 8-H), 3.08 (1 H, m, 3-H), 2.64 (1 H, d, $J_{2.3}$ 5.9, 2-H) and 1.96–1.23 (6 H, overlapping ms propane bridge).

***exo*-1-Hydroxy-11-trifluoromethyltetracyclo[6.3.0.0$^{2.11}$.0$^{3.7}$]-undec-9-ene 24.** δ_H 5.73 (1 H, dd, $J_{9.10}$ 5.9, $J_{9.8}$ 2.6, 9-H), 5.55 (1 H, d, 10-H), 3.16 (1 H, d, 8-H), 2.38–2.19 (2 H, overlapping ms, 3-H, 7-H), 2.27 (1 H, m, 2-H) and 1.96–1.23 (6 H, overlapping ms propane bridge); ν_{max}(liquid smear)/cm^{-1} of **23**–**24** mixture 3390s, 1453w and 733w.

Phenylurethanes

The crude mixture of adducts **23** and **24** (1.0 g) and phenyl isocyanate (2.0 g) were refluxed in hexane solution (30 ml). The reaction proceeded very slowly as judged by the appearance of **27** and **28** on TLC. After 7 h reflux and approximately 30% conversion to the phenylurethanes, the reaction was stopped and **27** and **28** were isolated from alumina flash chromatography (30% diethyl ether in light petroleum, bp 40–60 °C) in yields of 10 and 5%, respectively.

***endo*-1-Phenylcarbamyloxy-11-trifluoromethyltetracyclo-[6.3.0.0$^{2.11}$.0$^{3.7}$]undec-9-ene 27.** Mp 102–3 °C (decomp.); δ_H 7.33 (2 H, d, $J_{o.m}$ 7.7, *ortho* Hs), 7.24 (2 H, dd, $J_{m,p}$ 7.3, *meta* Hs), 7.02 (1 H, t, *para* H), 6.66 (1 H, br s, NH), 5.92 (1 H, dd, $J_{9.8}$ 2.6, $J_{9.10}$ 5.9, 9-H), 5.66 (1 H, d, 10-H), 3.64 (1 H, dddd, $J_{7.6}$ 3.3, $J_{7.8}$ 7.0, $J_{7.3}$ 8.4, $J_{7.6'}$ 11.0, 7-H), 3.28 (1 H, dd, 8-H), 3.20 (1 H, ddd, $J_{3.2}$ 7.0, $J_{3.4}$ 9.2, 3-H), 2.72 (1 H, d, 2-H) and 1.25–1.80 (6 H, overlapping ms in propane bridge); δ_C 151.51 (C=O), 136.97 (C-9), 136.30 (–NH–C), 128.05 (*meta* Cs), 124.15 (C-1), 123.68 (C-10), 122.82 (*para* C), 117.68 (*ortho* Cs), 88.93 (CF_3), 57.91 (C-8), 57.82 (C-7), 47.67 (C-3), 40.59 (C-2), 28.20 (C-11), 28.58, 28.43, 25.47 (propane bridge Cs); ν_{max}(Nujol mull)/cm^{-1} 3320m, 1751s, 1735s, 1602s, 1530s, 1170s, 1145s, 1119s and 801s (Found: M$^+$, 349.1290. Calc. for $C_{19}H_{18}NF_3O_2$: *M*, 349.1290).

***exo*-1-Phenylcarbamoyloxy-11-trifluoromethyltetracyclo-[6.3.0.0$^{2.11}$.0$^{3.7}$]undec-9-ene 28.** Mp 127–9 °C (decomp.); δ_H 7.33 (2 H, d, $J_{o.m}$ 7.7, *ortho* Hs), 7.22 (2 H, dd, $J_{m.p}$ 7.3, *meta* Hs), 7.00 (1 H, t, *para* H), 6.65 (1 H, br s, NH), 5.82 (1 H, dd, $J_{9.8}$ 2.6, $J_{9.10}$ 5.9, 9-H), 5.60 (1 H, d, 10-H), 3.33 (1 H, d, 8-H), 2.31 (1 H, s, 2-H), 2.31 (1 H, hidden signal), 2.21 (1 H, dd, $J_{3.7}$ 7.0, $J_{3.4}$ 12.0, 3-H) and 1.30–1.95 (6 H, overlapping ms in propane bridge); δ_C 151.11 (C=O), 136.31 (C-9), 135.41 (–NH–C), 128.04 (*meta* Cs), 123.29 (C-1), 122.74 (C-10), 120.38 (*para* C), 117.52 (*ortho* Cs), 84.25 (CF_3), 58.07 (C-8), 54.96 (C-7), 41.88 (C-3), 41.21 (C-2), 31.44, 29.43, 25.81, (propane bridge Cs), 28.69 (C-4); ν_{max}(Nujol mull)/cm^{-1} 3335m, 1751s, 1727s, 1603s, 1546s, 1535s, 1173s, 1119s and 801s (Found: M$^+$, 349.1290. Calc. for $C_{19}H_{18}NF_3O_2$: *M*, 349.1290).

Photoproducts from 3-trifluoromethylphenol–(*Z*)-cyclooctene

***endo*-1-Hydroxy-14-trifluoromethyltetracyclo-[9.3.0.0$^{2.14}$.0$^{3.10}$]tetradec-12-ene 29.** δ_H 5.79 (1 H, dd, $J_{12.11}$ 2.6, $J_{12.13}$ 5.9, 12-H), 5.67 (1 H, d, 13-H), 4.7–4.39 (1 H, br s, OH), 3.06 (1 H, dd, $J_{11.10}$ 5.5, 11-H), 2.82 (1 H, d, $J_{2.3}$ 7.0, 2-H), 2.68 (1 H, ddd, $J_{10.3}$ 9.5, 10-H), 2.59 (1 H, collapsed ddd, 3-H) and 2.0–1.0 (12 H, overlapping ms, hexane bridge protons); ν_{max}(liquid smear)/cm^{-1} of **29**–**30** mixture 3369s, 1463m, 1448m and 737s.

***exo*-1-Hydroxy-14-trifluoromethyltetracyclo[9.3.0.0$^{2.14}$.0$^{3.10}$]-tetradec-12-ene 30.** δ_H 5.71 (1 H, dd, $J_{12.11}$ 2.6, $J_{12.13}$ 5.9, 12-H), 5.57 (1 H, d, 13-H), 4.7–4.3 (1 H, br s, OH), 2.90 (1 H, d, 11-H), 2.19 (1 H, d, $J_{2.3}$ 1.1, 2-H) and 2.0–1.0 (14 H, overlapping ms 1-H, 8-H, hexane bridge protons).

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