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Intramolecular *meta* photocycloaddition of 3-benzyl(dimethylsila)prop-1-enes

David M. Amey, David C. Blakemore, Mike G.B. Drew, Andrew Gilbert *, Peter Heath

Department of Chemistry, The University of Reading, Whiteknights, P.O. Box 224, Reading RG6 6AD, UK

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Abstract

The regiochemistry of intramolecular *meta* photocycloaddition of 3-benzyl(dimethylsila)prop-1-enes is controlled by the silicon in the tether and the presence of an electron donor substituent on the phenyl ring. For 1′,3′-addition, the preferred formation of the angular rather than the linear triquinane isomer is interpreted in terms of an asymmetric orientation of the S_0 ethene and S_1 benzene inducing a non-synchronous addition which then promotes specific 2′,4′-cyclisation to give the cyclopropane ring of the dihydrosemibullvalene skeleton.

Keywords: Photocycloaddition; 3-Benzyl(dimethylsila)prop-1-enes; Intramolecular cycloaddition

1. Introduction

The intramolecular photocycloaddition of ethenes to the benzene ring continues to be a topic which attracts considerable interest [1,2]. The *meta* cycloaddition process [2], in particular, has been shown to have considerable synthetic potential as an access towards a number of polyquinanes and other naturally occurring compounds [3]. As shown in Scheme 1, for 5-phenylpent-1-ene derivatives having a 2′-electron donor substituent, the attack is at the 1′,3′-positions and both angular and linear triquinane isomers, **1** and **2** respectively, can be formed from the two modes of closure to give the cyclopropane ring in the photoadducts [4]. Although in principle these isomers may be interconverted thermally and/or photochemically by an ethenylcyclopropane–cyclopentene rearrangement, the general lack of any selectivity in photoadduct formation for many systems and the unpredictable nature of the interconversion can detract from the applicability and usefulness of the *meta* photocycloaddition process as a synthetic procedure.

During investigations into the photoreactions of arene–ethene non-conjugated bichromophores having a heteroatom in the tether, we observed that for 2′-methyl- and 2′-methoxy-derivatives of both 3-benzyloxyprop-1-enes [5] and *N*-protected 3-benzylazaprop-1-enes [6], the linear triquinane dihydrosemibullvalene **3** was greatly favoured over the angular isomer **4**. This feature indicated that for these bichromophores, there is a controlling influence which operates in the species prior to formation of the cyclopropane ring and which leads to discrimination between the isomers. We considered that for these ethers and *N*-protected amines, the smaller angles and shorter bond lengths in the $-CH_2-X-CH_2-$ tether compared to those of 5-phenylpent-1-enes, caused an asymmetry **5** in the orientation of the S_1 benzene ring and the S_0 ethene unit. The intramolecular cycloaddition is then not synchronous and crucially, the bonding between C-1′ and C-2 occurs before bonding between C-3′ and C-1. The result is that C-1′ achieves a tetrahedral geometry prior to C-3′ and cyclopropane ring formation occurs between C-2′ and C-6′ to give the linear adduct **3** in preference to cyclisation between C-2′ and C-4′ which would yield the angular isomer **4**. We sought to gain further information on asymmetry in the conformation preceding addition being the origin of this selectivity by an examination of the intramolecular *meta* photocycloaddition reactions of 3-benzyl(dimethylsila)-prop-1-enes. Molecular models suggested that the longer Si–C bonds compared to C–C bonds produced an asymmetry **6** in the precursor for the 1′,3′-addition of the ethene to the benzene ring. In agreement with this proposal, we reported in the preliminary account of this study [7], that the angular intramolecular adduct **7** was indeed the sole photoisomer from the 2′-methyl bichromophore **8**. In contrast, the 2′-methoxy derivative **9** did not appear to be subject to control from either the 1′,3′-directing influence of the substituent or asymmetry in the species preceding addition.

In the present paper, we discuss the factors which can control the modes of intramolecular *meta* photocycloaddition

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* Corresponding author.

