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Intramolecular photocycloaddition of a vinyl ether to CF_3-substituted 2-methoxy-5-phenylpent-1-enes

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Abstract

2-Methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene undergoes 2,6- and 1,3-*meta*-photocycloaddition on irradiation ($\lambda = 254$ nm). The methoxy group has the endo configuration in the photocycloadducts. Irradiation of the *para*- and *ortho*-CF_3-substituted 2-methoxy-5-phenylpent-1-enes leads to intramolecular *ortho*-photocycloadducts. The difference in product formation is related to the free enthalpy of electron transfer.

Keywords: Arene–alkene photoaddition; *Meta*-photocycloaddition; *Ortho*-photocycloaddition

1. Introduction

In the intramolecular *meta*-photocycloaddition of a vinyl ether to an arene, geometrical constraints force the oxygen atom to occupy either an endo or exo orientation, depending on its position relative to the double bond. In phenethyl vinyl ether (**1**) and (*Z*)-1-methoxy-5-phenylpent-1-ene (**2**), the oxygen atom can only approach the excited phenyl ring in the exo orientation. Both compounds yield *meta*-photocycloadducts on irradiation [1,2] (Fig. 1). Compound **1** gives one 2,6-adduct (**1a**) and its thermally rearranged product (**1c**, via a sigmatropic [1,5]-H shift) and two 1,3-*meta*-adducts (**1b** and **1d**). Compound **2** gives two 1,3-*meta*-adducts **2a** and **2b**. No 2,6-*meta*-adduct is formed owing to steric hindrance between the methoxy group and the hydrogen atoms on the α- and/or β-carbon atoms of the side chain, a phenomenon which is also observed for other *Z*-isomers [3–5]. On irradiation of (*E*)-1-methoxy-5-phenylpent-1-ene (**3**) and 2-methoxy-5-phenylpent-1-ene (**4**), in which the oxygen atom must approach the excited phenyl ring with an endo orientation (Fig. 2), intramolecular *meta*-photocycloaddition does not occur [2]. The reluctance of these two compounds to undergo *meta*-photocycloaddition is ascribed to the repulsive interaction between the endo oxygen atom and the negative charge which develops in the excited phenyl ring on approach of the alkene [2] (Fig. 2).

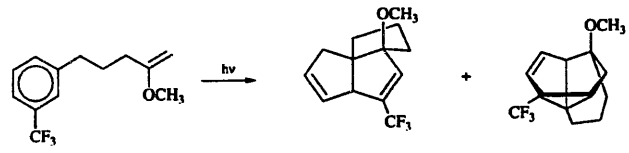
On irradiation of 5-(3-phenylpropyl)-2,3-dihydrofuran (**5**), no *meta*-adducts are found [6], in spite of the possible favourable secondary orbital interaction between the CH_2 group of the dihydrofuran ring and the excited benzene ring [7,8] (Fig. 3).

To decrease the repulsive interaction between the endo oxygen atom of the vinyl ether and the partial negative charge on the excited benzene ring, we decided to introduce an electron-withdrawing substituent at the *meta*-, *para*- and *ortho*-positions on the aryl ring in 2-methoxy-5-phenylpent-1-ene. We therefore synthesized and irradiated 2-methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene (**6**), 2-methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene (**7**) and 2-methoxy-5-[2-(trifluoromethyl)phenyl]pent-1-ene (**8**) (Fig. 4).

2. Results

2.1. 2-Methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene (6)

Irradiation of a 0.1% (v/v) solution of compound **6** in cyclohexane for 12 h yielded two major photoadducts **6a** and **6b** in a ratio of 41 : 32 and three minor products (together 9%) (Scheme 1). The initial ratio of the photoadducts



6 6a (41) 6b (32)

Scheme 1. Irradiation of 2-methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene (product ratios in parentheses).

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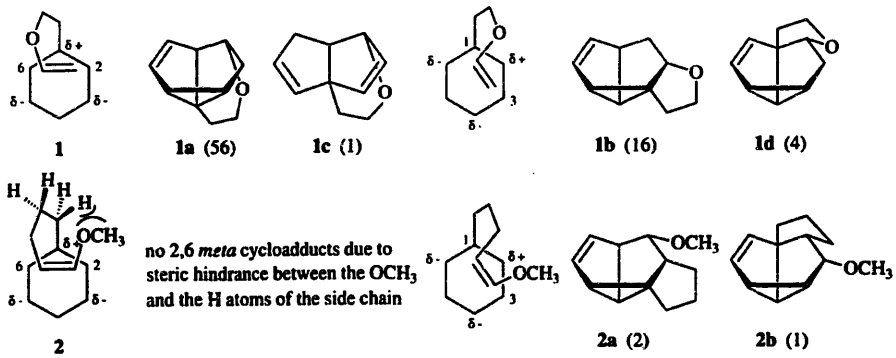


Fig. 1. Position of the oxygen atoms in 2,6- and 1,3-addition and photoadducts of compounds **1** and **2**.

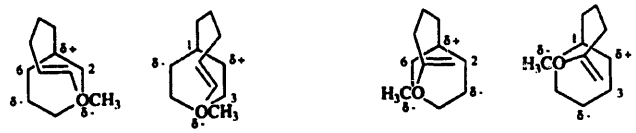


Fig. 2. Position of the oxygen atoms in 2,6- and 1,3-addition of compounds **3** and **4**.

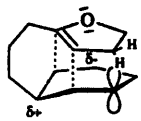


Fig. 3. Possible favoured endo addition by secondary orbital interaction.

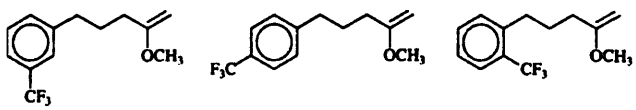


Fig. 4. *Meta*-, *para*- and *ortho*-CF_3-substituted 2-methoxy-5-phenylpent-1-enes.

6a : **6b** (extrapolated to $t=0$) was 1 : 1, and after 82% conversion of the starting material the ratio was 1.3 : 1. The product ratio was thus fairly constant in time. The adducts **6a** and **6b** were isolated by preparative gas chromatography (GC) and identified using ^1H nuclear magnetic resonance (NMR) (2D correlated spectroscopy (COSY) and J-resolved spectroscopy (JRES)), ^{19}F NMR, ^{13}C NMR (CH COSY) and gas chromatography/mass spectrometry (GC/MS). The ^1H NMR data are presented in Table 1 and Table 2 and the ^{13}C NMR data in Table 3.

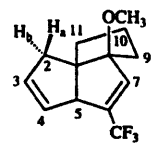
Photoproduct **6a**, 8-endo-methoxy-6-trifluoromethyltricyclo[6.3.0.$0^{1,5}$]undeca-3,6-diene, is a rearranged 1,3-*meta*-adduct (via a sigmatropic [1,5]-hydrogen shift), and **6b**, 5-endo-methoxy-8-trifluoromethyltetracyclo[5.4.0.$0^{1,8}$.$0^{5,11}$]-undec-9-ene, is a 2,6-*meta*-adduct.

