Use of arene 1,3-substituents to control cyclopropane ring formation during *meta* photocycloaddition of ethenes to the benzene ring

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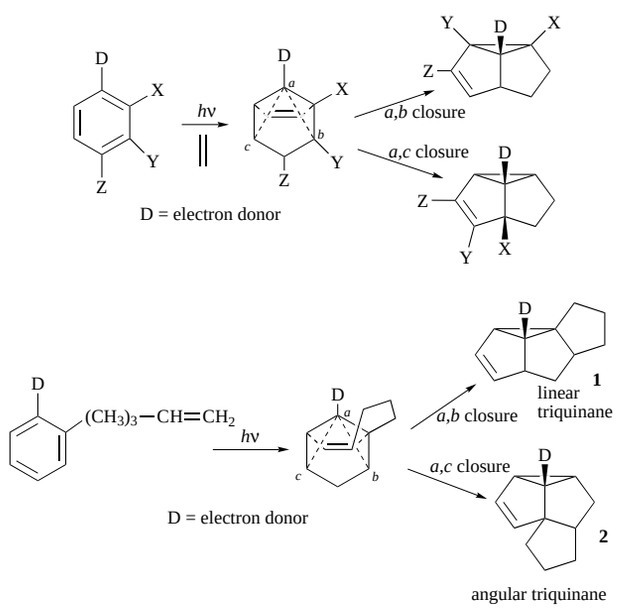
The 3-trifluoromethyl derivatives of benzyl alcohol, benzyltrimethylsilane and phenoxytrimethylsilane undergo 2,6-photocycloaddition to cyclopentene to give the 1,11-disubstituted-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]-undec-9-enes 7, 10, 11 and 12. This specificity in isomer formation is considered to originate from an intramolecular attractive interaction between the 1,3-substituents on the arenes during the addition of the ethene and this causes an asymmetric distortion of the C_6 ring which then controls the cyclopropane ring formation in the adduct. Similar reaction of 3-trifluoromethyl-phenol, -benzyl alcohol and -benzyltrimethylsilane, with vinyl acetate yields the 2-trifluoromethyl-*endo*-6-acetoxytricyclo[3.3.0.0^{2,8}]oct-3-enes 16, 17 and 18 respectively, showing that the directing influence of substituents on the arene dominates any effect of the acetoxy group on the photocycloaddition process. The control by Si···F interaction is not, however, significant during the intramolecular photocycloaddition of the bichromophores 19 and 20 and only the 1,6-bridged dihydrosemibullvalene 24 and products derived from *ortho* cycloaddition are respectively formed.

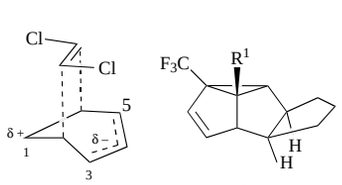
The *meta* photocycloaddition of ethenes to the benzene ring has attracted considerable attention both for its mechanistic interest[1] and for its use as a synthetic organic procedure.[2] As illustrated in Scheme 1, both the inter- and intra-molecular



Scheme 1

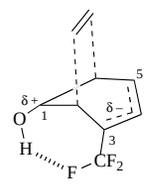
processes yield adduct isomers resulting from the two possible directions for the formation of the cyclopropane ring in the tricyclo[3.3.0.0^{2,8}]oct-3-ene (dihydrosemibullvalene) skeleton. In principle, a thermal or photochemical ethenylcyclopropane–cyclopentene rearrangement may interconvert the adduct isomers, but for most systems this procedure would not be viable for a synthetic application because there is insufficient difference between the thermodynamic stabilities or the absorption characteristics of the photoisomers to achieve the required selectivity. We have also found that attempts to use such interconversions to produce particular adduct isomers yield appreciable amounts of involatile materials.

The formation of two adduct isomers from the *meta* photocycloaddition of ethenes to the benzene ring detracts from the beneficial synthetic aspects of the process to introduce a considerable increase in molecular complexity in one step, and to give high product yields in short routes to a variety of polycyclic systems.[2] Control over the cyclopropane ring formation in the intermolecular *meta* photocycloaddition process is, however, observed with 1,2-dichloroethene as the addend.[3] In these

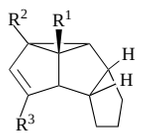


3

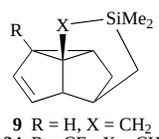
4 R^1 = OH
8 R^1 = CH_2OH
11 R^1 = CH_2SiMe_3



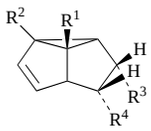
6



5 R^1= OH, R^2 = CF_3, R^3 = H
7 R^1 = CH_2OH, R^2 = CF_3, R^3 = H
10 R^1 = CH_2SiMe_3, R^2 = CF_3, R^3 = H
12 R^1 = $OSiMe_3$, R^2 = CF_3, R^3 = H
13 R^1 = $OSiMe_3$, R^2 = H, R^3 = CF_3



9 R = H, X = CH_2
24 R = CF_3, X = CH_2
25 R = H, X = O



14 R^1 = R^2 = R^4 = H, R^3 = OAc
16 R^1 = OH, R^2 = CF_3, R^3 = H, R^4 = OAc
17 R^1 = CH_2OH, R^2 = CF_3, R^3 = H, R^4 = OAc
18 R^1 = CH_2SiMe_3, R^2 = CF_3, R^3 = H, R^4 = OAc

additions, the *endo* chlorine substituent in the intermediate species **3** has a repulsive interaction with the developing allylic anion moiety in the C_6 ring which then becomes asymmetrically distorted so that the cyclisation is induced between C-1 and C-3

