

Selectivity and Charge Transfer in Photoreactions of Donor-Acceptor Systems. Part 10.† *meta* Photocycloadditions of *m*-Bis(trifluoromethyl)benzene and Trifluoromethyl Benzonitriles to Olefins

Gabi Weber, Jan Runsink, and Jochen Mattay*

Institut für Organische Chemie der RWTH Aachen, Prof.-Pirlet-Str. 1, D-5100 Aachen, West Germany

Photocycloadditions of *m*-bis(trifluoromethyl)benzene and *meta*- and *para*-trifluoromethylbenzonitriles to cyclopentene and cyclohexene yield preferentially 2,4- (from *meta* arene) and 2,5- (from *para* arene) disubstituted *meta* cycloadducts. This is in accordance with the correlation between reaction mode and free enthalpy of electron transfer, calculated by means of the Weller equation. The high regioselectivities of these *meta* cycloadditions support the involvement of dipolar intermediates which are stabilized in position 1' and/or 3' by the acceptor substituents. Products formed from *p*-trifluoromethylbenzonitrile usually have the cyclopentane ring in the 'normal' *endo* configuration whilst those from cycloadditions of *m*-bis(trifluoromethyl)benzene to cyclopentene or cyclohexene give rise to products with an *exo* configuration.‡ This is discussed in terms of steric hindrance with substituents in position 2 and 4 of the *meta* adducts (position 1' and 3' of the dipolar intermediate). *m*-Trifluoromethylbenzonitrile leads to products with diverse stereoselectivities; *i.e.* location of CN (CF₃) in position 2 of the *meta* adduct prefers the *exo* (*endo*) configuration of the cyclopentane ring. This effect may indicate an unsymmetrical approach of cyclopentene onto *m*-trifluoromethylbenzonitrile during the 4',6'-attack.

The photoreactions of olefins with singlet excited benzene or substituted benzene derivatives have been of interest for many years,¹ and recent results from this laboratory have shown the influence of charge transfer on the selectivity of product formation.²⁻⁴ A simplified version of an empirical correlation between the reaction mode and the free enthalpies of electron transfer (ΔG) based on the exciplex mechanism and the Weller equation,⁵ is given as follows:

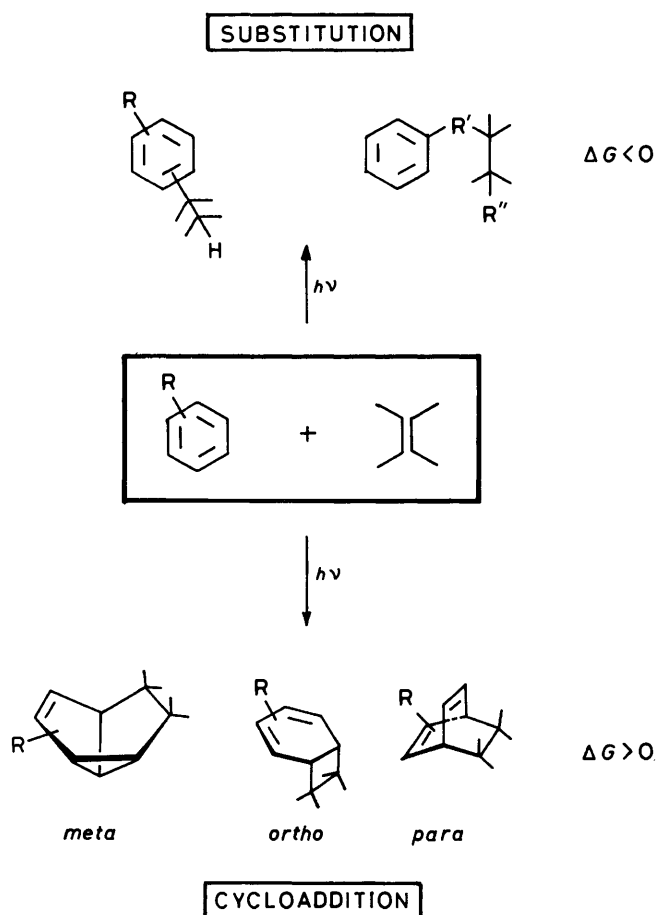
$$\Delta G = F[E_{\frac{1}{2}}^{\text{ox}}(\text{D}) - E_{\frac{1}{2}}^{\text{red}}(\text{A})] - \Delta E_{\text{excit}} + \Delta E_{\text{coul}}$$

where $E_{\frac{1}{2}}^{\text{ox}}(\text{D})$ = oxidation potential of the donor, $E_{\frac{1}{2}}^{\text{red}}(\text{A})$ = reduction potential of the acceptor, ΔE_{excit} = excitation energy of the electronically excited species, and ΔE_{coul} = coulombic interaction of the radical ion pair. If electron transfer becomes exergonic ($\Delta G < 0$) substitution reactions are preferred, whereas in systems of $\Delta G > 0$ the olefins undergo cycloaddition onto the arene ring.⁵

In the case of cycloadditions *meta* adducts are usually formed and dipolar intermediates ('zwitterions') have been proposed in addition to the exciplex^{2,4,5c,6,7} to explain this regioselectivity. Here we describe cycloaddition reactions of *m*-bis(trifluoromethyl)benzene (1) and *m*- and *p*-trifluoromethylbenzonitriles (2) and (3) with olefins such as cyclopentene (4) and cyclohexene (5).