2.2. 2-Methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene (7)

Irradiation of a 0.1% (v/v) solution of compound **7** in cyclohexane gave four products: **7a** (Scheme 2), **7b**, **7c** and **7d**. The concentration of **7a** did not increase further after 8 h

Table 1
Proton chemical shifts (in ppm relative to TMS) of compounds **6a** and **6b** (300 MHz, $CDCl_3$)

Proton	6a	Proton	6b
2^a	2.44 (dd)	2^a or 2^b	1.41 (m) or 1.67 (m)
2	2.01 (dd)	3^a or 3^b	1.45 (m) or 1.86 (m)
3–4	5.68–5.75 (m)	4^a or 4^b	1.30 (m) or 1.77 (m)
5	3.06–3.11 (m)	6^a	2.06 (d)
7	6.60 (q)	6^b	2.46 (dd)
9^a or 9^b	1.64 (m) or 2.21 (m)	7	2.57 (app. as t)
10^a or 10^b	1.57 (m) or 1.71 (m)	9	6.25 (app. as quint.) (F decoupling converts this quintet into a doublet)
11^a or 11^b	1.61 (m) or 1.89 (m)	10	6.23 (app. as dd)
OCH_3	3.19 (s)	11	3.03 (app. as t)
		OCH_3	3.23 (s)



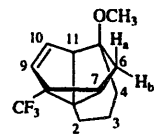
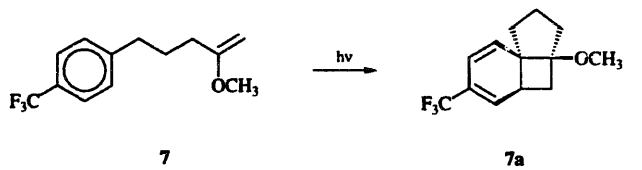


Table 2
Coupling constants (in hertz) of compounds **6a** and **6b** (300 MHz, $CDCl_3$)

J	**6a**	*J*	**6b**
2^a–2^b	16.1	6^a–6^b	13.7
2^a–3	6.1	6^b–7	2.3
2^b–3	2.0	7–11	2.1
7–CF_3	2.3	9–10	2.5
		9–CF_3	2.5
		10–11	1.9

Table 3
Carbon chemical shifts from ^{13}C APT (in ppm relative to TMS) of compounds **6a** and **6b** (75.5 MHz, $CDCl_3$)

Carbon	**6a**	**6b**
2	28.84	26.94
3	126.76	21.41
4	125.27	28.88
5	50.22	
6		31.74
7	141.59	46.50
9	33.18	142.30
10	20.50	136.82
11	29.70	49.35
OCH_3	49.00	49.08



7 **7a**

Scheme 2. Irradiation of 2-methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene.

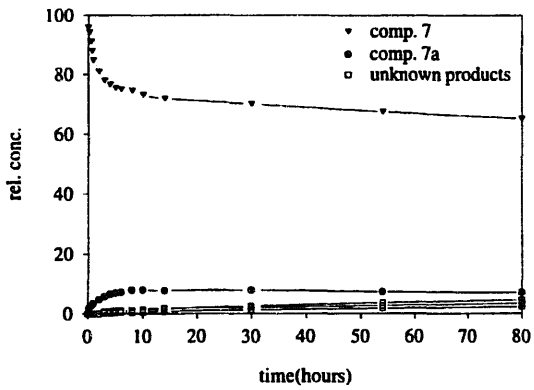
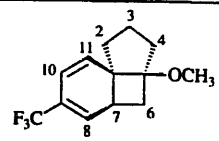


Fig. 5. Concentrations of **7**, **7a**, **7b**, **7c** and **7d** relative to an internal reference (ethyl caprylate) vs. irradiation time.

and decreased after 10 h (see Fig. 5). After 80 h of irradiation of compound **7**, there was still 65% of starting material left. Products **7b**, **7c** and **7d** were detected after 3 h irradiation time on GC. After 80 h, the ratio **7** : **7a** : **7b** : **7c** : **7d** was 65 : 7 : 3 : 4 : 2. Only product **7a** could be obtained in high purity with preparative GC and was identified by ^1H, ^{13}C and ^{19}F NMR and GC/MS. The ^1H NMR data are presented in Table 4 and the ^{13}C NMR data in Table 5.

Table 4
Proton chemical shifts (in ppm relative to TMS) of compound **7a** (600 MHz, $CDCl_3$)

Proton	**7a**
2^a or 2^b	1.75–1.82 (m) or 1.86 (ddt)
3^a or 3^b	1.90–1.94 (m) or 1.96–2.03 (m)
4^a or 4^b	1.60 (ddd) or 1.75–1.82 (m)
6^a and 6^b	2.25–2.32 (m)
7	2.51–2.56 (m)
8	6.07–6.10 (m)
10	5.97 (dd)
11	5.58 (app. as dt)
OCH_3	3.22 (s)



7a

Table 5
Carbon chemical shifts (in ppm relative to TMS) and ^{19}F coupling constants (in hertz) of compound **7a** (150.9 MHz, $CDCl_3$)

Carbon	**7a**	*J*
1	51.88	
2	37.15	
3	23.50	
4	39.16	
5	97.16	
6	39.56	
7	29.25	
8	127.50 (q)	8–CF_3 5.1
9	124.58 (q)	9–CF_3 30.5
10	117.94	
11	130.44	
CF_3	123.58 (q)	C–F 271.5
OCH_3	51.39	

Photoproduct **7a**, 9-trifluoromethyl-5-methoxytricyclo-[5.4.0.$0^{1,5}$]undeca-8,10-diene, is an *ortho*-adduct which has a broad structureless UV band with an absorption maximum at 277 nm in cyclohexane. Products **7b**, **7c** and **7d** could not be isolated, but GC/MS showed that they were isomers of the starting material. The UV absorption spectrum of the crude irradiation mixture after 15 min showed three bands at 259, 277 and 336 nm in cyclohexane. The absorption band at 259 nm belongs to compound **7**, that at 277 nm to compound **7a** and the band at 336 nm could be from a triene. This triene could be formed by photochemical ring opening of the diene **7a** [9] (see Section 3). Irradiation of the isolated *ortho*-adduct **7a** yielded four products. The retention times of these products on analytical GC and their masses were identical to those of compounds **7**, **7b**, **7c** and **7d**. ^1H NMR showed that the major product of this irradiation was compound **7**. After 15 min, the ratio **7** : **7a** : **7b** : **7c** : **7d** was 63 : 23 : 2 : 2 : 1 and after 90 min it became 60 : 8 : 4 : 9 : 5. After 15 min, the UV spectrum of the crude irradiation mix-

ture showed a broad structureless absorption maximum at 336 nm in cyclohexane.