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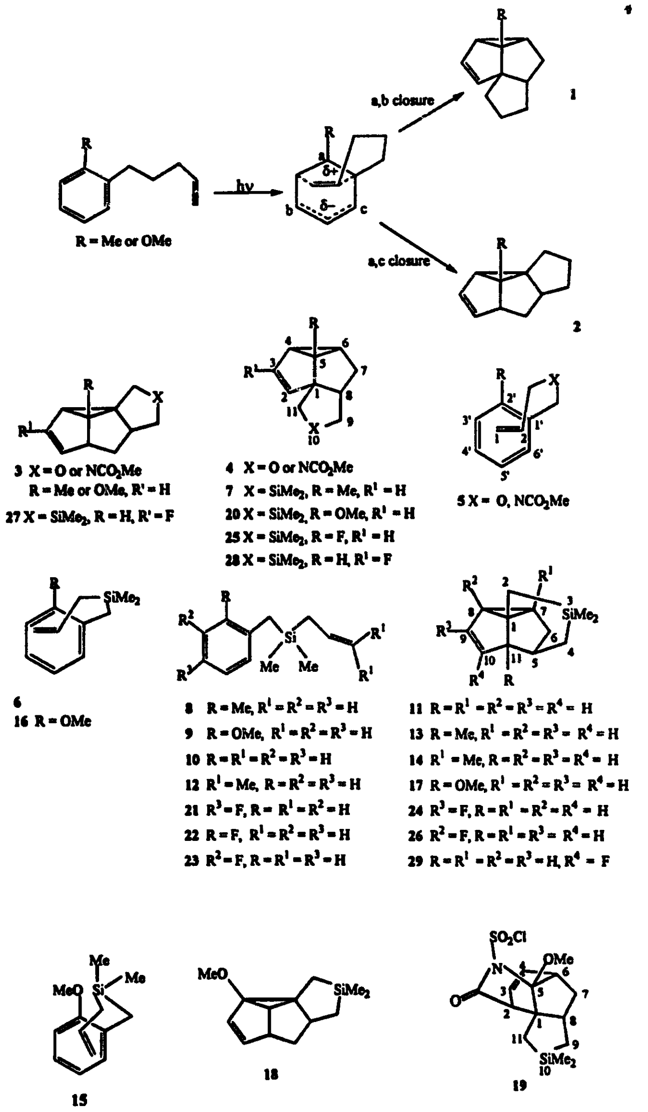

Scheme 1.

in bichromophores having a silicon atom in the tether and also present the details of our earlier preliminary report [7] together with the results of studies with fluoro-substituted derivatives of benzyl(dimethylsila)prop-1-ene. NMR spectral data are reported to support the earlier assignment of **7** but the structure for the photoisomer from the 2′-methoxy bichromophore has been reassigned following derivatisation and X-ray analysis.

2. Results and discussion

The 3-benzyl(dimethylsila)prop-1-enes were synthesised by the common route of coupling allylchlorodimethylsilane with the Grignard reagent of the appropriate benzyl bromide. The bichromophores were purified by flash chromatography and irradiated (254 nm) as 1% w/v solutions in cyclohexane under air.

The observed regiochemistry of *meta* photocycloaddition [4] is considered to arise from the addends being preferentially oriented to allow maximum substituent stabilisation of the developing polarity in the C_6 ring as the S_0 ethene approaches the S_1 benzenoid compound [8]. The ability of a silicon atom to stabilise a positive charge centre at a β-position [9] will, therefore be expected to direct the intramolecular addition of the 3-benzyl(dimethylsila)prop-1-enes to the 2′,6′-positions. Such control is indeed observed with the parent silicon-containing bichromophore **10** which gave the 1,6-bridged dihydrosemibullvalene **11** arising from 2′,6′-intramolecular cycloaddition in 60% yield. This 2′,6′-directing effect in **10** is appreciably greater than the stabilising influence of the alkane tether since for 5-phenylpent-1-ene, the ratio of products from 2′,6′- and 1′,3′-attack is approximately 5:2 respectively [10], but **11** is essentially the sole photoisomer from **10**. Interestingly, despite the longer C–Si bonds lengths, no evidence was obtained for the 1,7-bridged dihydrosemibullvalene from irradiation of **10**. This isomer can, in principle, be formed from the alternative direction of cyclopropane ring formation in the species following 2′,6′-intramolecular addition, but is not observed in 5-phenylpent-1-enes because of the considerable strain in the photoproduct.

Steric hindrance between the 3-methylene unit and a Z-methyl group at the 1-position in 5-phenylpent-1-enes destabilises the conformation leading to 2′,6′-attack and the intramolecular *meta* photocycloaddition then occurs solely at the 1′,3′-positions [11]. The photochemistry of **12** was examined to assess the competition between this directing effect and that of the silicon-containing tether. Considerable polymeric material was formed on irradiation of **12** and the solution became intense yellow (λ_{max} 310 nm) characteristic of a cyclo-octa-1,3,5-triene produced on ring opening of an *ortho* cycloadduct [12]. Five photoisomers ($M^+ = 218$ amu, MS/GC) in a combined yield of > 10% were detected but as judged from the ethenyl proton region in the NMR spectrum of this mixture, *meta* photoadducts had not been formed.