Results

Preparative irradiations ($\lambda = 254 \text{ nm}$) of solutions containing compounds (1), (2), or (3) (1M) as the aromatic compound and one of the olefins (4) or (5) (1M) in cyclohexane resulted in the formation of the products (6)–(21). The products listed in Scheme 2 and 3 represent 72, 83, 54, and 29% [from compounds (1) + (4), (1) + (5), (2) + (4), and (3) + (4) respectively] of the totally formed photoproducts in these reactions. In the reactions of (1) with (4) and (1) with (5) the main products were



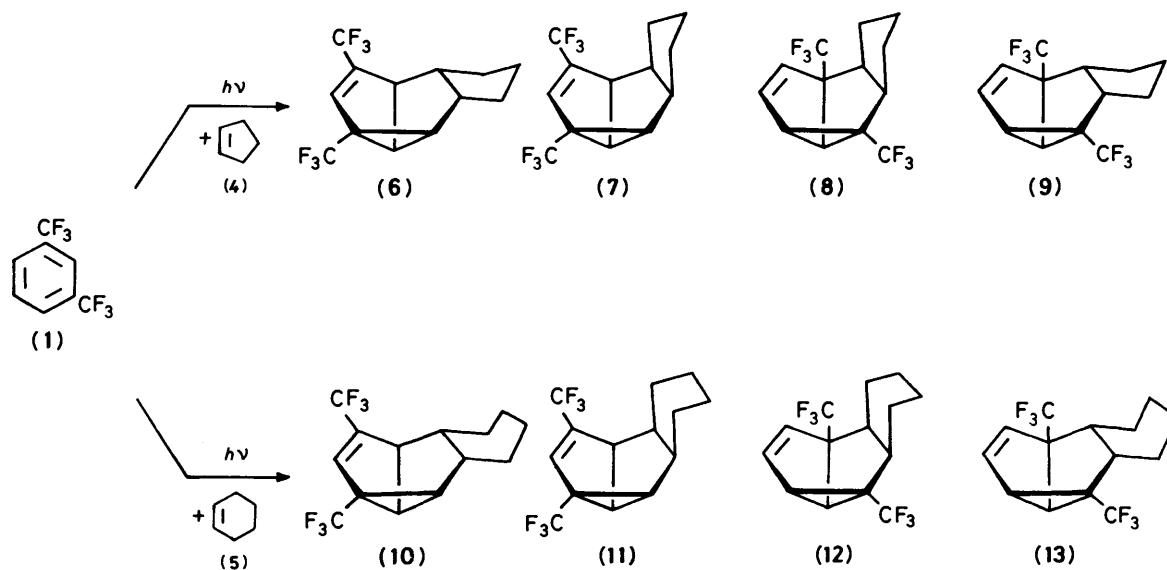
Scheme 1. Mode of reaction and photoinduced electron transfer

† For Part 9, see ref. 4b.

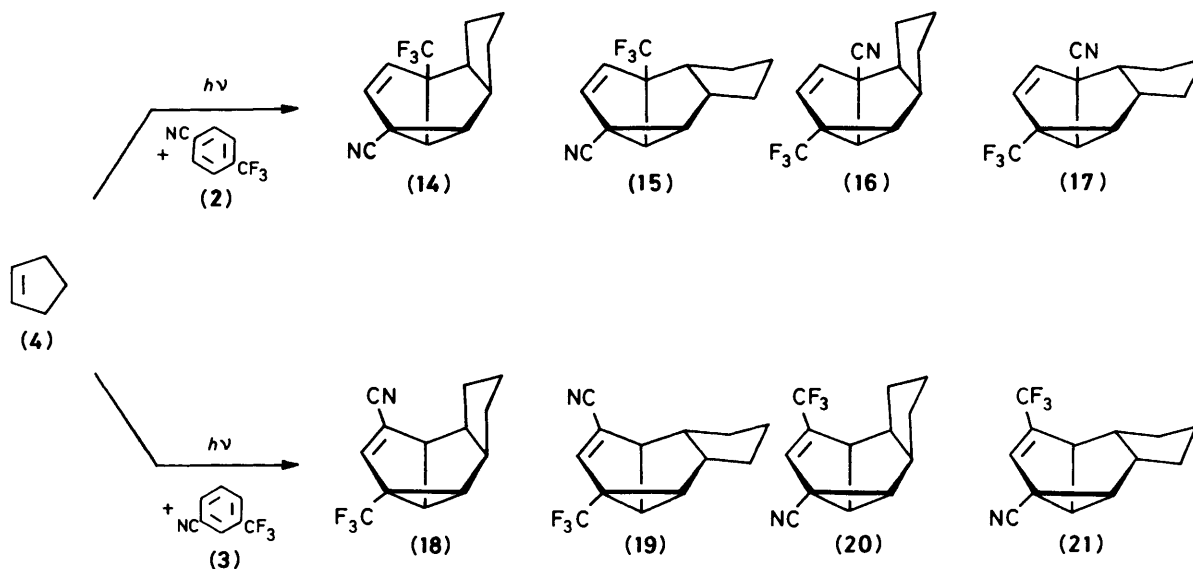
‡ In this paper the terms *exo* and *endo* are used to define the positions of the ethylenic substituents at carbons 1 and 8 of the 'tetracyclic' *meta* adducts (corresponds to carbons 6 and 7 of the 'tricyclic' *meta* adduct, *c.f.* Scheme 4) as described by J. March, 'Advanced Organic Chemistry,' J. Wiley, New York, 1985, p. 114.