2.3. 2-Methoxy-5-[2-(trifluoromethyl)phenyl]pent-1-ene (8)

A solution of 0.1% (v/v) of 2-methoxy-5-[2-(trifluoromethyl)phenyl]pent-1-ene (**8**) in cyclohexane was irradiated for 80 h. Analytical GC showed the presence of four photoproducts in the ratio **8a** : **8b** : **8c** : **8d** = 4 : 9 : 7 : 4. There was still 29% of starting material left after 80 h. After 2 h, the concentration of **8a** (15%) started to decrease until it eventually became 4% (Fig. 6). The photoproducts could not be separated by preparative GC or high performance liquid chromatography (HPLC). *N*-Phenylmaleimide was added to the product mixture in methanol and the solution was refluxed for 2 h. Analytical GC showed that only product **8a** reacted with *N*-phenylmaleimide. However, the addition product could not be obtained in sufficient amounts for NMR experiments. From GC/MS experiments, we know that the mass of each of the photoproducts is the same as that of the starting material **8**, and so the products must be isomers of **8**. The fragmentation patterns of the photoproducts from compound **8** are similar to those of the products from compound **7**, and so the structures of the products from **8** are probably similar to those formed from **7**. The retention times of the photoproducts of compound **8** are almost equal to the retention times of the photoproducts from compound **7** (**7a**, 0.75; **7b**, 1.26; **7c**, 1.30; **7d**, 1.31; **8a**, 0.85; **8b**, 1.18; **8c**, 1.23; **8d**, 1.25). Furthermore, the UV spectrum, after 2 h, showed an absorption maximum at 272 nm from compound **8** and a broad structureless absorption between 230 and 393 nm. The photochemical behaviour of compound **8** is thus almost identical to that of compound **7**, but the products are even less stable. However, on the basis of their masses, MS fragmentation patterns, retention times on GC, UV data and the reactivity of the primary photoproduct towards *N*-phenylmaleimide [10], we conclude that **8a** must be an *ortho*-adduct. It is known that *ortho*-adducts from arenes and alkenes are photochemically and thermally unstable [9,11–14]. The lability of such adducts further increases if donor and acceptor substituents are present [14].

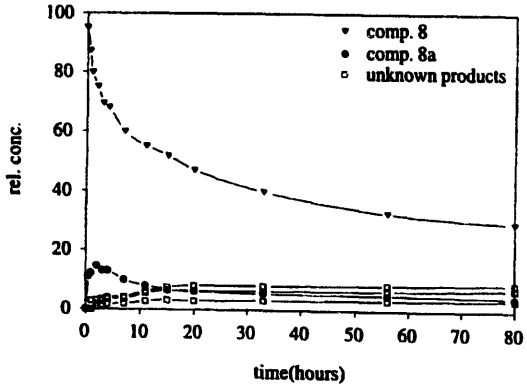


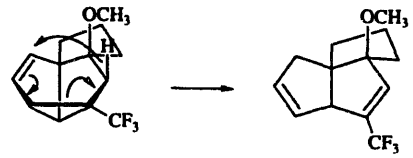
Fig. 6. Concentrations of **8**, **8a**, **8b**, **8c** and **8d** relative to an internal reference (ethyl caprylate) vs. irradiation time.

3. Discussion

The results of the irradiation experiments are summarized in Table 6. Two products, **6a** and **6b**, are formed on irradiation of compound **6** in a ratio of 41 : 32. Photoproduct **6a** is a rearranged 1,3-*meta*-adduct and **6b** is a 2,6-*meta*-adduct. During the addition of the alkene to the excited arene, the oxygen atom is forced to be situated endo to the phenyl ring. Product **6a** is formed from the primary 1,3-adduct **6ax** via a sigmatropic [1,5]-hydrogen shift (Scheme 3), a reaction known in the literature for compounds of this type [15]. In the present case, the [1,5]-hydrogen shift appears to occur during irradiation. In the 1,3-*meta*-photocycloaddition of compound **6**, addition of the alkene at positions 1 and 3 is more favourable than addition at positions 1 and 5 because, in the former situation, the CF_3 group resides at the carbon atom to which the addition occurs (Fig. 7). In the interaction between the alkene and the excited arene, the latter acts as an electrophile and there will be charge flow from the alkene to the aromatic ring. A developing negative charge at the site of addition can then be stabilized by an electron-withdrawing substituent [16]. Also, in the 1,5-addition, the CF_3 group will be situated, in the intermediate, at the centre position of the allylic moiety, which is not a favourable position for an electron-withdrawing substituent. Only one type of ring closure occurs, i.e. from carbon atom 4 to carbon atom 2. Osselton et al. [17] have proposed that the ring closure occurs preferentially on the side where the new σ-bond is further developed. It is known [18,19] that, in alkyl vinyl ethers, there is a $p-\pi$ conjugation in the vinyloxy system, which decreases the electron density on the oxygen atom and increases it on the β-carbon atom of the vinyl group. On the basis of this charge distribution, in combination with the electron-with-

Table 6
Summary of the results of the irradiation experiments

Compound	Mode
6	*Meta*-addition
7	*Ortho*-addition
8	*Ortho*-addition



6ax **6a**

Scheme 3. Formation of compound **6a** via a sigmatropic [1,5]-hydrogen shift.

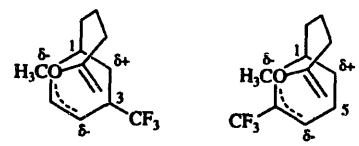


Fig. 7. Position of the alkene in the 1,3- and 1,5-addition of compound **6**.

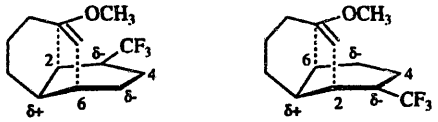
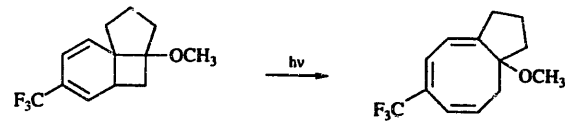


Fig. 8. Two different positions of the vinyl ether in the 2,6-addition of compound **6**.