There is also a conflict of directing influences in the bichromophore **8**. Thus while the methyl group directs the ethene attack to the 1′,3′-positions, the 2′,6′-positions would be favoured for reaction by the β-silicon effect in the tether. In view of the exclusive formation of **11**, however, it may have been expected that the latter influence would compete effectively and the 5- and 8-methyl-1,6-bridged dihydrosemibullvalenes **13** and **14** respectively would be formed preferentially. It is, however, to be noted that the former of these two possible isomers would be the less likely in view of the steric interaction between the $-SiMe_2-$ unit and the 2′-methyl group in the adduct precursor conformation. From ^1H NMR spectral data of the sole photoisomer from **8** (80% yield), it was deduced that, contrary to such expectations, the product had the angular triquinane structure **7**. Thus the β-silicon effect is readily overwhelmed by a combination of the stabilising influence of the methyl group on the developing positive charge and the lower strain in the triquinane adducts compared to the 1,6-bridged isomer. while the formation of **7** is in agreement with the asymmetry **6** in the conformation preceding a non-synchronous addition of the ethene moiety, it also requires prior to closure to an 8-membered ring in preference to a 5-membered ring. We have recently, however, noted that the ^{1}H NMR spectral assignment of structures of bridged dihydrosemibullvalenes from bichromophores having a heteroatom in the tether may not be straightforward and requires detailed data and analysis [13]. Evidence to discriminate between the possible substituted bridged dihydrosemibullvalene structures from the 2′-methyl bichromophore **8** was sought from NOe experiments. Irradiation of either of the two cyclopropyl protons at δ 2.07 and δ 2.22 (H-4 and H-6 respectively in **7**) produced an enhancement of the methyl signal (δ 1.05) of 6 and 8%, but had no effect on the methylene protons adjacent to the silicon.

As for the case of 5-phenylpent-1-enes and similar chromophores with oxygen or protected nitrogen in the 4-position of the tether, the 2′-methoxy group in **9** would be expected again to direct the photoaddition to the 1′,3′-positions of the benzene ring. In **9**, however, there is the possibility that a favourable bonding attractive interaction between the silicon and oxygen atoms could occur and this lead to addition from conformation **15**. Whether such a conformation is likely or would dominate over the methoxy-directed orientation of the intramolecular addition precursor **16** is presumably dependent on the distance between the silicon and oxygen atoms, but the 'locked' conformation **15** does also allow stabilisation of the developing positive charge at C-1′ by the β-silicon effect and this results in formation of the 5-methoxy-1,6-bridged adduct **17**. Irradiation of **9** did indeed produce only one photoisomer (85% yield) and from the ^{1}H NMR spectral data the linear triquinane structure **18** arising from unprecedented 1′,5′-intramolecular cycloaddition was initially deduced [7]. However, a subsequent more detailed analysis of these data led to the conclusion that the structure of the photoisomer of **9** was either the 1,6-bridged dihydrosemibullvalene **17** from the 'locked' conformation **15** or the angular triquinane **20** arising from methoxy group direction of the ethene attack the 1′,3′-positions and non-synchronous addition from the asymmetric conformation **16**. The problem of discrimination between **17** and **20** is similar to that we encountered to distinguish between 1,6-bridged adducts and linear triquinanes from 3-benzyloxyprop-1-enes, but in the latter case, the matter was resolved by NMR techniques [13]. However, no unambiguous assignment for the photoisomer **9** could be made in this case and furthermore, NOe experiments did not produce conclusive data. The elucidation of the structure of the photoisomer from **9** was achieved by X-ray crystallographic analysis. The crystalline derivative that proved to be the most suitable for the structural identification was that obtained from the reaction of the intramolecular photocycloadduct with *N*-chlorosulphonyl isocyanate. The X-ray analysis of a single crystal (Fig. 1) allowed structure **19** to be assigned to the derivative: this arises from a regiospecific homo Diels Alder addition of the isocyanate across the ethenylcyclopropane moiety of the 1-methoxy-5,6-bridged dihydrosemibullvalene **20** and survival of the $-SO_2Cl$ grouping during the work-up procedure. Thus the intramolecular *meta* photocycloaddition of **9** is specifically directed by the methoxy group and involves addition to the arene 1′,3′-positions with no significant influence from a silicon–oxygen bonding interaction does not apparently play any role in directing the photoreactions of the bichromophore. The exclusive formation of the angular triquinane skeleton is again accounted for by asymmetry in the S_1 benzene–S_0 ethene conformation of **9** and this results in a non-synchronous addition which then leads to preferential cyclisation between C-1 and C-3′.

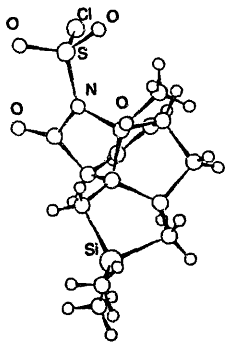

Fig. 1. Crystal structue of **19**.