2,4-disubstituted *meta* cycloadducts with the cyclopentene or cyclohexene ring in the *exo*-configuration [(6)/(10): 41/47% yield at 80/20% conversion].

The remaining unidentified products of the reaction of compounds (1) and (4) (28%) consisted of mainly 1:1 and 2:1



Scheme 2. Products of the photoreaction between *m*-bis(trifluoromethyl)benzene (1) and cyclopentene (4)/cyclohexene (5)



Scheme 3. Isolated products of the photoreactions between cyclopentene (4) and *p*-trifluoromethylbenzonitrile (2)/*m*-trifluoromethylbenzonitrile (3)

adducts of (1) and (4), as shown by means of g.c.m.s. During irradiation of (1) and (5) only 1:1 adducts were observed.

In the photoreactions (2) and (3) the colourless solutions turned dark brown during irradiation and the reaction was therefore stopped after 48 h. At low conversions only the products listed in Scheme 3 could be identified. Table 1 represents the yield of the identified products (6)–(21).

N.m.r. Analysis.—The n.m.r. data of the analysed products of the photoreactions are listed in Tables 2–7. The products (6)–(15) gave n.m.r. spectra typical of *meta* cycloadducts^{2,4,6–9} whilst the chemical shifts of 6-H and 7-H allowed the *endo* and the *exo* orientations of the cyclopentene and cyclohexene ring to be distinguished. The *endo* position generally causes a downfield shift of about 1 p.p.m. This is in accordance with the ¹H n.m.r.

Table 1. Yield of the photoproducts

Arene + Olefin	Product yield (%)				Conversion (%)
	(6)/41	(7)/16	(8)/9	(9)/6	
(1) + (4) ^a	(6)/41	(7)/16	(8)/9	(9)/6	83
(1) + (5) ^b	(10)/47	(11)/19	(12)/13	(13)/3	20
(2) + (4) ^c	(14)/28	(15)/18	(16)/5	(17)/4	7
(3) + (4) ^d	(18)/6	(19)/3	(20)/7	(21)/13	12

^a 28% of the unidentified products are 1:1 and 2:1 adducts (see text) examined by means of g.c.m.s. and ¹⁹F n.m.r. ^b In addition, formation of 9 unidentified products according to ¹⁹F n.m.r. ^c In addition, formation of 16 unidentified products, two main products in 14/16% yield. ^d In addition, formation of 15 unidentified products, 11 with 5% yield.

Table 2. ^1H N.m.r. spectroscopic data [δ_{H} (p.p.m.) and J (Hz)] of compounds (6)–(12) (CDCl_3/TMS , 90 MHz)

Proton	(6)	(7)	(8)	(9)	(10)	(11)**	(12)**
1-H	3.00 dd $J_{1,5}$ 5 Hz $J_{1,8}$ 7 Hz	3.2–3.3 m	3.2 d $J_{1,2}$ 7.5 Hz	2.9 d $J_{1,2}$ 7.5 Hz	3.07 dd $J_{1,5}$ 5.4 Hz $J_{1,8}$ 7.8 Hz	3.2 dd* $J_{1,5}$ 6 Hz $J_{1,8}$ 5 Hz	3.10 d $J_{1,2}$ 7.6 Hz
2-H	—	—	2.45 dd $J_{2,3}$ 1.5 Hz	2.65 dd $J_{2,3}$ 1.5 Hz	—	—	2.43 dd $J_{2,3}$ 1.8 Hz
3-H	6.10 q $J_{3-\text{CF}_3}$ 1.8 Hz	6.25 q $J_{3-\text{CF}_3}$ 1.7 Hz	5.9 dd $J_{3,4}$ 6 Hz	5.75 dd $J_{3,4}$ 5 Hz	6.19 q $J_{3-\text{CF}_3}$ 1.7 Hz	6.16 q $J_{3-\text{CF}_3}$ 1.8 Hz	5.85 dd $J_{3,4}$ 5.5 Hz
4-H	—	—	5.85 d	5.7 d	—	—	5.76 dq $J_{4-\text{CF}_3}$ 0.5 Hz
5-H	3.32 d	3.4 m	—	—	3.03 d	3.4 dd* $J_{5,6}$ 6 Hz	—
6-H	2.5–2.6 m	3.2–3.3 m	3.3–3.7 m	2.3–2.6 m	2.0–2.2 m	2.6–2.7 m	2.6–2.9 m
7-H	2.05 d	2.5–2.6 m	—	—	2.0–2.2 m	2.6–2.7 m	—
8-H	1.4–1.9 m	1.4–2.0 m	1.4–2.1 m	1.4–2.0 m	1.1–1.9 m	1.2–1.9 m	1.2–2.9 m
Ring (6H) or (8H)	—	—	—	—	—	—	—