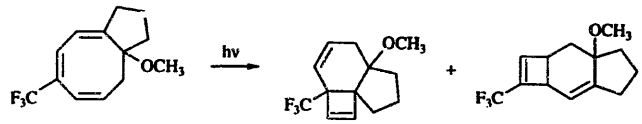
drawing properties of the CF_3 group when it is on the same side as the β-carbon atom, we can assume that, on this side, the formation of the σ-bond between the alkene and the arene (carbon atom 3) may run ahead of that on the other side. Carbon atom 3 of the arene will attain sp^3 character earlier than the other carbon at the addition site and will draw its neighbours (carbon atoms 2 and 4) closer together, thus causing the ring closure to take place from carbon atom 4 to carbon atom 2. In the 2,6-addition, leading to **6b**, the oxygen atom is situated above carbon atom 5 of the benzene ring. It is understandable that the vinyl ether does not approach the excited phenyl ring in such a way that the oxygen atom is situated above carbon atom 3, because extra negative charge develops at this position due to the electron-withdrawing CF_3 group (Fig. 8). Repulsion between the lone pairs of the oxygen atom of the methoxy group and the partial negative charge on the benzene carbon atom will discourage this approach. The fact that no photoadducts are found for (*E*)-1-methoxy-5-phenylpent-1-ene and 2-methoxy-5-phenylpent-1-ene is ascribed to the repulsive interaction between the oxygen atom and the negative charge which develops on approach of the alkene to the phenyl ring [2]. This repulsion is probably decreased in the presence of an electron-withdrawing substituent on the arene. Two factors may contribute to this effect. The first may be that the electron-withdrawing CF_3 group is capable of reducing the charge at the carbon atoms above which the oxygen atom is situated (para to CF_3 in the 1,3-addition and meta to CF_3 in the 2,6-addition). Secondly, the CF_3 group turns the arene into a better electron acceptor than toluene, and this may lead to increased charge transfer from the alkene to the arene making the oxygen atom less negative than in the molecule without a CF_3 group.

Only one *ortho*-adduct **7a** is obtained from the irradiation of compound **7** and no *meta*-adducts are formed. Three other products are detected on GC which are probably secondary products formed from the *ortho*-photoadduct. The diene **7a** may be converted into a triene by photochemical ring opening [9] (Scheme 4). The UV spectrum of the crude irradiation mixture shows three absorption bands at 259, 277 and 336 nm. The absorption band at 259 nm belongs to compound **7**, that at 277 nm to compound **7a** and the band at 336 nm may be from a triene. It is known from the literature [9,11–13] that a triene of this type can undergo photocyclization (Scheme 5). Irradiation of the isolated *ortho*-adduct **7a** yields compound **7** [9,11,12] and the secondary photoadducts **7b**, **7c** and **7d**. On irradiation of **7**, a quasi-stationary state is reached with approximately 65% **7** and 8% **7a** (see Fig. 5). If **7a** is irradiated, approximately the same ratio is reached. Thus the equilibrium **7** ⇄ **7a** strongly lies to the left,



7a

Scheme 4. Photochemical ring opening of diene **7a** to a triene.



Scheme 5. Conversion of a triene by photochemical cyclization.

which is probably mainly due to the fact that the absorption coefficient of **7a** is much larger than that of **7**.

Irradiation of compound **8** yields four photoproducts which could not be isolated; however, it was concluded that the reaction mixture consists of an *ortho*-adduct and its ensuing reaction products. As observed for irradiation of compound **7**, *ortho*-photocycloaddition is the major reaction mode on irradiation of **8**.

From studies by Bryce-Smith et al. [20], Houk [8], Mattay [21] and van der Hart et al. [22], it is known that *ortho*-addition is favoured over *meta*-addition when the donor–acceptor properties of the reactants are different. The donor–acceptor properties have been used by Mattay [21] by considering the equation for the free enthalpy (ΔG) of complete electron transfer

$$\Delta G = F[E^{ox}_{1/2}(D) - E^{red}_{1/2}(A)] - \Delta E_{0-0} + \Delta E_{coul}$$

in which F is the Faraday constant (9.648×10^4 C mol^{-1}), $E^{ox}_{1/2}(D)$ is the oxidation potential of the donor (in volts, measured in acetonitrile), $E^{red}_{1/2}(A)$ is the reduction potential of the acceptor (in volts, measured in acetonitrile), ΔE_{0-0} is the excitation energy (in J mol^{-1}) and ΔE_{coul} is the coulombic interaction energy (in J mol^{-1}) of D^+ and A^- in a given solvent. The coulombic term has been written by Mattay [21] as follows

$$\Delta E_{coul} = \frac{e^2 N}{4\pi\epsilon_0 a}\left[\frac{1}{\epsilon} - \frac{2}{37.5}\right]$$

where $e = 1.602 \times 10^{-19}$ C, $N = 6.023 \times 10^{23}$ mol^{-1}, $\epsilon_0 = 8.854 \times 10^{-12}$ F m^{-1}, ϵ is the dielectric constant of the solvent and a is the encounter distance. The coulombic interaction energy pertains to a D^+/A^- ion pair at an encounter distance a, which was taken to be 7 Å. In the intermolecular photocycloaddition, the ΔG value correlates with the mode of reaction. At smaller ΔG values, more electron transfer takes place and *ortho*-addition becomes favoured. The boundaries of the ΔG areas vary for a particular arene with a range of alkenes and a particular alkene with a range of arenes. Use of the coulombic interaction term in the equation for ΔG implies that we are dealing with complete electron transfer. In *meta*- and *ortho*-cycloaddition this is probably not the case because a larger solvent dependence would be expected [23]. Incorporation of the complete coulombic term is therefore

Table 7
Reduction potentials and excitation energies of *meta*-, *para*- and *ortho*-CF_3-substituted toluenes

Compound	$E^{red}_{1/2}$ (V) [a]	ΔE_{0-0} (eV)
6 (*meta*-CF_3)	−2.69 (−3.19)	4.56
7 (*para*-CF_3)	−2.29 (−2.64)	4.59
8 (*ortho*-CF_3)	−2.30 (−2.56)	4.56

[a] Reduction potentials were measured by cyclic voltammetry at a Pt electrode vs. an $Ag/AgNO_3$ electrode in acetonitrile and were recalculated vs. a saturated calomel electrode (SCE); second reduction potential in parentheses.

questionable and we could consider the use of a correction factor. However, we assume that in our case this is not important because the coulombic interaction is identical for the three compounds studied. We therefore take it to be a constant (C). In our compounds, the alkene is always the same and the arenes differ in the position of the CF_3 substituent relative to the alkyl chain. In these systems, the arene is the electron acceptor and the alkene is the donor. To obtain an estimate of the ΔG values for compounds **6**, **7** and **8**, we have used 2-methoxypropene as a model alkene and 2-, 3- and 4-(trifluoromethyl)toluene as the arene.

In Table 7, the reduction potentials and excitation energies of 2-, 3- and 4-(trifluoromethyl)toluene are given. The excitation energy of the *para*-CF_3-substituted toluene differs only slightly (0.03 eV) from that of the other two isomers. The reduction potentials of the *para*- and *ortho*-CF_3-substituted toluenes are the same and less negative than the reduction potential of the *meta*-CF_3-substituted toluene.

The oxidation potentials were calculated by Miller's formula [24] from the *IP* values (calculated semiempirically using MOPAC93 [25] with AM1 parametrization) (see Table 8).