rather than between C-1 and C-5. This feature has also been used to control the intramolecular process and (*E*)-1-chloro-5-phenylpent-1-ene and 2-chloro-5-phenylpent-1-ene give specific access to the angular and linear triquinane † skeleta respectively.[4] Furthermore, we have recently shown that 5-phenylpent-1-enes having heteroatoms at the 4-position undergo highly selective intramolecular addition to give either the linear[5,6] or the angular[7] triquinane systems **1** and **2** respectively. This feature is rationalised in terms of asymmetry in the bichromophore conformation leading to adduct formation, and this induces a non-synchronous addition which greatly favours one or other of the cyclisations yielding the cyclopropane ring in the dihydrosemibullvalene skeleton. We have also recently observed that while there is little selectivity in the cyclopropane ring formation from the *meta* photocycloaddition of cyclopentene to 3-(trifluoromethyl)anisole,[8] the corresponding 2,6-photocycloaddition of cycloalkenes to 3-(trifluoromethyl)phenol yields solely the *exo* and *endo* 1-hydroxy-2-(trifluoromethyl)dihydrosemibullvalenes **4** and **5** respectively and none of the alternative 1-hydroxy-4-trifluoromethyl isomers.[9] This regiospecificity in the cyclisation to give the cyclopropane ring is accounted for in terms of the distortion of the C_6 ring from planarity during the *meta* addition of the ethene, producing a sufficiently close approach of the hydroxy hydrogen and fluorine atoms to allow intramolecular hydrogen bonding which then causes a twist in the C_6 ring as in **6** and this leads specifically to bonding between C-1 and C-3.

In the present paper, we present and discuss the results of studies designed to assess whether the attractive interaction between 1,3-substituents on the arene, which has been noted in the one case of 3-(trifluoromethyl)phenol and cycloalkenes, is a general feature for distorting the C_6 ring and one which can be used to give the needed control over isomer formation in both inter- and intra-molecular *meta* photocycloaddition of ethenes to the benzene ring.

Results and discussion

The high regioselectivity of the inter- and intra-molecular *meta* photocycloaddition of ethenes to the benzene ring is accounted for by a mechanism in which polarity develops in the S_1 arene on approach of the S_0 ethene.[1] The addends orient to maximise stabilisation of these developing charges by the substituents on the benzene ring. Thus electron donor substituents direct addition to the 2,6-positions and 2,4-addition is favoured with respect to electron acceptor substituents. These directing influences act in concert for 3-(trifluoromethyl)phenol and, as noted above, the intramolecular hydrogen bonding which becomes possible between the substituents during the addition is considered to asymmetrically distort the C_6 ring and lead to specific 1,3-intramolecular cyclisation to give the cyclopropane ring in the dihydrosemibullvalene skeleton. An increase in the number of units between the interacting substituents should facilitate this hydrogen bond formation and may thereby reduce the distortion in the C_6 ring during the addition. The effect on the specificity of the reaction of easing the structural constraints was investigated by examining the photoaddition of cyclopentene to 3-(trifluoromethyl)benzyl alcohol.

3-(Trifluoromethyl)benzyl alcohol–cyclopentene

There are numerous published accounts of the *meta* photocycloaddition of a variety of ethenes to a wide range of substituted benzenes,[1] but the only reported example of such an intermolecular reaction of a benzyl compound is the addition of cyclopentene to 3-(methoxymethyl)anisole.[10] In this system, the photoaddition is directed by the methoxy substituent specifically to the 2,6-positions. We have observed in the present investigation that while photoaddition of cyclopentene does occur readily to benzyl methyl ether in acetonitrile, under similar conditions, and also in solvents of low polarity, benzyl alcohol is essentially photostable. It is widely accepted that the *meta* photocycloaddition arises from the S_1 state of the benzenoid compound,[1] and the low photoreactivity of benzyl alcohol in *meta* cycloaddition may thus be indicated by its low fluorescence quantum yield (0.07) and high intersystem crossing efficiency (0.51).[11] We estimate that the quantum yield of fluorescence of 3-(trifluoromethyl)benzyl alcohol is approximately six-fold greater than that of the parent alcohol. A study of the photochemistry of the 3-trifluoromethyl derivative of the alcohol thus has the interest of determining not only whether hydrogen bonding between the 1,3-substituents is sufficient to distort the C_6 ring and maintain the control over isomer formation, but also if the *meta* photocycloaddition would be promoted in this derivative.

Monitoring the irradiation (254 nm) of solutions of 3-(trifluoromethyl)benzyl alcohol and cyclopentene in acetonitrile by GC, indicated the rapid formation of essentially only one product (a 1 : 1 adduct—GC–MS) during the complete consumption of the arene. The ^{1}H NMR spectrum of the crude reaction product at low or high conversion was consistent with the presence of a single major product and from detailed analysis of these data and their comparision with those of *meta* photocycloadducts of related structure,[9] the *endo*-1-hydroxymethyl-11-(trifluoromethyl)tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene structure **7** was assigned. Thus, although compared to 3-(trifluoromethyl)phenol, hydrogen bonding with fluorine may be expected to be facilitated during the 2,6-photoaddition to 3-(trifluoromethyl)benzyl alcohol, there is evidently still sufficient distortion induced in the C_6 ring to promote specific 1,3-cyclisation and give solely the 1,2-disubstituted dihydrosemibullvalene skeleton. The thermal stability of **7** in comparison to the corresponding adducts from 3-(trifluoromethyl)phenol is readily accounted for by the latter undergoing a facile 1,5-sigmatropic shift of the hydroxy hydrogen to yield the isomeric ketone.[9] The absence of the *exo*-isomer **8** in readily detectable amounts may be explained in terms of the orientation of the addends leading to this adduct being unfavourable as a result of the type of steric interactions discussed in the formation of 1-substituted dihydrosemibullvalenes from cyclopentene and alkyl benzenes.[12]

In order to assess whether a through space interaction between silicon and fluorine atoms could be used in a similar manner to hydrogen bonding to control the cyclopropane ring formation during *meta* photocycloaddition to the benzene ring, we examined the photoreactions of 3-trifluoromethyl substituted benzyl- and phenoxy-trimethylsilanes with cyclopentene.