** 270 MHz, * Reversed assignment possible.

Table 3. ^{19}F N.m.r. spectroscopic data [δ_{F} (p.p.m.) and J (Hz)] of compounds (6)–(13) (in CDCl_3 against $\text{CFCl}_3/\text{CDCl}_3$)

CF_3 -position	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
2	–68.2 s	–68.8 s	—	—	–68.1 s	–68.4 s	—	—
4	–64.0 d $J_{1,6}$ 1.6 Hz	–61.7 d $J_{1,4}$ 1.4 Hz	—	—	–64.1 d $J_{1,8}$ 1.8 Hz	–61.5 d $J_{1,4}$ 1.4 Hz	—	—
5	—	—	–70.3 s	–64.3 s	—	—	–69.5 s	–64.7 s
6	—	—	–72.9 s	–69.5 s	—	—	–71.4 s	–70.4 s

Table 4. ^{13}C N.m.r. spectroscopic data [δ_{C} (p.p.m.) and J (Hz)] of compounds (7) and (10)–(12) [(11), (12) in C_6D_6 ; (7), (13) in $\text{C}_6\text{D}_6/\text{CCl}_4$]

	(6)	(10)	(11)	(12)
CF_3	J_{123} 74 J_{276} 0 Hz	125.04 J_{271} 2 Hz	125.22 272.0 Hz	126.57 J_{279} 1 Hz
CF_3	120.05 J_{268} 0 Hz	122.72 J_{271} 9 Hz	122.96 J_{269} 8 Hz	126.25 J_{262} 8 Hz
C-1	41.85 s*	43.91 m*	48.96	42.51 $J_{3,0}$ 3 Hz
C-2	46.49 $^2J_{32}$ 0 Hz	45.05 $^2J_{26}$ 4 Hz	covered	34.10 q $J_{3,4}$ 4 Hz
C-3	127.41 m	131.46 $J_{5,5}$ 5 Hz $J_{2,0}$ 2 Hz	132.60 qq $J_{5,7}$ 5 Hz $J_{1,9}$ 9 Hz	132.24 s 68.43 q $^2J_{27}$ 3 Hz
C-4	139.58 q $^2J_{32}$ 0 Hz	137.27 q $^2J_{32}$ 9 Hz	143.5 q $^2J_{33}$ 7 Hz	132.70 q $J_{2,4}$ 4 Hz
C-5	53.01 s	55.55 s	53.78	50.57 s
C-6	57.94 s	52.11 s	50.53 q	38.21 s
C-7	41.86 s	34.14 s	39.92 s	43.92
C-8	40.70 s*	35.90 s*	43.10 s	21.77 s
CH_2 cyclopentane or cyclohexane ring	32.50 s 31.03 s 26.54 s	29.94 s 27.47 s 24.73 s 22.90 s	29.20 s 25.95 q $J_{1,9}$ 9 Hz 24.97 s 22.56 q $J_{1,4}$ 4 Hz	26.56 s 24.54 q $J_{1,2}$ 2 Hz 23.64 s 21.77 s

* Reversed assignment possible.

data of *meta* cycloadducts of α,α,α -trifluorotoluene and cyclopentene⁸ or 1,3-dioxole.^{4,6}

The ^{19}F n.m.r. spectra provides information about regio- and stereoselectivities based on the following features: (i) If CF_3 is in position 5, the *exo* configuration of the ring will cause a downfield shift of the F-signal, (ii) CF_3 in position 4 generates a doublet at *ca.* –64 p.p.m. (*exo*) and –61 to –62 p.p.m. (*endo*)

Table 5. ^1H N.m.r. spectroscopic data [δ_{H} (p.p.m.) and J (Hz)] of compounds (14) and (15) (in CDCl_3/TMS)

Proton	(14)	(15)
1-H	3.53 d $J_{1,8}$ 7.5 Hz	3.19 d $J_{1,8}$ 7.0 Hz
2-H	—	—
3-H	5.90 d	5.75 d
4-H	5.75 d $J_{3,4}$ 5.7 Hz	5.55 d $J_{3,4}$ 5.7 Hz
5-H	—	—
6-H	2.8–3.2 m	2.8–3.2 m
7-H	2.52 dd $J_{8,7}$ 6.6 Hz	2.24 d
8-H	—	—
cyclopentane ring (6 H)	1.4–2.0 Hz	1.4–2.0 Hz

with an F,H-coupling constant of 1.4–1.9 Hz, (iii) The ^{13}C n.m.r. signals of C-atoms which bear a CF_3 group have a C,F-coupling constant of *ca.* 30 Hz, whereas CF_3 itself has a coupling constant of *ca.* 270 Hz.