From the first six entries in Table 8, it can be seen that the calculated ionization potentials are close to the experimental *IP* values (largest difference is 0.17 V). The oxidation potential of ethyl vinyl ether measured by Mattay [21] differs from the oxidation potential obtained from the *IP* value. By comparison of the oxidation potential of methyl vinyl ether (2.21 V) with that of ethyl vinyl ether calculated from the experimental *IP* value (2.22 V) and that measured by Mattay [21] (1.44 V), we conclude that 2.22 V is a better value for the oxidation potential of ethyl vinyl ether.

Table 9
Free enthalpies of electron transfer in compounds **6**, **7** and **8** calculated from $E^{ox}_{1/2}$ and $E^{red}_{1/2}$ of isolated model chromophores

Compound	$\Delta G - C$ (eV)
6	0.15
7	−0.28
8	−0.24

In Table 9, the $\Delta G - C$ values of compounds **6**, **7** and **8** are given, which were calculated using the reduction and oxidation potentials and the excitation energies of the isolated chromophores given in Table 7 and Table 8. The coulombic term, which is assumed to be identical for the three pairs, has been taken as a constant (C).

The ΔG value for compound **6** is approximately 0.4 eV higher than that of **7** and **8**, which means that, in the excited state, between the two chromophores of compound **6** there is less electron transfer. Compound **6** gave *meta*-adducts on irradiation and compounds **7** and **8** gave *ortho*-adducts. Thus, for these systems, there seems to be a relation between the ΔG value (calculated from the donor–acceptor properties of the isolated chromophores) and the mode of the addition reaction. To our knowledge, this is the first example of such a relation in an intramolecular photocycloaddition reaction.

4. Experimental details

All starting materials were obtained commercially (Aldrich Chemicals N.V., Belgium and Janssen Chimica, Netherlands). All commercial compounds were used without further purification. The ^1H NMR spectra of all the synthesized compounds were recorded on a JEOL FX200 Fourier Transform NMR spectrometer at 200 MHz in $CDCl_3$ with tetramethylsilane (TMS) as internal reference. Irradiations were carried out in quartz vessels in a Rayonet Photochemical

Table 8
Experimental and calculated ionization potentials and oxidation potentials

Compound	IP_{exp} (eV)	IP_{calc} (eV) [a]	$E^{ox}_{1/2}$ (V) [b] (from IP_{exp})	$E^{ox}_{1/2}$ (V) [b] (from IP_{calc})	Reference
Propene	9.74	9.72	2.76	2.74	[21]
Ethyl vinyl ether	9.15	8.99	2.22	2.07	[26]
			1.44 [c]		[21]
Methyl vinyl ether	9.14	9.07	2.21	2.14	[26]
(*Z*)-1,2-Dimethoxyethene	7.97	8.12	1.13	1.27	[20]
(*E*)-1,2-Dimethoxyethene	8.04	8.21	1.20	1.35	[20]
(*Z*)-2-Methoxybut-2-ene	8.25	8.31	1.39	1.44	[26]
2-Methoxypropene		8.93		2.02	

[a] From semiempirical calculations using MOPAC93 with AM1 parametrization; *IP* is the difference between ΔH_f of the ionized molecule (the geometry was not allowed to relax) and ΔH_f of the neutral molecule, divided by 23.06.
[b] Calculated by means of Miller's formula [24] unless otherwise indicated.
[c] Oxidation potential taken from Ref. [21].

Reactor RPR200 fitted with eight 254 nm lamps, placed in a room cooled to 4 °C. All irradiations were carried out with commercially available cyclohexane (Uvasol, Merck), under an argon atmosphere, and K_2CO_3 (approximately 2% w/v) was added to all solutions. Analytical irradiations were carried out in a merry-go-round with one Hanau TNN 15/32 Hg lamp. Analyses of the mixtures of the photoproducts were performed on a Varian 3400 Gas Chromatograph (column, 25 m; OV 101; carrier gas, H_2). The products of the irradiation of compounds **6** and **7** were separated using a preparative gas chromatograph, ATI Unicam 610 Series (column, 6 m×8 mm; 40–60 mesh; 10% carbowax on Chromosorb W NAW; carrier gas, H_2). The mass spectra of the photoproducts were recorded on a Finnigan MAT with an ion trap detector (model 700) and a United Packard Gas Chromatograph (model 438a). ^{1}H NMR spectra of the photoadducts were taken on a Bruker WM300 or Bruker DMX-600 NMR spectrometer at 300 MHz or 600 MHz. ^{13}C NMR was performed on a Bruker WM300 or Bruker DMX-600 spectrometer operating at 75.5 MHz or 150.9 MHz. All spectra were recorded in $CDCl_3$ with TMS as internal reference. The connectivities of the protons of the photoproducts were obtained by decoupling and/or COSY and JResolve 2D ^{1}H NMR experiments. The assignments of the carbon atoms were obtained from ^{13}C attached proton test (APT) and ^{1}H–^{13}C COSY experiments. Chemical shift values (δ) are given in parts per million (ppm) relative to TMS and coupling constants (J) are given in hertz. Reduction potentials were obtained by cyclic voltammetry at a Pt electrode using an Autolab Potentiostat controlled by a General Purpose Electrochemical System 3.3 (GPES3, Eco Chemie, Utrecht, Netherlands) software package. Measurements were carried out using an $Ag/AgNO_3$ reference and a Pt counter-electrode in water-free acetonitrile. Concentrations of 1 mM were used and scans were taken from −2.00 V to −4.00 V at a rate of 100 mV s^{-1}. Acetonitrile (HPLC grade, Rathburn Chemicals Limited) was dried twice over activated aluminium oxide [27]. The supporting electrode was 0.1 M tetrabutylammonium hexafluorophosphate which was purified by repeated crystallization from ethyl acetate. The salt was dried under vacuum at 70 °C and stored under vacuum over P_2O_5. 4-(Trifluoromethyl)toluene was obtained from Aldrich Chemicals N.V., Belgium.

4.1. Synthesis of the starting materials

4.1.1. 2-Methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene (6)

4.1.1.1. 3-[3-(Trifluoromethyl)phenyl]propan-1-ol

To 1.8 g (74.1 mmol) of magnesium turnings in 15 ml of anhydrous diethyl ether, 9.0 g (46 mmol) of 3-(trifluoromethyl)benzyl chloride in 30 ml of anhydrous diethyl ether was added dropwise. After standing for 45 min, ethylene oxide (from 2-bromoethanol and potassium hydroxide) was added dropwise at 0 °C over a period of 2 h. The green suspension was poured, after stirring for 30 min at room temperature, into 100 ml of 20% sulphuric acid. The organic layer was washed with brine and dried over magnesium sulphate. The crude product was purified twice by column chromatography (first eluent, petroleum ether (40–60 °C); second eluent, diethyl ether), yielding 7.2 g (35 mmol) of 3-[3-(trifluoromethyl)phenyl]propan-1-ol (purity, 91%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.89 (quint., 2H, H2), 2.50 (bs, 1H, OH), 2.75 (t, 2H, H3), 3.65 (t, 2H, H1), 7.35–7.44 (m, 4H, aromatic).