Aryltrimethylsilane systems

Previous literature describing the *meta* photoaddition reactions of ethenes to arylsilanes is limited to the report of the 2,6-addition of cyclopentene, 2,2-dimethyl-1,3-dioxole and vinylene carbonate to phenoxytrimethylsilane.[13] The $-CH_2SiMe_3$ substituent on the benzene ring may also be expected to direct *meta* photocycloaddition of ethenes to the 2,6-positions as a result of the β-stabilising effect of silicon[14] on the developing positive charge at the 1-position of the S_1 arene on approach of the ethene. Surprisingly, however, irradiated solutions of benzyltrimethylsilane in the presence of cyclopentene gave no evidence for *meta* cycloadduct formation. This lack of reactivity is unexpected particularly since 3-(benzyldimethylsilyl)prop-1-ene efficiently undergoes the intramolecular process to give solely the 1,6-bridged dihydrosemibullvalene **9**.[5] Whatever feature inhibits the addition of the cyclopentene to photoexcited benzyltrimethylsilane can evidently be overcome, as in the benzyl alcohol system, by the 3-trifluoromethyl substituent. Thus, irradiation of the alkene with 3-(trifluoromethyl)benzyl-

† IUPAC names of the linear and angular triquinanes **1** and **2** are tetracyclo[6.3.0.0^{2,6}.0^{2,11}]undec-9-ene and tetracyclo[6.3.0.0^{4,8}.0^{2,11}]-undec-9-ene, respectively.

trimethylsilane, in which the photoaddition-directing influences of the two substituents again act in concert gave good yields of the 1,2-substituted dihydrosemibullvalene isomers **10** and **11** in a ratio of 1.6 : 1 respectively. This specificity in the cyclopropane ring formation during the 2,6-photoaddition of cyclopentene to 3-(trifluoromethyl)benzyltrimethylsilane is accounted for by the intramolecular attractive interaction between the silicon and fluorine atoms which asymmetrically distorts the C_6 ring in a similar manner to that depicted in **6** for the addition to 3-(trifluoromethyl)phenol, and thus cyclisation between C-1 and C-3 is again favoured. Nevertheless, in view of the *endo* specificity observed for the addition of cyclopentene to 3-(trifluoromethyl)benzyl alcohol, the formation of both stereoisomers from the benzylsilane is not readily explained since steric influences preventing an *exo* approach of the addends may have been expected to be more pronounced in the latter than in the former system.

A further point of interest in the silyl systems was what influence the presence of the oxygen–silicon bond would have on the Si···F interaction between the 1,3-substituents. Any reduction in the effectiveness of this interaction to control the direction of formation of the cyclopropane ring as a result of lone pair donation from the oxygen into the low energy d-orbitals of the silicon would be evident by the formation of both the 1,2- and the 1,4-disubstituted dihydrosemibullvalene isomers as for other 1,3-disubstituted benzenes.[1] The photoaddition of cyclopentene to 3-(trifluoromethyl)phenoxytrimethylsilane, however, occurred with high selectivity to give the 1,2-disubstituted dihydrosemibullvalene **12** in good yield. In particular, none of the 1,4-isomer **13** was detected by ^{1}H NMR spectroscopy and hence the control over the cyclopropane ring formation by interaction between the 1,3-substituents remains dominant. The *endo* specificity in the formation of **12** may have been predicted as this stereoisomer is formed in more than 90% yield in the photoadditions of cyclopentene to phenoxytrimethylsilane[13] and is the sole adduct from the reaction of diphenyl ether and of isopropyl and *tert*-butyl phenyl ethers with this ethene.[12] In all these cases, the inefficiency of the *exo* addition can be readily understood in terms of steric inhibition of this orientation of the S_1 arene and S_0 ethene. These observations, however, make the 1.6 : 1 ratio of the *endo* and the *exo* isomers **10** and **11** respectively from 3-(trifluoromethyl)benzyltrimethylsilane all the more surprising since there is no apparent feature in this system to overcome the corresponding steric effects and to promote an *exo* orientation of the addends.

There are now two approaches which can be applied to direct and control the cyclopropane ring formation in the intermolecular *meta* photocycloaddition of ethenes to the benzene ring. Whether the '*endo* effect' of a substituent on the ethene[6] or the attractive interaction of the 1,3-groups on the benzene ring outlined above would provide the more dominant control in a competitive situation is of interest particularly for addend pairs to be used to access targeted polyfunctional dihydrosemibullvalene systems. In order to assess the relative efficiencies of these two directing influences, we studied the photocycloaddition of vinyl acetate to the 3-(trifluoromethyl) derivatives of phenol, benzyl alcohol, benzyltrimethylsilane and phenoxytrimethylsilane.

Photocycloadditions of vinyl acetate to 1,3-disubstituted benzenes

Vinyl acetate was chosen for this study since in its *meta* photocycloaddition to the benzene ring, the *endo* addition is greatly preferred and, furthermore, there is high selectivity (≈80% overall) for the 7-*endo*-acetate isomer **14**.[15] The latter feature is rationalised by the same arguments used to explain the specific formation of the 7-*endo*-chloro isomers of the dihydrosemibullvalenes from the photoaddition of (*E*)-1,2-dichoroethene to benzenes.[7] Thus in the *endo* orientation of the S_0 vinyl acetate and the S_1 benzene, cyclisation to give the cyclopropane ring occurs with high selectivity between C-1 and C-3 rather than between C-1 and C-5. On the reasonable assumption that the 1,3-disubstituted benzenes and vinyl acetate will align to minimise steric interactions, then in the addition precursor **15** the directing influences of the substituents on the benzene ring and on the ethene are in competition: the former would give the dihydrosemibullvalene with a 6-*endo*-acetate and the latter with a 7-*endo*-acetate substituent.