Based on these arguments structural assignments can be made even from product mixtures; the ^{19}F n.m.r. spectra of the crude reaction mixture of (1) + (5) gave chemical shifts characteristic of the CF_3 groups of product (13). Comparison of the ^{19}F n.m.r. data (Table 3) shows clearly that compounds (8) and (12), and compounds (9) and (13) have the same regio- and stereoselectivity.

The ^1H n.m.r. data of the *meta* adducts from the reaction of (2) and (4) showed signals for two olefinic protons, whereas the ^{19}F n.m.r. showed only singlets. Therefore, the substitution pattern is reduced to 2-CN, 5- CF_3 or *vice versa*. On comparison with other *meta* cycloadducts one expects only a large coupling constant ($J_{1,8}$) for the *endo* orientation. By this argument compound (14) has the *endo* and (15) the *exo* configuration. Compounds (16)–(21) were identified from the enriched

Table 6. ^{13}C N.m.r. spectroscopic data [δ_{C} (p.p.m.) and J (Hz)] of components (14), (15) (in CDCl_3/TMS)

	(14)	(15)
CF_3	122.78	122.78
CN	110.18 m	110.18 m
C-1	41.91 q $J_{2.5}$ Hz	40.64 q $J_{2.3}$ Hz
C-2	50.86 q $J_{1.5}$ Hz	covered
C-3	129.66 s	125.84 s
C-4	133.99 q $J_{2.4}$ Hz	133.55 q $J_{2.5}$ Hz
C-5	66.59 q $^2J_{30}$ Hz	66.2 q $^2J_{28}$ Hz
C-6	61.78 q $J_{1.3}$ Hz	covered
C-7	42.68 s	covered
C-8	28.67 $J_{1.5}$ Hz	covered
cyclopentane (ring $3 \times \text{CH}_2$)	30.05 29.61 25.81	31.12 29.68 25.50

Table 7. ^{19}F N.m.r. spectroscopic data [δ_{F} (p.p.m.) and J (Hz)] of compounds (14)–(21) (in CDCl_3 against $\text{CFCl}_3/\text{CDCl}_3$) and CN position

CF_3 -position	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)
2	CN*	CN*	-70.2 s	-68.1 s	-67.9 s	-67.4 s	CN*	CN*
4	—	—	—	—	CN*	CN*	-61.5 d	-63.8 d
5	-72.9 s	-69.2 s	CN*	CN*	—	—	—	—

* The statements about the position of the CN group are given by the *meta* and *para* substitution of (2) and (3).

Table 8. Redox-potentials, excitation energies, and calculated ΔG values

Arene	Acceptor		Donor		G/eV^a	(Acc. + Donor)
	$E_{1/2}^{\text{red}}/\text{V}$	$E_{\text{excit}}/\text{eV}$	Olefin	$E_{1/2}^{\text{ox}}/\text{V}$		
(1)	-2.51	4.47	(4)	1.83	0.78	[(1) + (4)]
(2)	-2.18	4.31	(5)	1.72	0.67	[(1) + (5)]
(3)	-2.39	4.35			0.61	[(2) + (4)]
					0.78	[(3) + (4)]

^a E_{coul} (cyclohexane) = 0.91 eV.

fractions of preparative g.c. separations according to a similar analysis of the n.m.r. data.

Discussion

Photoinduced Charge Separation (Charge Transfer and Mode of Reaction).—Recent results from this laboratory showed that charge transfer may influence the selectivity of product formation in photoreactions between electron donor and acceptor molecules.⁵

The photoreactions described here show a significant selectivity for the *meta* cycloaddition. The redox potentials, the excitation energies, and the calculated ΔG values (shown in Table 8) further confirm our proposal that cycloaddition is the preferred reaction mode for an endergonic electron transfer.

Since electron transfer becomes exergonic with 1,3-dioxole as the donor reactant,* no cycloadducts were formed upon irradiation.† The absence of substitution products may reflect

* $\Delta G = -0.29/-0.52$ eV for 1,3-dioxole + (1) or (3)/(2) in cyclohexane according to the Weller equation.

† Even after 230 h irradiation only a few of the arenes were consumed and a maximum 1% of products could be detected by means of g.c.

the dominance of back electron transfer rather than heterolytic cleavage into a benzylic radical and a fluoride anion, a process which was observed in photoreactions with α,α,α -trifluorotoluene.⁴

Regio- and Stereoselectivities of Cycloadditions.—In addition to the exciplex, dipolar intermediates have been proposed in order to explain the high regioselectivities of photocycloadditions with acceptor and donor substituted benzenes.^{2,4,6,7} For convenience, the dipolar intermediate is represented as a 'zwitterion' (Scheme 4).

CF_3 and CN as acceptor substituents are able to stabilize a negative charge in position 2 or 4 of the dipolar intermediate and therefore mainly 2,4-disubstituted *meta* cycloadducts are formed by 4',6'-attack‡ of the olefin onto the arene. 1'-3'-Attack, which led to 5,8-substituted *meta* adducts, is observed to a smaller extent.