4.1.1.2. 1-Bromo-3-[3-(trifluoromethyl)phenyl]propane

Bromine (5.5 g, 34 mmol) was added dropwise to 10.6 g (34 mmol) of triphenyl phosphite at 0 °C [28]. After 7.0 g (34 mmol) of 3-[3-(trifluoromethyl)phenyl]propan-1-ol had been added to the red solid, the orange solution was kept at 85 °C for 1 h. The orange mixture was poured into 100 ml of 10% sodium hydroxide solution and extracted twice with diethyl ether. Purification by column chromatography (eluent, 10% diethyl ether in petroleum ether (40–60 °C)) gave 7.1 g (27 mmol) of 1-bromo-3-[3-(trifluoromethyl)-phenyl]propane (purity, 88%).

^{1}H NMR ($CDCl_3$, TMS) δ: 2.17 (quint., 2H, H2), 2.84 (t, 2H, H3), 3.38 (t, 2H, H1), 7.37–7.47 (m, 4H, aromatic).

4.1.1.3. 4-[3-(Trifluoromethyl)phenyl]butanoic acid

The Grignard reagent from 7.0 g (26 mmol) of 1-bromo-3-[3-(trifluoromethyl)phenyl]propane and 0.89 g (37 mmol) of magnesium in 20 ml of anhydrous diethyl ether, after refluxing for 1 h, was poured onto 100 g of solid carbon dioxide. After the addition of 200 ml of 50% hydrochloric acid and extraction of the water layer with diethyl ether, the organic layer was washed four times with 5% sodium hydroxide solution. After acidification with hydrochloric acid, the water layer was extracted with diethyl ether. The organic layer was dried over magnesium sulphate and evaporation of the solvent gave 3.9 g (17 mmol) of 4-[3-(trifluoromethyl)phenyl]butanoic acid (purity, 88%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.97 (quint., 2H, H3), 2.39 (t, 2H, H2), 2.73 (t, 2H, H4), 7.36–7.46 (m, 4H, aromatic), 11.62 (s, 1H, COOH).

4.1.1.4. Methyl 4-[3-(trifluoromethyl)phenyl]butanoate

Esterification of 3.9 g (17 mmol) of 4-[3-(trifluoromethyl)phenyl]butanoic acid with 2.4 ml of sulphuric acid in 70 ml of methanol yielded, after refluxing for 3.5 h, 3.4 g (14 mmol) of methyl 4-[3-(trifluoromethyl)phenyl]butanoate (purity, 96%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.98 (quint., 2H, H3), 2.28 (t, 2H, H2), 2.72 (t, 2H, H4), 3.58 (s, 3H, $COOCH_3$), 7.36–7.46 (m, 4H, aromatic).

4.1.1.5. 2-Methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene (6)

Following Okazoe et al. [29], 2-methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene was prepared as follows. A solution of 10.7 g (56 mmol) of $TiCl_4$ in 30 ml of dichloro-

methane was added at 0 °C to 40 ml of tetrahydrofuran (THF). To the yellow solution, a solution of 13.0 g (112 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in 4 ml of dichloromethane was added dropwise at 20 °C. After stirring for 10 min, 8.0 g (122 mmol) of zinc dust was added and the mixture was stirred for another 30 min. A solution of 5.6 g (32 mmol) of dibromomethane and 1.8 g (7.4 mmol) of methyl 4-[3-(trifluoromethyl)-phenyl]butanoate in 15 ml of THF was added dropwise to the dark blue mixture and stirred at 25 °C for 24 h. To the dark brown mixture was added 40 ml of saturated potassium carbonate solution. The supernatant was then decanted and the greyish black residue was washed with three portions of diethyl ether (3 × 100 ml). The organic fractions were combined, the solvent was removed and, after filtering, the residue was washed three times with 50 ml of pentane. After combination of the organic fractions and removal of the solvent, the yellow liquid was purified by column chromatography (silica; 230–499 mesh; eluent, 20% diethyl ether in heptane) yielding 0.76 g (3.1 mmol) of 2-methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene (purity, 93%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.83 (quint., 2H, H4), 2.14 (t, 2H, H3), 2.67 (t, 2H, H5), 3.53 (s, 3H, OCH_3), 3.87 (d, 1H, H1^a), 3.90 (d, 1H, H1^b), 7.34–7.46 (m, 4H, aromatic).

4.1.2. 2-Methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene (7)

4.1.2.1. Diethyl [4-(trifluoromethyl)benzyl]malonate

Diethyl malonate (16.4 g, 0.1 mol) was added rapidly to a solution of 2.4 g (0.1 mol) of sodium dissolved in 52 ml of dry ethanol following Reid and Ruhoff [30]. After heating the solution to 60 °C, 24.4 g (0.1 mol) of 4-(trifluoromethyl)benzyl bromide was added dropwise at such a rate that the ethanol solution refluxed gently. Diethyl ether was added to the reaction mixture after completion of the reaction (30 min reflux, GC). Washing with water and concentration yielded 29.9 g of a mixture of two products (1 : 1). This mixture was used as obtained in the next step. No accurate chemical shift values could be obtained from the ^{1}H NMR spectrum due to overlap.

4.1.2.2. Ethyl 3-[4-(trifluoromethyl)phenyl]propanoate

Diethyl [4-(trifluoromethyl)benzyl]malonate was decarbalkoxylated according to a method described by Krapcho et al. [31]. Thus a solution of 5.9 g (0.1 mol) of sodium chloride, 3.7 g (0.2 mol) of water and 5.9 g of crude diester in 85 ml of dimethyl sulphoxide (DMSO) was heated at 175 °C for 6 h. Addition of water to the reaction mixture, extraction with diethyl ether and evaporation gave 22.2 g of two products (1 : 1). This mixture was used as obtained in the next step. Due to overlap in the ^{1}H NMR spectrum, no accurate chemical shifts could be obtained.

4.1.2.3. 3-[4-(Trifluoromethyl)phenyl]propan-1-ol

A solution of 22.2 g of crude ethyl 3-[4-(trifluoromethyl)phenyl]propanoate in 90 ml of anhydrous diethyl ether was added dropwise to a suspension of 4.1 g (0.11 mol) of lithium aluminium hydride in 175 ml of anhydrous diethyl ether at reflux temperature. After 45 min, 30 ml of ice–water was slowly added to the mixture. To the grey suspension, 150 ml of 10% sulphuric acid was added, and the clear organic layer was separated and washed three times with 75 ml of diethyl ether. The organic layer was then washed with water and dried over magnesium sulphate. Evaporation of the solvent gave 19.1 g of alcohol (purity, 60%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.62 (bs, 1H, OH), 1.90 (quint., 2H, H2), 2.78 (t, 2H, H3), 3.68 (t, 2H, H1), 7.33–7.56 (m, 4H, aromatic).