There is little influence of the trifluoromethyl group on the direction of cyclopropane ring formation during *meta* photocycloaddition of cyclopentene to trifluoromethylbenzene[16] and, in this study, we have observed a similar lack of selectivity in the reaction of vinyl acetate with this arene. Indeed, the only notable features of the latter process are that the multi-component adduct mixture is formed with high efficiency and has a pronounced aroma of bananas! In contrast, although no photoaddition of vinyl acetate occurred to the phenoxytrimethylsilane, the other three 1,3-disubstituted arenes reacted efficiently and with high selectivity. In all three systems one major photoadduct (GC–MS) was formed and this comprised approximately 80% of the reaction mixture.

The ethenyl region in the ^{1}H NMR spectrum of the crude product from the phenol comprised an intense finely split singlet at δ 5.79 and weak doublet and double doublet signals characteristic of those for *meta* photocycloadducts. The major product crystallised from hexane and gave spectral data consistent with a 1 : 1 adduct. However, although the proton integral values and general form of the ^{1}H NMR spectrum were consistent with a 1,2,6- or 1,2,7-trisubstituted dihydrosemibullvalene, the same chemical shifts of the two ethenyl protons (H-3 and H-4) and the absence of their coupling to H-5 are unexpected for this structure. The ethenyl protons in the *exo*- and *endo*-1-hydroxy-2-trifluoromethyl adducts, isomers of cyclopentene with 3-(trifluoromethyl)phenol, have δ-value differences of 0.22 and 0.26 respectively.[9] The equivalency of the two ethenyl protons in the vinyl acetate adduct may possibly arise from deshielding of H-4 by a 6-*endo*-acetate group. The stereochemistry and the position of the acetate substituent could not, however, be unambiguously assigned from the spectral data, but X-ray crystallographic analysis of a single crystal of this major adduct confirmed not only the 1-hydroxy-2-trifluoromethyl substitution on the dihydrosemibullvalene but also that the acetate grouping did indeed reside at the 6-*endo*-position.[17] Structure **16** for this photoadduct shows that the principal pathway for the photocycloaddition of vinyl acetate to 3-(trifluoromethyl)phenol involves an *endo* approach of the addends as in **15** with subsequent control of the cyclopropane formation arising from interaction of the 1,3-substituents during the addition to the benzene ring. As indicated by the ^{1}H NMR spectra of the crude adduct mixtures, small amounts of the 7-*endo*-acetate isomer may well have been present, resulting from control in the cyclopropane formation by the acetate group but the quantities of the minor reaction products did not realistically allow their isolation in the purities required for conclusive spectral identification.

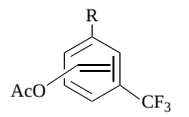
The major photoproducts from the photoaddition of vinyl acetate to 3-(trifluoromethyl)-benzyl alcohol and -benzyltrimethylsilane were assigned the *endo*-6-acetate structures **17** and **18** respectively from detailed analyses of their ^{1}H NMR spectral data. For the latter adduct, however, the signals of H-3 and H-4 in the dihydrosemibullvalene skeleton had different δ-values and the couplings of these protons could readily be discerned.

The results with the vinyl acetate addend show that the interaction between 1,3-substituents on the benzene ring during intermolecular *meta* photocycloaddition of ethenes is a dominant feature in directing the cyclisation to give the cyclopropane ring, and results in a high selectivity in isomer formation. In principle, the directing influence of Si···F interaction during the *meta* addition could be used to direct the corresponding intramolecular process of arene–ethene bichromophores. To

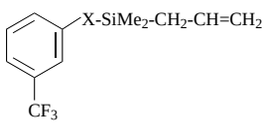
assess this possibility we examined the photoreactions of the 3′-(trifluoromethyl)-substituted 3-(benzyldimethylsilyl)- and 3-(phenoxydimethylsilyl)-prop-1-enes **19** and **20** respectively.

Intramolecular photoreactions of (aryldimethylsilyl)propenes

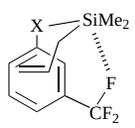
We have recently described the intramolecular *meta* photocycloaddition reactions of several 3-(benzyldimethylsilyl)prop-1-enes and noted (*i*) that the β-silicon stabilisation of the developing positive charge in the S_1 benzene ring is more effective than an alkane tether in directing the addition to the 2′,6′-positions, and (*ii*) that the charge stabilising influences of 2′-methyl-, methoxy- or fluoro-substituents dominate the photoaddition which then gives solely angular triquinanes by specific 1′,5′-addition.[7] The 3′-trifluoromethyl substituent on the benzene of **19** and **20** reinforces the directing influence of the



15 R = OH, CH_2OH, CH_2SiMe_3, or $OSiMe_3$



19 X = CH_2
20 X = O



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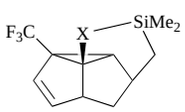

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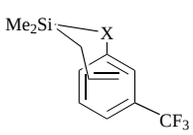

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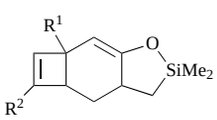

26 R^1 = H, or CF_3
R^2 = CF_3, or H

β-silicon effect and, as in the intermolecular addition, 2′,6′-attack is to be expected for the intramolecular addition. However, the conformation **21** is required for the reaction precursor in order to allow Si···F interaction to occur during intramolecular addition, and the directing influence of the substituents would then give the 1,7-bridged dihydrosemibullvalene **22** by a 1′,3′-closure. Such bridged isomers have not been observed from intramolecular *meta* photocycloaddition of arene–ethene bichromophores having three units between the chromophores probably because of the considerable strain in this system. The long C–Si bonds in the present bichromophores may, however, relieve the strain in the 1,7-bridged dihydrosemibullvalenes. Thus there is a conflict between the substituent directing influence and the adduct thermodynamic stability for photoaddition proceeding from the conformation **21**. The alternative conformation **23** retains the reinforcing influences of the substituent and the tether on the 2′,6′-positions for cycloaddition but from past precedent, only the 1,6-bridged dihydrosemibullvalene **24** will be formed as a result of the strain in the 1,7-bridged isomer. Indeed irradiation of 3-[(3-trifluoromethyl)-benzyldimethylsilyl)]prop-1-ene produced only the one intramolecular adduct **24** which suggests that although the conformation **21** is favoured by an interaction of the substituents in the ground state, it does not lead to cycloaddition and the sole intramolecular adduct arises from the less sterically congested orientation **23**.