Another possible mode of attack at positions 2' and 6' of the arene does not occur here. In that case CF_3 as an acceptor substituent would be located at the positive centre of the dipolar intermediate. 1-Substituted *meta* adducts have only been observed with donor substituted arenes.^{6,7,9}

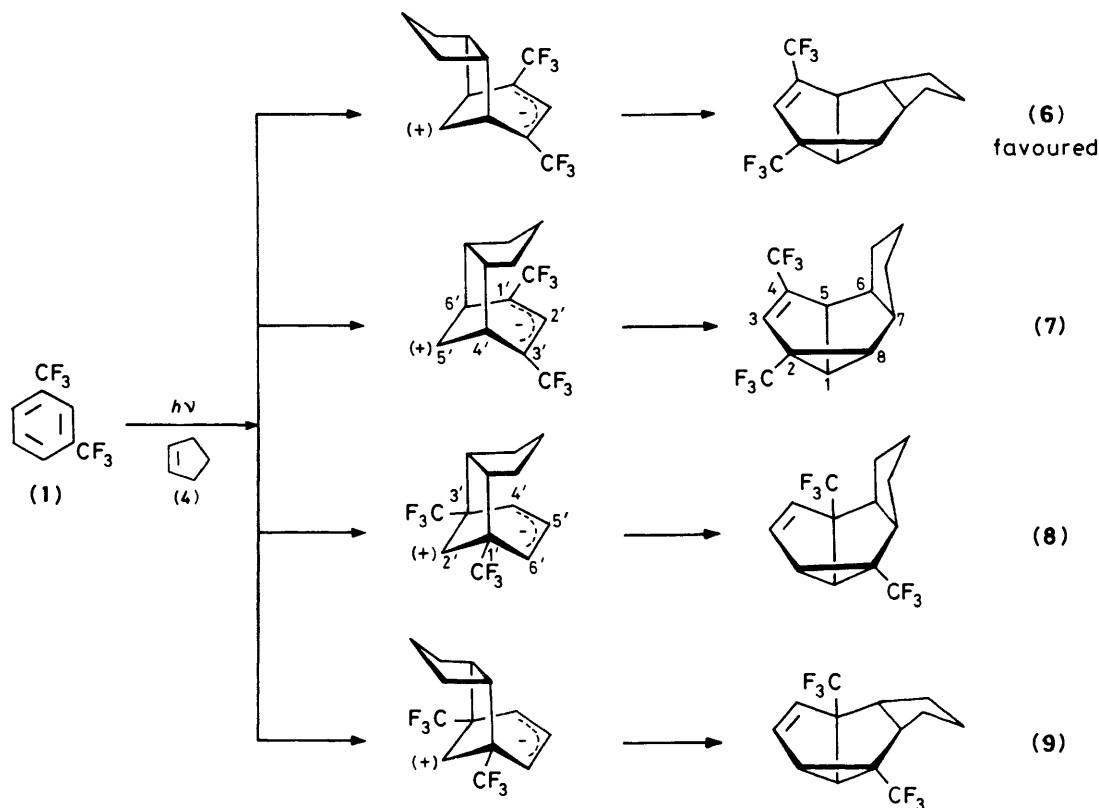
In the reaction of compounds (2) and (4), *meta* cycloadducts with CN located in position 2 and CF_3 in position 5 are preferred. The opposite substitution pattern is only observed in the minor products. The CN group in position 4 and accordingly the CF_3 in position 8 should be the most stable isomer due to the possible mesomeric effect between CN and the π -bond. Although such an arrangement was not observed one of the two unidentified products could have this substitution.

In the case of reaction between compounds (3) and (4) only a few of the main products could be isolated. All of them are 2,4-disubstituted *meta* cycloadducts which support the hypothesis of the stabilization effect of acceptor substituents in positions 2 and 4.

With simple alkenes *endo* stereoselectivity is observed in most *meta* cycloadditions. This has been rationalized on the basis of secondary orbital interactions in the exciplex state by Houk.¹⁰ In contrast, stereoselectivity turns to *exo* in photoreactions with cyclopentene (4) and cyclohexene (5) as the donor and compound (1) as the acceptor compound. Similar effects have only been observed in photoreactions with enol ethers, e.g. with 1,3-dioxoles, and have been rationalized on the basis of an electronic repulsion in the *endo* configuration.^{2,4-6} Table 9 shows the preferred stereoselectivities of some selected photoreactions between acceptor and donor compounds.

The stereoselectivities of the products of the reaction between compounds (1) and (4) clearly differ from those of the other reactions with cyclopentene. The same applies to cyclohexene. According to molecular models of the dipolar intermediates which result from a 4',6'-attack of the olefin onto (1), sterical hindrance between the CF_3 substituent in positions 2 and 4 and the five- or six-membered ring causes the *endo* configuration to be less favourable (Scheme 4).

‡ See Scheme 4.