A fluorine substituent can direct the regiochemistry of *meta* photocycloaddition as a result of its ability to stabilise both a positive charge by an electron-donor resonance effect, and a negative charge in the β-position by a strong electron-withdrawing inductive effect. Which of the two effects control the sites of ethene attack in the intramolecular *meta* photocycloaddition depends upon the position of substitution but both have a greater influence than the alkyl tether 2′,6′-directed attack [14]. Thus for 2′-fluoro-5-phenylpent-1-enes, the 1′,3′-addition is exclusive, whereas, the 3′-fluoro substituent directs the ethene attack to the 1′,5′-positions specifically, and only the 1,6-bridged dihydrosemibullvalene arises from the 4′-isomer as the directing influence of the substituent and the tether act in concert. We studied the photochemistry of the fluoro-substituted bichromophores **21**, **22**, and **23** in order to assess the competing influences of the β-silicon effect and the 1′,3′- and 1′,5′-direction of the addition by a fluoro substituent in the benzene ring. Furthermore, any influence on the precursor conformation of a bonding silicon–fluorine interaction (possible in **22**) would be evident from these studies. The results of irradiation of **21**, **22**, and **23** are given in Table 1.

As expected, and analogous to the photochemistry of 5-(4′-fluorophenyl)pent-1-ene [15], irradiation of the bichromophore **21** yielded only the one photoisomer **24** (32% yield) since the influences of the fluorine substituent and the β-silicon effect reinforce one another in directing the intramolecular addition. 2′-fluorophenylpent-1-enes yield both linear and angular triquinane photoisomers with a marked preference for the former [14], but again, it is apparent by the formation of the angular isomer **25** as the sole intramolecular *meta* cycloadduct from **22** that there is a powerful controlling influence of the silicon over the cyclopropane ring

Table 1
Intramolecular photoreactions of fluoro-substituted benzyl(dimethylsila)prop-1-enes

Bichromophore	Photoisomer	GC retention time [b]	Yield (%)
21	**24**	1.12	30%
22 [a]	**25**	1.14	32%
23	**26, 27, 28, 29**	1.05, 1.10 [c]	28% (total)

[a] A minor photoproduct was formed from **22** which was labile under the conditions of isolation that do not affect *meta* cycloadducts.

[b] Times relative to the starting bichromophore.

[c] This second component comprised the three major photoisomers of **23**.

formation which is once again attributed to asymmetry in the orientation of the chromophores in the conformation of the addition precursor. In contrast to the specific 1′,5′-directing influence of the 3′-fluoro substituent in the hydrocarbon bichromophore [14], the tether in **23** also has an influence on the selectivity of the regiochemistry of the intramolecular photoaddition and this leads to a relatively complex mixture of photoisomers from **23** (GC/MS, $M^+ = 208$ amu). Of the four isomers which predominate the mixture, only the minor product was separated chromatographically and isolated in high purity: this was assigned the 1,6-bridged dihydrosemibullvalene structure **26** formed from the control of the intramolecular photoaddition by the β-silicon effect of the tether. However, extracted ^{1}H NMR spectral data of enriched mixtures of the other three photoisomers and their comparison with those of fluorinated intra- and intermolecular *meta* photocycloadducts [14–16], allowed structural assignments to be made for two of the more major photoproducts. Thus, for example, the doublet at δ 4.56 ($J = 2.6$ Hz) in the most abundant isomer is assigned to the ethenyl proton in the linear triquinane **27**, and the singlet at δ 4.54 is consistent with the angular triquinane structure **28**. The doublet at δ 4.98 ($J = 2.6$ Hz) is assigned to a 3-proton adjacent to fluorine in the dihydrosemibullvalene skeleton and the 1,6-bridged structure **29** is tentatively deduced for the fourth photoisomer. It is, therefore, apparent that although a major influence on the intramolecular addition of **23** arises from the fluorine substituent as for the hydrocarbon bichromophore, the β-silicon effect does compete for the regiochemical control of the reaction.

To summarize, the directing influences of silicon at the 4-position of 5-phenylpent-1-enes on the regiochemistry of intramolecular *meta* photocycloaddition are in agreement with the proposed mechanism for this process. Despite inducing specificity in the parent bichromophore, the β-silicon effect does not compete with the 1′,3′-directing influence of 2′-electron donating substituents. In such bichromophores, however, only angular triquinanes result from the 1′,3′-addition; a feature which is rationalised in terms of asymmetry of the benzene–ethene orientation in the bichromophore conformation which precedes the addition. However, for the 3′-fluoro-bichromophore, both 1,5- and 2,6-additions occur showing that the β-silicon effect of the tether can compete to some extent with the fluorine stabilisation of an adjacent negative charge.