We confirmed the preliminary report by Fleming *et al.*[18] that 3-(phenoxydimethylsilyl)prop-1-ene undergoes intramolecular 2′,6′-cycloaddition to give the 1,6-bridged adduct **25**. However, although irradiation of the 3′-trifluoromethyl derivative **20** seemingly gave only one 1:1 adduct (GC–MS), the ^{1}H NMR spectrum of the crude product indicated the presence of two major and several minor components. The mixture was not successfully resolved chromatographically but from the ^{1}H NMR spectra of enriched fractions, it was apparent that intramolecular *meta* cycloaddition had not occurred. Instead the data were very similar to those reported for arene–ethene bichromophore photoisomers (*e.g.* **26** from **20**) derived from initial intramolecular *ortho* photocycloaddition.[19,20] Such a reaction is greatly preferred from irradiation of 4-phenoxybut-1-enes having electron withdrawing substituents (*e.g.* –CN and $-CO-CH_3$) in the 2′- or 4′-positions,[19,20] but the corresponding 3′-isomers are reported to be essentially photostable.[20] This latter observation and the present results with **20** are all the more surprising in view of the ready intermolecular *meta* photocycloaddition of cyclopentene to 3-cyanoanisole[8,21] and the addition of the cycloalkene to 3-(trifluoromethyl)phenoxytrimethylsilane described above.

From the present study it is evident that appropriate substituents at the 1,3-positions of the benzene ring interact during intermolecular *meta* photocycloaddition and this feature can be used to induce a specific closure which yields the cyclopropane ring so that isomer formation is controlled. The other directing influence on this process from the substituent on the ethene is outweighed by the effect from the arene substituents and hence single isomers of polyfunctionalised dihydrosemibullvalenes can be obtained. The effect of 1,3-substituents does not, however, operate in the intramolecular process and this is dominated by the control from the stabilising influence of the substituents on the charges which develop in the C_6 ring during the addition.

Experimental

Photochemical and analytical methods

Solutions of the benzenoid compounds (0.3 mol dm^{-3}) and cyclopentene (1.0 mol dm^{-3}) in cyclohexane, dioxane or acetonitrile 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. The intramolecular reactions of 3-(phenoxydimethylsilyl)prop-1-ene and of the bichromophores **19** and **20** were carried out as 1% w/v solutions in the above solvents. The photoaddition reactions were monitored by capillary column gas chromatography (Perkin-Elmer 8410, OV101, 12 m, 80–150 °C), TLC (Camlab Polygram G/UV precoated alumina or silica sheets using varying proportions of 40–60 °C light petroleum and diethyl ether as eluent) and NMR spectroscopy (JEOL EX400 and Bruker WM250 spectrometers), and were continued to complete consumption of the arene. Separation and purification of the photoproducts involved flash chromatography on ICN silica 32–63 (Park Scientific Ltd.). This procedure gave the intermolecular *meta* photocycloadducts **7**, **12**, **16** and **17**, and the intramolecular photoisomers **24** and **25** with high purity as shown by ^{1}H NMR spectroscopy, TLC and GC. The yields of the adducts were not optimised, and those quoted are of the photoproducts following their separation and purification by chromatography. All adducts deteriorated to some extent on standing at room temperature and gave variable results on combustion analysis. In-house accurate mass spectral measurements were, therefore, recorded soon after separation and following chromatographic purity assurance.

NMR spectra of the photoproducts were recorded on the above instrumentation using tetramethylsilane as the 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 of liquid films were recorded on a Perkin-Elmer 881 spectrometer.

Starting materials

3-(Trifluoromethyl)benzyltrimethylsilane. The compound was synthesised by reaction of the Grignard reagent, formed from 3-(trifluoromethyl)benzyl bromide, with chlorotrimethyl silane.

Dry diethyl ether (100 ml) was added to magnesium powder (0.51 g, 21.0 mmol) and a crystal of iodine under nitrogen and the mixture cooled to 0 °C. 3-(Trifluoromethyl)benzyl bromide (1.0 g, 4.2 mmol) dissolved in dry diethyl ether (25 ml) was added dropwise to the stirred mixture over 1 h. Chlorotrimethylsilane (0.53 ml, 4.2 mmol) in dry diethyl ether (25 ml) was then added to the stirred mixture at 0 °C over 1 h. The reaction was allowed to warm to room temperature and saturated ammonium chloride solution added. The diethyl ether layer was separated and dried over anhydrous magnesium sulfate. Removal of the diethyl ether and short-path distillation of the oil gave 3-(trifluoromethyl)benzyltrimethylsilane (0.67 g, 69%); δ_H 7.26–7.08 (4 H, m, 2-, 4-, 5-, 6-H), 2.08 (2 H, s, PhCH_2), 0.00 [9 H, s, Si(CH_3)$_3$]; δ_C 142.50 (*C*F$_3$), 130.52 (C-3), 129.46 (C-4), 124.89 (C-2), 124.85 (C-5), 124.03 (C-6), 123.99 (C-1), 65.03 (*C*H$_2$SiMe$_3$), 0.00 [Si(*C*H$_3$)$_3$]; ν_{max}/cm^{-1}: 3030m, 2919s, 1676m, 1331s (Found: M$^+$, 232.0872. Calc. for $C_{11}H_{15}SiF_3$: *M*, 232.0895).