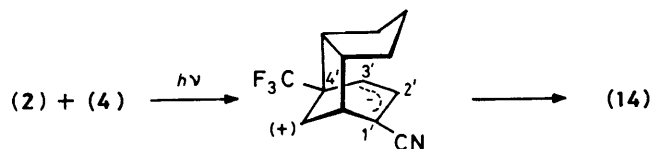
Scheme 4. Product formation *via* dipolar intermediates (Note: The dipolar character of the *meta*-bonded intermediates of a bicyclo[3.2.1]octene-type depend on stabilization by donor and/or acceptor substituents. For convenience, these dipolar intermediates are represented as zwitterions)

Table 9. Preferred stereoselectivity of *meta* cycloadducts

Acceptor	Donor	
	1,3-Dioxole	Cyclopentene
Benzene	<i>exo</i> ²	<i>endo</i> ¹¹
α,α,α -Trifluorotoluene	<i>exo</i> ^{4b}	<i>endo</i> ⁸
<i>m</i> -Bis(trifluoromethyl)benzene	—	<i>exo</i>
<i>p</i> -Trifluoromethylbenzotrile	—	<i>endo</i>
Anisole	<i>exo</i> ⁶	<i>endo</i> ¹²

In contrast, the corresponding 1',3'-attack leads preferentially to intermediates of *endo*-configuration and, consequently, to compound (8) [from (4)] or (12) [from (5)]. Substituents in positions 5 and 8 do not alter the normal *endo* stereoselectivity significantly (see Scheme 4).

The reaction of compound (2) with (4) mainly yields products of *endo* configuration. Only one substituent is located on the 'allylic part' of the intermediate (see Scheme 5). Obviously, this arrangement of the substituents does not cause such a large steric hindrance to the cyclopentane ring. This corresponds with studies of the α,α,α -trifluorotoluene/cyclopentene system by Cornelisse.⁸



Scheme 5. 1',4'-Substituent arrangement in the dipolar intermediate does not cause significant steric hindrance in the *endo* configuration (see note of Scheme 4)

In the case of the reaction of (3) with (4) the ratio of stereoisomers from 4',6'-attack partly depends on the final step of *meta* cycloaddition, *i.e.* the formation of the cyclopropane ring. If the CN group is located on the cyclopropane [position 2 in (21)] and, consequently, the CF₃ group is at the π -bond [position 4 in (21)], the *exo* configuration is preferred. The opposite substitution pattern favours the *endo* configuration (18). These diverse stereoselectivities might indicate an unsymmetrical approach of cyclopentene onto *m*-trifluoromethylbenzotrile during the 4',6'-attack.

Experimental

General.—*m*-Bis(trifluoromethyl)benzene was purchased from Riedel-de Haen (99%), *m*- and *p*-trifluoromethylbenzotrile from Janssen (99% and 95%), and, cyclopentene and cyclohexene (both 98%) from Merck and BASF, respectively. Spectrophotometric grade solvents (Uvasol from Merck) were used for quantitative measurements. For preparative procedures, the solvents were purified by standard methods. Analytical g.c. was carried out on a Carlo Erba Fractovap 2101 using OV 101 and OV 17 glass columns, 10% and 5% on Chromosorb WAW DMCS 80/100 mesh. Preparative g.c. was carried out using one of the following methods: (A) Honeywell Brown Elektronik, Model 720, 10m OV 101 glass column, 10% on Chromosorb WAW DMCS 80/100 mesh; (B) Hupe APG 402, 10m and 20m Carbowachs 20M on Gaschrom P, 45/60 mesh; (C) PYE Unicam GCV Chromatograph, 4m OV 101, 10% on Chromosorb WAW DMCS 80/100 mesh.

Analytical h.p.l.c. was carried out on a Perkin-Elmer Ser. 3-LC-65 T, Chromosorb Si 60, and preparative h.p.l.c. on a Gilson-303 Chromatograph, Dynamax Modular Macro-HPLC column system, Si 60.

For both h.p.l.c. methods, mixtures of 3 and 5% AcOEt in

hexane were used as eluates. Details of the measurement of the electrochemical redox potential are given in ref. 5a.

^1H and ^{13}C n.m.r. spectra were recorded on Varian EM 390 (90 MHz), WH 270 Bruker (270 MHz), and Varian CFT 20 (20 MHz) spectrometers. ^{19}F N.m.r. spectra were recorded on a Bruker WP 80 SY spectrometer. G.c.m.s. was carried out using a Varian 3700 instrument, 15m OV 101, kapillar, and a Varian MAT 212 instrument, 70eV, 250 °C, 3 kV.

Irradiation Conditions and Work-up.—Preparative irradiations were carried out in a photoreactor from Gräntzel (quartz) containing a solution of the aromatic compounds [(1), (2) or (3)] (1M; 100 ml) and the olefin (4) or (5) in cyclohexane under N_2 . Potassium carbonate (ca. 2 g) was added in order to prevent acid-catalysed decompositions of the products. The reaction mixture was checked by analytical g.c. The photoreactions of (1) + (4)/(5)/(2)/(3) + (4) were stopped for work-up after 64/72/48/48 h respectively. After irradiation, the solutions were examined by means of g.c.m.s. and the solvent was removed by distillation at room temperature. The residue was examined by means of ^{19}F n.m.r. spectra and g.c.m.s.