4.1.2.4. 1-Bromo-3-[4-(trifluoromethyl)phenyl]propane

Substitution of the hydroxyl group was performed using bromine and triphenyl phosphite, as described for the synthesis of 1-bromo-3-[3-(trifluoromethyl)phenyl]propane. After column chromatography (eluent, 30% diethyl ether in petroleum ether (40–60 °C)), 12.3 g (46 mmol) of 1-bromo-3-[4-(trifluoromethyl)phenyl]propane (purity, 85%) was obtained.

^{1}H NMR ($CDCl_3$, TMS) δ: 2.17 (quint., 2H, H2), 2.85 (t, 2H, H3), 3.39 (t, 2H, H1), 7.29–7.60 (m, 4H, aromatic).

4.1.2.5. 1-Cyano-3-[4-(trifluoromethyl)phenyl]propane

Sodium cyanide (3.9 g, 81 mmol) was dissolved in 7 ml of water and 9 ml of ethanol at a temperature of 70 °C. 1-Bromo-3-[4-(trifluoromethyl)phenyl]propane (12.3 g, 46 mmol) was added dropwise at the same temperature [32]. After heating for another 3 h, diethyl ether was added to the reaction mixture, the organic layer was washed with brine and concentration yielded 9.1 g (43 mmol) of 1-cyano-3-[4-(trifluoromethyl)phenyl]propane (purity, 80%).

^{1}H NMR ($CDCl_3$, TMS) δ: 2.01 (quint., 2H, H2), 2.35 (t, 2H, H1), 2.86 (t, 2H, H3), 7.29–7.64 (m, 4H, aromatic).

4.1.2.6. Methyl 4-[4-(trifluoromethyl)phenyl]butanoate

Sulphuric acid (18.2 g), methanol (15.2 g) and 1-cyano-3-[4-(trifluoromethyl)phenyl]propane (9.1 g, 43 mmol) were refluxed overnight. The reaction mixture was quenched with 50 ml of water and extracted with diethyl ether; the organic layer was washed with concentrated sodium bicarbonate solution and dried over magnesium sulphate. Purification of the ester by column chromatography (eluent, 20% diethyl ether in petroleum ether (40–60 °C)) gave 6.4 g (26 mmol) of methyl 4-[4-(trifluoromethyl)phenyl]butanoate (purity, 87%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.97 (quint., 2H, H3), 2.34 (t, 2H, H2), 2.71 (t, 2H, H4), 3.67 (s, 3H, $COOCH_3$), 7.27–7.56 (m, 4H, aromatic).

4.1.2.7. 2-Methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene (7)

The reaction of 2.0 g (8.1 mmol) of ester with Lombardo's reagent, as described for the synthesis of 2-methoxy-5-[3-(trifluoromethyl)phenyl]pent-1-ene, gave 450 mg (1.8 mmol) of 2-methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene (purity, 95%).

^{1}H NMR ($CDCl_3$, TMS) δ: 1.85 (quint., 2H, H4), 2.13 (t, 2H, H3), 2.67 (t, 2H, H5), 3.53 (s, 3H, OCH_3), 3.88 (dd, 2H, $H1^a+H1^b$), 7.26–7.54 (m, 4H, aromatic).

4.1.3. 2-Methoxy-5-[2-(trifluoromethyl)phenyl]pent-1-ene (8)

2-Methoxy-5-[2-(trifluoromethyl)phenyl]pent-1-ene (**8**) was prepared analogously to the *para*-CF_3-substituted 2-methoxy-5-phenylpent-1-ene **7**.

4.1.3.1. Diethyl [2-(trifluoromethyl)benzyl]malonate

Purity, 64%. ^{1}H NMR ($CDCl_3$, TMS) δ: 1.25 (t, 6H, $(OCH_2\underline{CH_3})_2$), 3.43 (d, 2H, benzylic), 3.70 (t, 1H, $CH(COOEt)_2$), 4.17 (q, 4H, $(O\underline{CH_2}CH_3)_2$), 7.33–7.63 (m, 4H, aromatic).

4.1.3.2. Ethyl 3-[2-(trifluoromethyl)phenyl]propanoate

Purity, 61%. ^{1}H NMR ($CDCl_3$, TMS) δ: 1.25 (t, 3H, $OCH_2\underline{CH_3}$), 2.62 (t, 2H, H2), 3.14 (t, 2H, H3), 4.15 (q, 2H, $O\underline{CH_2}CH_3$), 7.31–7.64 (m, 4H, aromatic).

4.1.3.3. 3-[2-(Trifluoromethyl)phenyl]propan-1-ol

Purity, 73%. ^{1}H NMR ($CDCl_3$, TMS) δ: 1.89 (quint., 2H, H2), 2.09 (bs, 1H, OH), 2.87 (t, 2H, H3), 3.72 (dt, 2H, H1), 7.32–7.63 (m, 4H, aromatic).

4.1.3.4. 1-Bromo-3-[2-(trifluoromethyl)phenyl]propane

Purity, 84%. ^{1}H NMR ($CDCl_3$, TMS) δ: 2.17 (quint., 2H, H2), 2.95 (t, 2H, H3), 3.45 (t, 2H, H1), 7.30–7.65 (m, 4H, aromatic).

4.1.3.5. 1-Cyano-3-[2-(trifluoromethyl)phenyl]propane

Purity, 78%. ^{1}H NMR ($CDCl_3$, TMS) δ: 1.99 (quint., 2H, H2), 2.40 (t, 2H, H1), 2.94 (t, 2H, H3), 7.30–7.68 (m, 4H, aromatic).

4.1.3.6. Methyl 4-[2-(trifluoromethyl)phenyl]butanoate

Purity, 87%. ^{1}H NMR ($CDCl_3$, TMS) δ: 1.96 (quint., 2H, H3), 2.40 (t, 2H, H2), 2.82 (t, 2H, H4), 3.68 (s, 3H, $COOCH_3$), 7.29–7.63 (m, 4H, aromatic).

4.1.3.7. 2-Methoxy-5-[2-(trifluoromethyl)phenyl]pent-1-ene (8)

Purity, 96%. ^{1}H NMR ($CDCl_3$, TMS) δ: 1.82 (quint., 2H, H4), 2.20 (t, 2H, H3), 2.78 (t, 2H, H5), 3.54 (s, 3H, OCH_3), 3.89 (s, 2H, $H1^a+H1^b$), 7.30–7.62 (m, 4H, aromatic).