3-[3-(Trifluoromethyl)benzyldimethylsilyl]prop-1-ene 19. This bichromophore was synthesised as outlined above with the Grignard reagent being treated with allylchlorodimethylsilane. δ_H 7.35–7.17 (4 H, m, 2′-, 4′-, 5′-, 6′-H), 5.77 (1 H, ddt, $J_{2,1a}$ 16.1, $J_{2,1b}$ 11.0, $J_{2,3}$ 8.0, 2-H), 4.90 (1 H, m, 1a-H), 4.86 (1 H, m, $J_{1b,3}$ 1.1, 1b-H), 2.18 (2 H, s, PhCH_2), 1.55 (2 H, dt, 3-H), 0.08 (3 H, s, SiMe$_A$), 0.01 (3 H, s, SiMe$_B$); δ_C 141.24 (*C*F$_3$), 134.53, 134.34, 131.45, 128.66, 124.71, 121.01 (C-1′, C-2′, C-3′, C-4′, C-5′ C-6′), 113.77 (C-1), 113.40 (C-2), 25.29 (Ph*C*H$_2$), 22.62 (C-3), −3.99 [Si(*C*H$_3$)$_2$]; ν_{max}/cm^{-1} 3078 (arene C-H), 2918 (C-H), 1677 (C=C), 1331 (C–Si) (Found M$^+$, 258.1048. Calc. for $C_{13}H_{17}SiF_3$: *M*, 258.1051).

Synthesis of 3-(phenoxydimethylsilyl)prop-1-ene. Phenol (0.70 g, 7.4 mmol) and triethylamine (0.75 g, 7.4 mmol) were dissolved in dry dichloromethane, and stirred under an atmosphere of nitrogen at 0 °C. Allylchlorodimethylsilane (1.0 g, 7.4 mmol) was dissolved in dry dichloromethane (10.0 ml) and added dropwise over 30 min to the former solution. The resulting mixture was allowed to warm to room temperature and stirred overnight. The mixture was then rotary evaporated. The residue was washed with light petroleum (bp 40–60 °C) and filtered. The solvent was evaporated from the filtrate to give an oil which was purified by flash chromatography (1.3 g, 90.2%). δ_H 7.20–6.85 (5 H, m, 2′-, 3′-, 4′-, 5′-, 6′-H), 5.82 (1 H, ddt, $J_{2,1a}$ 17.6, $J_{2,1b}$ 10.0, $J_{2,3}$ 7.6, 2-H), 4.96 (1 H, ddd, $J_{1a,1b}$ 6.0, $J_{1a,3}$ 1.6, 1a-H), 4.92 (1 H, ddd, $J_{1b,3}$ 1.6, 1b-H), 1.77 (2 H, d, 3-H), 0.00 (6 H, SiMe$_2$); δ_C 133.36, 129.57, 121.72, 120.24 (1′-, 2′-, 3′-, 4′-, 5′-, 6′-C), 114.52 (1-C), 113.50 (2-C), 24.58 (3-C), 0.00 (Si*C*H$_3$), −1.70 (Si*C*H$_3$); ν_{max}/cm^{-1} 2958m, 1596m, 1252s (Found: M$^+$, 192.0962. Calc. for $C_{11}H_{16}SiO_2$: *M*, 192.0970).

3-[3-(Trifluoromethyl)phenoxydimethylsilyl]prop-1-ene 20. 3-(Trifluoromethyl)phenol (2.0 g, 12.3 mmol) and distilled triethylamine (1.2 g, 12.3 mmol) were dissolved in dry dichloromethane (35 ml) and cooled to 0 °C under a nitrogen atmosphere. To this yellow solution was added dropwise over 30 min a solution of allylchlorodimethylsilane (1.7 g, 12.3 mmol) in dry dichloromethane (15 ml). The solution was allowed to warm to room temperature and the dichloromethane removed by rotary evaporation. The residue was extracted with light petroleum (bp 60–80 °C) (100 ml) and purified by flash chromatography (1.9 g, 59.1%). δ_H 7.27–6.91 (4 H, m, 2′-, 4′-, 5′-, 6′-H), 5.71 (1 H, ddt, $J_{2,1a}$ 16.9, $J_{2,1b}$ 10.3, $J_{2,3b}$ 9.9, 2-H), 4.88 (1 H, m, $J_{1a,3}$ 1.5, $J_{1a,1b}$ 7.0, 1a-H), 4.79 (1 H, ddd, $J_{1b,3}$ 1.5, 1b-H), 1.69 (1 H, d, $J_{3a,3b}$ 8.1, 3a-H), 1.49 (1 H, dd, 3b-H), 0.21 (6 H, s, SiMe$_2$); δ_C 155.41 (*C*F$_3$), 132.86, 130.10, 123.49, 118.43 (C-1′, C-2′, C-3′, C-4′, C-5′, C-6′), 114.96 (C-1), 113.40 (C-2), 24.45 (C-3), 0.00 (Si*C*H$_3$) −1.72 (Si*C*H$_3$) (Found M$^+$, 260.0844. Calc. for $C_{12}H_{15}SiOF_3$: *M*, 260.0844).