3. Experimental details

3.1. Photochemical and analytical methods

Preparative irradiations were of 1% w/v solutions of the bichromophores in cyclohexane or dioxane under air in 50 cm × 1.25 cm (i.d.) quartz tubes in a reactor fitted with six 18 W low pressure mercury arc lamps. Progress of the reaction was monitored by GC using a Hewlett-Packard 5790A Chromatograph fitted with a flame ionisation detector and a 12 m BP1 (SGE OV1 equivalent) bonded phase capillary column. 2,2,4,4,6,8,8-Heptamethylnonane was used as the GC standard to assess percentage conversion of the bichromophores and yields of the photoisomers. Product mixtures were also analyzed by TLC using Camlab Plygram G/UV precoated sheets and varying proportions of 40–60 b.p. light petroleum ether as eluent. Separation and purification of the photoisomers were achieved by flash chromatography on ICN silica 32–63 (Park Scientific Ltd). NMR spectra were recorded on a Joel 400 spectrometer with tetramethylsilane as an internal standard and in $CDCl_3$ solution: coupling constants are given in Hz. IR spectra were obtained using a Perkin-Elmer 881 spectrophotometer and were of liquid films. High resolution mass spectral data were obtained on a Fisons VG Autospec instrument operating in EI and CI (NH_3) modes after chromatographic purity assurance of the samples.

3.2. Bichromophores

The benzyl(dimethylsila)prop-1-enes were synthesised by the common method of reaction of allylchlorodimethylsilane with the appropriate benzyl magnesium bromide: the synthesis of 2′-fluorobenzyl[dimethylsila]prop-1-ene **22** is given to illustrate the procedure. Magnesium powder (0.27 g, 11.1 mmol), a small crystal of iodine and sodium dried diethyl ether (20 ml) were stirred together under a stream of nitrogen. A solution of 2′-fluorobenzyl bromide (2.0 g, 10.6 mmol) in sodium dried diethyl ether (10 ml) was added dropwise to the slurry at a speed to keep the solvent under gentle reflux (*ca.* 30 min). The mixture was refluxed for a further 2 hrs and then allowed to cool to room temperature. A solution of allylchlorodimethylsilane (1.43 g, 10.6 mmol) in sodium dried diethyl ether (20 ml) was added dropwise to the stirred solution of the Grignard reagent over 30 min. The reaction mixture was stirred overnight and a saturated solution (50 ml) of ammonium chloride was added. The organic layer was washed with water, dried over anhydrous magnesium sulphate, and the diethyl ether removed to give the crude bichromophore (2.05 g, 92.8%) as a yellow oil. Purification of the bichromophores was achieved by flash chromatography using ICN silica 32–63 (Park Scientific Ltd).

3.2.1. 3-Benzyl(dimethylsila)prop-1-ene **10**

δ_H 7.27–6.96 (5 H, overlapping m's, 2′-, 3′-, 4′-, 5′-, 6′-H), 5.76 (1 H, ddt, $J_{2,1a}$ 15.8, $J_{2,1b}$ 11.4, $J_{2,3}$ 8.4, 2-H), 4.87 (1 H, dt $J_{1a,3}$ 1.1, 1a-H), 4.86 (1 H, dt, $J_{1b,3}$ 1.1, 1b-H), 2.12 (2H, s, –CH_2–Si–), 1.53 (2 H, dt, allylic –CH_2–), and −0.02 (6 H, s, 2×Me); δ_C 140.23, 134.97, 128.46, 128.40, 124.25, 113.48, 25.33, 22.95, and −3.75; ν_{max}/cm^{-1} 1631s, 1249s. (Found: M^+, 190.1179. Calc. for $C_{12}H_{18}Si$ *M*, 190.1178).

3.2.2. 3-(2′-Methylbenzyl[dimethylsila])prop-1-ene **8**

δ_H 7.12–6.96 (4 H, overlapping m's, 3′-, 4′-, 5′-, 6′-H), 5.76 (1H, ddt, $J_{2,1a}$ 16.1, $J_{2,1b}$ 10.6, $J_{2,3}$ 8.1, 2-H), 4.88 (dt, $J_{1a,3}$ 1.1, 1a-H), 4.87 (1 H, dt, $J_{1b,3}$ 1.1, 1b-H), 2.24(3 H, s, 2′-Me), 2.14 (2 H, s, –CH_2– Si–), 1.57 (2 H, dt, allylic –CH_2–), 0.00 (6 H, s, 2×Me); δ_C 138.46, 134.67, 134.55, 130.14, 128.75, 125.66, 124.18, 113.26, 23.26, 21.78, 20.34, −3.55; ν_{max}/cm^{-1} 1631s, 1249s. (Found: M^+, 204.1339. Calc. for $C_{13}H_{20}Si$: *M*, 204.1325).