4.1.4. 2-(Trifluoromethyl)toluene

2-(Trifluoromethyl)benzyl chloride (2 g, 0.01 mol) in 10 ml of anhydrous THF was added dropwise to a suspension of 0.39 g (0.01 mol) of $LiAlH_4$ in 16 ml of anhydrous THF at reflux temperature. After 30 min, 30 ml of ice–water was added slowly to the mixture. A portion of 15 ml of 10% sulphuric acid was added to the grey solution and the organic layer was separated and washed with water and brine. After drying over magnesium sulphate and evaporation of the solvent, the yield was 1.2 g (7.5 mmol) of 2-(trifluoromethyl)toluene. The compound was purified by preparative gas chromatography (purity, better than 99%).

^{1}H NMR ($CDCl_3$, TMS) δ: 2.49 (s, 3H, CH_3), 7.23–7.62 (m, 4H, aromatic). GC/MS (electron impact) *m/z*: 160.

4.1.5. 3-(Trifluoromethyl)toluene

Reduction of 3-(trifluoromethyl)benzyl chloride as described for 2-(trifluoromethyl)toluene yielded 0.9 g (5.6 mmol) of 3-(trifluoromethyl)toluene. Purification was performed by preparative GC (purity, better than 99%).

^{1}H NMR ($CDCl_3$, TMS) δ: 2.41 (s, 3H, CH_3), 7.33–7.42 (m, 4H, aromatic). GC/MS (electron impact) *m/z*: 160.

4.1.6. 4-(Trifluoromethyl)toluene

^{1}H NMR ($CDCl_3$, TMS) δ: 2.41 (s, 3H, CH_3), 7.27 (d, 2H, aromatic), 7.50 (d, 2H, aromatic). GC/MS (electron impact) *m/z*: 160.

4.2. Photoproducts

4.2.1. Products from 2-methoxy-5-[3-(trifluoromethyl)-phenyl]pent-1-ene (6)

Irradiation of 2-methoxy-5-[3-(trifluoromethyl)phenyl]-pent-1-ene (**6**) for 12 h gave two major photoadducts (**6a** (41%) and **6b** (32%)) and three minor products (together, 9%). On analytical GC, under the conditions used (detection temperature/injection temperature, 250 °C; column temperature, 5 min at 100 °C and then a rise in temperature at 20 °C min^{-1}), the retention times of the major products relative to the starting material were 0.65 for **6a** and 0.74 for **6b**. The products were isolated by preparative GC and identified by NMR and MS. The adducts are all isomers of the starting material.

Compound **6a**: 8-endo-methoxy-6-trifluoromethyltricyclo[6.3.0.$0^{1,5}$]undeca-3,6-diene. GC/MS (electron impact) *m/z* (relative abundance): 244 (44), 229 (11), 215 (37), 212 (100), 175 (22), 159 (34), 147 (50), 115 (25), 72 (28). ^{1}H NMR (300 MHz, $CDCl_3$): details in Table 1 and Table 2. ^{13}C NMR (75.5 MHz, $CDCl_3$): details in Table 3.

Compound **6b**: 5-endo-methoxy-8-trifluoromethyltetracyclo[5.4.0.$0^{1,8}$.$0^{5,11}$]undec-9-ene. GC/MS (electron impact) *m/z* (relative abundance): 244 (17), 229 (7), 212 (19), 175 (13), 172 (39), 159 (20), 115 (11), 72 (100). ^{1}H NMR (300 MHz, $CDCl_3$): details in Table 1 and Table 2. ^{13}C NMR (75.5 MHz, $CDCl_3$): details in Table 3.

4.2.2. Products from 2-methoxy-5-[4-(trifluoromethyl)-phenyl]pent-1-ene (7)

Four photoproducts from 2-methoxy-5-[4-(trifluoromethyl)phenyl]pent-1-ene (**7**) were detected on analytical GC. On analytical GC, under the conditions used (detection temperature/injection temperature, 250 °C; column temperature, 10 min at 100 °C and then a rise in temperature at 20 °C min^{-1}), the retention times of the products relative to the starting material were 0.75 for **7a**, 1.26 for **7b**, 1.30 for **7c** and 1.31 for **7d**. Only product **7a** could be isolated by preparative GC and identified by NMR and MS. The other photoproducts could not be isolated, but GC/MS showed that they were isomers of the starting material.

Compound **7a**: 9-trifluoromethyl-5-methoxytricyclo-[5.4.0.$0^{1,5}$]undeca-8,10-diene. GC/MS (electron impact) *m/z* (relative abundance): 244 (4), 213 (9), 175 (4), 159 (8), 133 (9), 109 (9), 72 (100). ^1H NMR (600 MHz, $CDCl_3$): details in Table 4. ^{13}C NMR (150.9 MHz, $CDCl_3$): details in Table 5. UV (cyclohexane): $\lambda_{max} = 277$ nm.

Compound **7b**. GC/MS (electron impact) *m/z* (relative abundance): 244 (100), 229 (22), 212 (13), 197 (18), 175 (29), 159 (21), 143 (18), 128 (24), 115 (29), 91 (26), 77 (20), 69 (24).

Compound **7c**. GC/MS (electron impact) *m/z* (relative abundance): 244 (100), 229 (38), 212 (13), 197 (27), 185 (18), 175 (41), 159 (13), 143 (20), 133 (22), 115 (24), 91 (26), 77 (29), 51 (33).

Compound **7d**. GC/MS (electron impact) *m/z* (relative abundance): 244 (100), 229 (29), 212 (18), 197 (23), 184 (20), 175 (40), 159 (20), 143 (17), 133 (24), 115 (36), 91 (31), 77 (21), 69 (19).

4.2.3. Products from 2-methoxy-5-[2-(trifluoromethyl)-phenyl]pent-1-ene (8)

On analytical GC, four photoadducts were detected on irradiation of compound **8**. On analytical GC, under the conditions used (detection temperature/injection temperature, 250 °C; column temperature, 10 min at 100 °C and then a rise in temperature at 20 °C min^{-1}), the retention times of the products relative to the starting material were 0.85 for **8a**, 1.18 for **8b**, 1.23 for **8c** and 1.25 for **8d**. None of these products could be isolated because of their instability, but GC/MS showed that they were isomers of the starting material.

Compound **8a**. GC/MS (electron impact) *m/z* (relative abundance): 244 (4), 213 (5), 175 (11), 159 (8), 143 (7), 133 (11), 109 (14), 72 (100).

Compound **8b**. GC/MS (electron impact) *m/z* (relative abundance): 244 (71), 229 (31), 197 (19), 175 (100), 159 (13), 143 (24), 128 (28), 115 (30), 91 (27), 77 (28).

Compound **8c**. GC/MS (electron impact) *m/z* (relative abundance): 244 (95), 229 (25), 197 (18), 175 (100), 159 (15), 143 (22), 143 (22), 115 (31), 91 (22), 77 (24), 51 (27).

Compound **8d**. GC/MS (electron impact) *m/z* (relative abundance): 244 (100), 229 (22), 197 (10), 175 (93), 159 (18), 143 (19), 133 (24), 115 (33), 91 (24), 77 (23), 51 (25).

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