Photoproducts

***endo*-1-Hydroxymethyl-11-(trifluoromethyl)tetracyclo-[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene 7.** Compound **7** was prepared in 90% yield; δ_H 5.82 (1 H, dd, $J_{9,10}$ 5.9, $J_{9,8}$ 2.6, 9-H), 5.60 (1 H, d, 10-H), 3.40 (1 H, dd, $J_{CH,OH}$ 13.9, $J_{OH,CF}$ 7.0, O*H*), 3.15 (1 H, dddd, $J_{7,bridge}$ 10.8, $J_{7,bridge}$ 3.2, 7-H), 3.07 (1 H, d, $J_{7,8}$ 7.7, 8-H), 2.95 (1 H, dddd, $J_{3,bridge}$ 12.1, $J_{3,7}$ 7.6, 3-H), 2.19 (1 H, d, $J_{2,3}$ 7.3, 2-H), 1.80–1.34 (6 H, m, cyclopentane ring Hs), 1.12 (2 H, t, CH_2OH); δ_C 153.66, 138.34, 125.96, 123.63, 66.59, 57.74, 49.20, 39.55, 29.67, 29.89, 28.06, 26.82, 14.97 (Found: M$^+$, 244.1074. Calc. for $C_{13}H_{15}OF_3$: *M*, 244.0997).

1-Trimethylsilylmethyl-11-(trifluoromethyl)tetracyclo-[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene, *endo* isomer 10. Despite extensive chromatography, the sample (14%) still contained trace amounts of **11** by GC. δ_H 5.84 (1 H, dd, $J_{9,10}$ 5.9, J$_{9,8}$ 2.6, 9-H), 5.69 (1 H, d, 10-H), 3.17 (1 H, dddd, $J_{7,bridge}$ 10.6, $J_{7,bridge}$ 3.3, 7-H), 3.08 (1H, dd, $J_{3,bridge}$ 10.0, $J_{3,7}$ 8.4, 3-H), 2.88 (1 H, ddd, $J_{8,7}$ 7.0, $J_{8,F}$ 7.0, 8-H), 2.10 (1 H, d, $J_{2,3}$ 7.0, $J_{2,F}$ 7.0, 2-H), 1.92–1.27 (6 H, m, cyclopropane ring Hs), 1.57 (2 H, s, CH_2SiMe$_3$), 0.10 (3 H, s, Si*Me*), 0.07 (3 H, s, Si*Me*), 0.04 (3 H, s, Si*Me*); δ_C 137.43, 126.72, 126.63, 61.14, 57.70, 49.08, 39.83, 29.39, 30.21, 27.14, 26.54, 14.14, 1.04; *m*/*z* 300 (M$^+$, 11%).

***exo*-Isomer 11.** Despite extensive chromatography, the sample (6%) still contained small amounts of **10** by GC. δ_H 5.79 (1 H, dd, $J_{9,10}$ 5.9, $J_{9,8}$ 2.6, 9-H), 5.66 (1 H, d, 10-H), 3.25 (1 H, m, $J_{7,bridge}$ 7.5, $J_{7,bridge}$ 3.1, 7-H), 3.08 (1 H, m, $J_{3,bridge}$ 10.5, 3-H), 2.81 (1 H, dd, $J_{8,F}$ 7.0, 8-H), 2.05 (1 H, d, $J_{2,F}$ 7.0, 2-H), 1.90-1.23 (6 H, m, cyclopropane ring Hs), 1.56 (2 H, s, CH_2SiMe$_3$), 0.10 (3 H, s, Si*Me*), 0.07 (3 H, s, Si*Me*), 0.04 (3 H, s, Si*Me*); δ_C 137.82, 126.92, 60.42, 59.82, 49.91, 41.15, 30.76, 30.23, 30.16, 27.10, 17.06, 1.48, 0.46; *m*/*z* 300 (M$^+$, 8%).

***endo*-1-Trimethylsilyloxy-11-(trifluoromethyl)tetracyclo-[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene 12.** Compound **12** was prepared in 67% yield; δ_H 5.66 (1 H, dd, $J_{9,8}$ 3.0, 9-H), 5.49 (1 H, d, $J_{10,9}$ 5.9, 10-H), 3.16 (1 H, m, $J_{7,bridge}$ 9.2, $J_{7,bridge}$ 4.6, 7-H), 2.92 (1 H, dd, $J_{3,bridge}$ 10.0, $J_{3,7}$ 8.5, 3-H), 2.36 (1 H, d, $J_{8,7}$ 7.0, 8-H), 1.90 (1 H, br s, 2-H), 1.60–1.10 (6 H, m, cyclopentane ring Hs), 0.10 [3 H, s, Si(CH_3)] and −0.04 [6 H, s, Si(CH_3)$_2$]; δ_C 136.40, 125.71, 116.43, 60.47, 58.22, 48.54, 29.51, 29.29, 26.69, 1.86, 0.74 (Found: M$^+$, 302.1317. Calc. for $C_{15}H_{21}SiOF_3$: *M*, 302.1314).

1-Hydroxy-2-trifluoromethyl-*endo*-6-acetoxytricyclo-[3.3.0.0^{2,8}]oct-3-ene 16. Compound **16** was prepared in 40% yield; mp 80–82 °C; δ_H 5.93 (2 H, br s, 3-H, 4-H), 5.33 (1 H, ddd, $J_{6,7}$ 7.0, $J_{6,7'}$ 9.5, 6-H), 3.49 (1 H, d, $J_{5,6}$ 5.5, 5-H), 2.43 (1 H, d, $J_{8,7'}$ 5.5, 8-H), 2.43 (1 H, dd, $J_{7,7'}$ 14.7, 7-H), 2.02 (3 H, s, CH_3), 1.47 (1 H, ddd, 7′-H), (signal for −O*H* not clearly discerned); δ_C 170.34, 132.43, 125.13, 125.06, 79.60, 57.36, 30.88, 30.84, 26.80, 20.84; ν_{max}(Nujol)/cm^{-1} 3413m, 1736s, 1246s, 1045s, 735s (Found: C, 52.12; H, 4.29%; M$^+$, 248.0590. Calc. for $C_{11}H_{11}F_3O_3$: C, 53.23; H, 4.47; *M*, 248.0660).