3.2.3. 3-(2′-Methoxybenzyl[dimethylsila])prop-1-ene **9**

δ_H 7.13–6.82 (4 H, overlapping m's, 3′-, 4′-, 5′-, 6′-H), 5.82 (1 H, ddt, $J_{2,1a}$ 16.6, $J_{2,1b}$ 10.4, $J_{2,3}$ 8.2, 2-H), 4.90 (1 H, dt, $J_{1a,3}$ 1.1, 1a-H), 4.89 (1 H, dt, $J_{1b,3}$ 1.1, 1b-H), 3.82 (3 H, s, OMe), 2.16 (2H, s, –CH_2–Si–), 1.56 (2 H, dt, allylic –CH_2–), 0.00 (6 H, s, 2×Me); δ_C 135.35, 129.72, 128.91, 125.33, 125.15, 120.43, 113.04, 109.98, 54.99, 23.41, 18.95, −3.53; ν_{max}/cm^{-1} 1631m, 1243s. (Found: M^+, 220.1287. Calc. for $C_{13}H_{20}SiO$: *M*, 220.1284).

3.2.4. 2-Methyl-4-benzyl[dimethylsila]but-2-ene **12**

δ_H 7.29–7.01 5 H, overlapping m's, 2′-, 3′-, 4′-, 5′-, 6′-H) 5.17 (1 H, t of septets, $J_{3,4}$ 8.4, $J_{3,Me}$ 1.5, 3-H), 2.14 (2 H, s, –CH_2–Si–), 1.75 (3 H, d, Me), 1.59 (3 H, d, Me), 1.45 (2 H, d, allylic –CH_2–), 0.00 (6 H, s, 2×Me); δ_C 140.27, 129.30, 128.13, 123.88, 119.38, 25.82, 25.44, 17.65, 16.75, −3.73; ν_{max}/cm^{-1} 1248s. (Found: M^+, 218.1491. Calc. for $C_{14}H_{22}Si$: *M*, 218.1492).

3.2.5. 3-(4′-Fluorobenzyl[dimethylsila])prop-1-ene **21**

δ_H 6.98–6.91 (4 H, overlapping m's, 2′-, 3′-, 5′-, 6′-H), 5.78 (1 H, ddt, $J_{2,1a}$ 17.6, $J_{2,1b}$ 13.6, $J_{2,3}$ 8.1, 2-H), 4.90 (1 H, m, 1a-H), 4.87 (1 H, ddt, $J_{1b,3}$ 1.1, 1b-H), 2.09 (2 H, s, –CH_2–Si–), 1.55 (2 H, dt, 3-H), 0.00 (6 H, s, 2×Me); δ_C 134.52, 129.18, 129.10, 115.02, 113.34, 24.06, 22.59, 4.09; ν_{max}/cm^{-1} 1630s, 1250s. (Found: M^+, 208.1085. Calc. for $C_{12}H_{17}SiF$: *M*, 208.1083).

3.2.6. 3-(2′-Fluorobenzyl[diimethylsila])prop-1-ene **22**

δ_H 7.36–6.88 (4 H, overlapping m's, 3′-, 4′-, 5′-, 6′-H), 5.78 (1 H, ddt, $J_{2,1a}$ 16.5, $J_{2,1b}$ 10.6, $J_{3,2}$ 8.4, 2-H), 4.88 (1 H, ddt, $J_{1a,3}$ 1.46, 1a-H), 4.84 (1 H, m, 1b-H), 2.04 (2 H, s, –CH_2–Si–), 1.47 (2 H, dt, 3-H), 0.00 (6 H, s, 2×Me); δ_C 134.55, 130.41, 125.62, 125.55, 123.76, 123.72, 115.16, 113.31, 22.82, 17.68, 3.97; ν_{max}/cm^{-1} 1632s, 1257s. (Found: M^+, 208.1079. Calc. for $C_{12}H_{17}SiF$: *M*, 208.1083).

3.2.7. 3-(3′-Fluorobenzyl[dimethylsila])prop-1-ene **23**

δ_H 7.17 (1 H, m, $J_{4',5'}$ 8.1, $J_{4',F}$ 6.6, 4′-H), 6.78 (2 H, m, 2′, 5′-H), 6.71 (1 H, dt, $J_{6',5'}$ 10.2, $J_{6',2'}$ 2.2, 6′-H), 5.77 (1 H, m, $J_{2,1a}$ 17.6, $J_{2,1b}$ 9.5, $J_{2,3}$ 8.4, 2-H), 4.91 (1 H, dt, $J_{1a,3}$ 1.1, 1a-H), 4.86 (1 H, m $J_{1b,3}$ 1.1, 1b-H), 2.12 (2 H, s, –CH_2–Si–), 1.54 (2 H, dt, $J_{3,2}$ 3.7, $J_{3,1}$, 1.5, 3-H), 0.00 (6 H, s, 2×Me); δ_C 164.01, 161.72, 143.50, 134.39, 129.48, 123.76, 114.77, 110.85, 25.15, 22.61, 4.03; ν_{max}/cm^{-1} 1631s, 1254s. (Found: M^+, 208.1083. Calc. for $C_{12}H_{17}SiF$: *M*, 208.1083).

3.3. Photoproducts

The spectral data for the intramolecular *meta* photocycloadducts **7** and **11** from the bichromophores **8** and **10** respectively have been previously reported [7].

3.3.1. 5-Methoxy-10[dimethylsila]tetracyclo-[6.3.0.0^{1,5}.0^{4,6}]undec-2-ene **20**

δ_H 5.47 (1 H, dd, $J_{3,2}$ 5.6, $J_{3,4}$ 1.9 3-H), 5.43 (1 H, dd, $J_{2,4}$ 1.9, 2-H), 3.37 (3 H, s, OMe), 2.23, (1 H, dt, $J_{4,6}$ 8.5, 4-H), 2.12–2.00 (2 H, overlapping m's, 6-H and 8-H), 1.67 (1 H, dd, $J_{7exo,7endo}$ 13.2, $J_{exo,8}$ 6.3, 7exo-H), 1.50 (1 H, ddd, $J_{7endo,8}$ 5.5, $J_{7endo,6}$ 1.5, 7endo-H), 1.19 (1 H, d, $J_{11,11'}$ 15.4, 11-H), 0.87 (1 H, dd, $J_{9,9'}$ 14.3, $J_{9,8}$ 12.2, 9-H), 0.68 (1 H, dd, $J_{9',8}$ 6.8, 9′-H), 0.67 (1 H, d, 11′-H), 0.07 (6 H, s, 2×Me); δ_C 141.11, 124.03, 91.57, 68.42, 37.09, 36.61, 31.24, 19.00, 17.56, 1.28, 0.00. (Found: M^+, 220.1287. Calc. for $C_{13}H_{20}SiO$: *M*, 220.1284).

Diels–Alder adduct **19** of **20** with *N*-chlorosulphonyl isocyanate. This adduct was synthesised by stirring the photoadduct **20** with an equimolar quantity of *N*-chloroisocyanate at 0 °C, under an atmosphere of nitrogen, over a 12 h period. Followed by work up with sodium bicarbonate solution and extraction of the organic layer.

M.p. 74.3 °C; {positions numbered as for **20**) δ_H 6.17 (1 H, dd, $J_{4,3}$ 8.8, $J_{4,6}$ 5.9, 4-H), 5.67 (1 H, dd, $J_{3,2}$ 5.9, 3-H), 3.67 (3 H, s, OMe), 3.40 (1 H, overlapping dd, $J_{6,7}$ 5.5, 6-H), 2.90 (1 H, d, 2-H), 2.53 (1 H, overlapping dd, $J_{7,8}$ 8.1, 17-H), 2.44 (1 H, dd, $J_{7',9}$ 12.8, 7′-H), 1.75–1.64 (3 H, overlapping m's 8-H, 11-H, 11′-H), 1.13 (2 H, m $J_{9,8}$ 8.1, 9-H, 9′-H), 0.23 (3 H, s, Me), 0.10 (3 H, s, Me); δ_C 172.12, 135.69, 122.17, 96.11, 61.04, 59.81, 52.71, 44.01, 42.16, 38.74, 22.10, 14.93, 1.89, 1.21. (Found: C, 46.61; H, 6.06; N, 3.83. Calc. for $C_{14}H_{21}NO_4SiSCl$: C, 46.33; H, 5.83; N, 3.86%. Found: M^+, 362.0645. Calc. for $C_{14}H_{21}NO_4SiSCl$: *M*, 362.0649).

3.3.1.1. Crystal data **19**

$C_{14}H_{21}NO_4SiSCl$, $M = 362.02$. Wavelength 0.71070 Å, monoclinic, $P2_1/c$, $a = 10.063(7)$ Å, $b = 12.018(7)$ Å, $c = 14.974(9)$ Å, $\beta = 104.68(1)°$, $U = 1752(2)$ Å^3, $Z = 4$, $dc = 1365$ Mg m^{-3}, $\mu = 0.419$ mm^{-1}, $F(000)$ 756, reflections collected 5511, independent reflections 3066 [R(int) = 0.0661], refined on F^2 to $R1 = 0.0797$, $wR2 = 0.2129$ for data with $I > 2\sigma(I)$. Data for the crystals were collected on a Marresearch Image Plate using Mo Kα radiation. The crystal was positioned at 75 mm from the Image Plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [11]. The structure was solved using direct methods with the Shelx86 program [12]. In the structure, the non-hydrogen atoms were refined wiht anisotropic thermal parameters. The hydrogen atoms were included in geometric positions. The structure was refined using Shelxl [13]. All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading.