1-Hydroxymethyl-2-trifluoromethyl-*endo*-6-acetoxytricyclo-[3.3.0.0^{2,8}]oct-3-ene 17. Compound **17** was prepared in 53% yield; δ_H 5.81 (2 H, br s, 3-, 4-H), 5.15 (1 H, ddd, $J_{6,7'}$ 8.1, $J_{6,7}$ 5.5, 6-H), 3.48 (1 H, d, $J_{5,6}$ 7.0, 5-H), 2.40 (1 H, ddd, $J_{7,7'}$ 13.6, 7-H), 2.05 (1 H, d, $J_{8,7}$ 6.6, 8-H), 2.01 (3 H, s, CH_3OCO), 1.63 (2 H, s, CH_2OH), 1.63–1.57 (1 H, m, 7′-H), (signal for −O*H* not clearly discerned); δ_C 170.46, 133.86, 125.80, 81.32, 80.83, 65.88, 61.41, 53.95, 51.55, 30.06, 28.06, 26.50, 20.88, 15.29 (Found: M$^+$, 262.0824. Calc. for $C_{12}H_{13}O_3F_3$; *M*, 262.0813).

1-Trimethylsilylmethyl-2-trifluoromethyl-*endo*-6-acetoxytricyclo[3.3.0.0^{2,8}]oct-3-ene 18. Despite extensive chromatography, the sample (11.6%) still contained trace amounts of unknown impurities by GC; δ_H 5.78 (1 H, d, $J_{4,3}$ 5.5, 4-H), 5.73 (1 H, dd, $J_{3,5}$ 1.1, 3-H), 5.15 (1 H, ddd, $J_{6,7'}$ 9.0, $J_{6,7}$ 7.0, 6-H), 3.11 (1 H, d, $J_{5,6}$ 5.0, 5-H), 2.37 (1 H, ddd, $J_{7,7'}$ 14.5, 7-H), 2.00 (3 H, s, CH_3OCO), 1.87 (1 H, d, $J_{8,7}$ 5.5, 8-H), 1.61 (1 H, dd, 7′-H), 1.43 (2 H, s, CH_2SiMe$_3$), 0.11 (3 H, s, Si*Me*), 0.09 (3 H, s, Si*Me*), 0.08 (3 H, s, Si*Me*); δ_C 171.08, 133.53 (d, $J_{4,F}$ 9.2, C-4), 126.99, 126.59, 80.78 (d, $J_{6,F}$ 7.3, C-6), 57.58 (d, $J_{5,F}$ 5.5, C-5), 29.92, 27.52, 26.11, 21.49, 14.92, 0.00; *m*/*z* 316 (M$^+$ 10%).

3-Dimethylsilyl-8-(trifluoromethyl)tetracyclo[5.4.0.0^{1,8}.0^{5,11}]-undec-9-ene 24. Compound **24** was prepared in 27% yield; δ_H 5.70 (1 H, d, $J_{9,10}$ 5.9, 9-H), 5.41 (1 H, dd, $J_{10,11}$ 2.9, 10-H), 2.25

(1 H, br s, 5-H), 2.16 (1 H, br s, 11-H), 1.75 (1 H, ddd, $J_{6endo,6exo}$ 14.0, $J_{6endo,5}$ 4.4, $J_{6endo,7}$ 2.0, 6_{endo}-H), 1.67 (1 H, ddd, $J_{6exo,7}$ 6.0, $J_{6exo,5}$ 2.0, 6_{exo}-H), 1.42 (1 H, d, $J_{2,2'}$ 13.9, 2-H), 1.22 (1 H, d, *7-H), 0.97 (1 H, d, 2′*-H), 0.76 (1 H, dd, $J_{4,4'}$ 13.2, $J_{4,5}$ 5.9, 4-H), 0.56 (1 H, dd, $J_{4',5}$ 2.0, 4′-H), 0.12 (3 H, s, Si*Me*), 0.06 (3 H, s, Si*Me*); δ_C 137.65, 123.02, 59.00, 49.12, 32.42, 31.96, 23.58, 22.61, 16.09, −4.00 (Found: M^+, 258.1045. Calc. for $C_{13}H_{17}SiF_3$: *M*, 258.1051).

2-Oxa-3-(dimethylsilyl)tetracyclo[5.4.0.0^{1,8}.0^{5,11}]undec-9-ene 25. Compound **25** was prepared in 20% yield; δ_H 5.60 (1 H, dd, $J_{9,10}$ 5.9, $J_{9,8}$ 2.6, 9-H), 5.54 (1 H, ddd, $J_{10,11}$ 2.4, $J_{10,8}$ 1.2, 10-H), 2.78 (1 H, dd, $J_{8,7}$ 6.6, 8-H), 2.65 (1 H, m, 5-H), 2.62 (1 H, m, 11-H), 1.70 (1 H, td, $J_{7,6exo}$ 7.2, $J_{7,6endo}$ 2.4, 7-H), 1.62 (1 H, ddd, $J_{6endo,6exo}$ 12.8, $J_{6endo,5}$ 6.4, 6_{endo}-H), 1.47 (1 H, ddd, $J_{6exo,5}$ 2.1, 6_{exo}-H), 1.10 (1 H, dd, $J_{4,4'}$ 15.2, $J_{4,5}$ 1.6, 4-H), 0.69 (1 H, dd, $J_{4',5}$ 2.0, 4′-H), 0.30 (3 H, s, Si*Me*), 0.26 (3 H, s, Si*Me*); δ_C 127.56, 115.26, 62.32, 50.52, 41.92, 34.52, 29.09, 28.39, 21.66, 1.69, 1.51 (Found: M^+, 192.0962. Calc. for $C_{11}H_{16}SiO$: *M*, 192.0970).

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