3.3.2. 3-[Dimethylsila]-9-fluoro-tetracyclo-[5.4.0.0$^{1.8}$.O$^{5.11}$.]undec-9-ene 24

δ_H 4.52 (1 H, dd, $J_{10,11}$ 2.6, $J_{10,8}$ 1.1, 10-H), 2.36 (1 H, s, 8-H), 1.99 (1 H, d, $J_{11,F}$ 6.6, 11-H), 1.92 (1 H, m, $J_{5,F}$ 6.6, 5-H), 1.74 (1 H, d, $J_{6,6'}$ 13.6, 6-H), 1.56 (1 H, ddd, $J_{6',7}$ 6.2, $J_{6',}$F 2.2, 6′-H), 1.45 (1 H, d, $J_{4,4'}$ 13.6, 4-H), 1.12 (1 H, m, $J_{7,11}$ 2.2, 7-H), 0.78 (1 H, ddd, $J_{2,2'}$ 14.7, $J_{2,8}$ 1.5, 2-H), 0.76 (1 H, d, 4′-H), 0.59 (1 H, dd, 2′-H), 0.08 (3 H, s, Me_A), 0.05 (3 H, s, Me_B); δ_C 159.57, 99.40, 55.57, 51.12, 45.55, 36.35, 31,26, 26.65, 22.12, 21.59, 1.25, 1.20. (Found: M^+, 208.1086. Calc. for $C_{12}H_{17}SiF$: M, 208.1083).

3.3.3. 5-Fluoro-10-[dimethylsila]tetracyclo-[6.3.0.0$^{1.5}$.O$^{4.6}$]undec-2-ene 25

δ_H 5.35 (1 H, dt, $J_{3,2}$ 5.5, $J_{3,4}$ 2.2, $J_{3,F}$ 2.2, 3-H), 5.31 (1 H, dt, $J_{2,F}$ 2.2, $J_{2,4}$ 2.2, 2-H), 2.36 (1 H, ddt, $J_{4,F}$ 12.8, $J_{4,6}$ 7.0, 4-H), 2.2 (1 H, ddd, $J_{6,F}$ 14.5, $J_{6,7exo}$ 6.2, 6-H), 2.03 (1 H, m, 8-H), 1.63 (1 H, dd, $J_{7exo,7endo}$ 13.6, 7_{exo}-H), 1.40 (1 H, m, 7_{endo}-H), 1.14 (1 H, t, $J_{11,11'}$ 7.0, $J_{11,F}$ 7.0, 11-H), 0.79–0.70 (2 H, m, 9-H, 9′-H), 0.67 (1 H, dd $J_{11',F}$ 1.8, 11′-H), 0.10 (3 H, s, Me_A), 0.09 (3 H, s, Me_B); δ_C 140.84, 123.43, 56.77, 39.59,, 34.57, 31.42, 19.31, 16.77, 1.06, 1.02. (Found: M^+, 208.1081. Calc. for $C_{12}H_{17}SiF$: M, 208.1083).

3.3.4. 3-[dimethylsila]-8-fluoro-tetracyclo-[5.4.0.0$^{1.8}$.O$^{5.11}$.]undec-9-ene 26

δ_H 5.86 (1 H, d, $J_{9,10}$ 6.2, 9-H), 5.41 (1 H, m, $J_{10,9}$ 6.2, $J_{10,F}$ 4.4, $J_{10,11}$ 2.2, 10-H), 2.43 (1 H, d, 11-H), 2.30 (1 H, d, $J_{7,6'}$ 2.6, 7-H), 1.65 (1 H, m, $J_{5,6}$ 8.4, $J_{5,F}$ 4.0, 5-H), 1.56 (1 H, d, $J_{6,6'}$ 6.2, 6-H), 1.48 (1 H, dd, 6′-H), 1.40 (1 H, d, $J_{4,4'}$ 13.9, 4-H), 1.14 (1 H, d, 4′-H), 0.88 (1 H, m, $J_{2,F}$ 2.2, 2-H), 0.68 (1 H, dd, $J_{2',2}$ 14.6, $J_{2',F}$ 2.2, 2′-H), 0.22 (3 H, s, Me_A), 0.11 (3 H, s, Me_B): δ_C 128.39, 127.70, 61.98, 46.82, 31.54, 31.36, 22.65, 16.70, 4.03, 1.04. (Found: M^+, 208.1090. Calc. for $C_{12}H_{17}SiF$: M, 208.1083).

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