Product Isolation.—In order to remove polymeric materials the reaction mixtures were either filtered over basic Al_2O_3 [(1) + (5) and (3) + (4)] or distilled at 60–80 °C/0.1 mmHg [(1) + (4) and (2) + (4)]. In the former cases the products were separated first by h.p.l.c. and after that by preparative g.c. Separation of the products from (1) + (4) and (2) + (4) by means of h.p.l.c. failed and the mixtures were, therefore, only separated using preparative g.c. The isolated fractions were analysed by mean of ^1H , ^{13}C , and ^{19}F n.m.r. spectroscopy and were found to be at least 96% pure. Irradiations for analytical purposes were performed in a 'merry-go-round' apparatus (from H. Mangels, Bornheim-Roisdorf) which was fitted with a TNN-15W-lamp (Heraeus).

Photoproducts.*—The reaction between compounds (1) + (4) gave the following products. 4,6-Bis(trifluoromethyl)-*exo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (6), m/z 282 (M^{++} , 5.8%), 253 (5.4), 213 ($M^{++} - \text{CF}_3$, 3.4), 171 (2.4), 82 (5.9), 81 (CCF_3^+ , 100), 80 (55.2), 79 (27.3), 67 (18.4), 53 (5.8), and 41 (9.5); 4,6-Bis(trifluoromethyl)-*endo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (7), m/z 282 (M^{++} , 6.0%), 253 (9.0), 213 ($M^{++} - \text{CF}_3$, 4.5), 171 (3.3), 82 (6.2), 81 (CCF_3 , 100), 80 (63.4), 79 (31.5), 67 (26.3), 53 (6.7), and 41 (11.4); 2,7-Bis(trifluoromethyl)-*exo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (8), m/z 282 (M^{++} , 42.2%), 253 (9.3), 241 (15.3), 214 (CF_3PhCF_3 , 8.5), 213 ($M^{++} - \text{CF}_3$, 56.3), 185 (16.5), 173 (9.9), 172 (14.9), 171 (8.7), 149 (59.1), 148 (89.5), 147 (20.9), 135 (16.7), 115 (14.6), 109 (10.1), 79 (48.7), 68 (45.4), 67 (100), 66 (16.0), 53 (5.8), and 41 (26.6); and 2,7-Bis(trifluoromethyl)-*endo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (9), m/z 282 (M^{++} , 5.1%), 253 (3.2), 241 (4.6), 213 ($M^{++} - \text{CF}_3$, 16.7), 185 (11.0), 171 (7.7), 149 (100), 148 (66.1), 129 (25.2), 109 (9.6), 81 (CCF_3 , 13.5), 80 (12.9), 79 (34.6), 68 (26.8), 67 (47.5), 66 (11.2), 53 (4.9), and 41 (25.0).

The reaction between compounds (1) + (5) gave the following products. 4,6-Bis(trifluoromethyl)-*exo*-tetracyclo[6.4.0.0^{2.4}.0^{3.7}]dodec-5-ene (10), m/z 296 (M^{++} , 21.9%), 227 ($M^{++} - \text{CF}_3$, 18.4), 95 (100), 94 ($\text{CF}_3\text{C}=\text{CH}^+$, 52.0), 81 (CCF_3^+ , 34.7), 79 (29.6), 67 (35.4), 55 (12.1), and 41 (22.3); 4,6-Bis(trifluoromethyl)-*endo*-tetracyclo[6.4.0.0^{2.4}.0^{3.7}]dodec-5-ene (11), m/z 296 (M^{++} , 31.0%), 227 ($M^{++} - \text{CF}_3$, 22.2), 95 (100), 94 ($\text{CF}_3\text{C}=\text{CH}^+$, 63.4), 93 ($94^+ - \text{H}$, 16.4), 81 (CCF_3^+ , 44.4), 80 (12.1), 79 (32.6), 67 (42.7), 55 (11.5), 54

(9.4), and 41 (23.5); 2,7-Bis(trifluoromethyl)-*exo*-tetracyclo[6.4.0.0^{2.4}.0^{3.7}]dodec-5-ene (12), m/z 296 (M^{++} , 89.8%), 255 (16.7), 254 (10.3), 227 ($M^{++} - \text{CF}_3$, 100), 199 (23.1), 195 ($\text{CF}_3\text{PhCF}_2^+$, 9.3), 185 (31.5), 163 (27.5), 162 (50.6), 93 (29.0), 81 (CCF_3^+ , 45.1), 79 (38.8), 67 (64.2), 55 (18.8), 54 (30.4), and 41 (48.3); and 2,7-Bis(trifluoromethyl)-*endo*-tetracyclo[6.4.0.0^{2.4}.0^{3.7}]dodec-5-ene (13), m/z 296 (M^{++} , 30.8%), 255 (8.1), 227 ($M^{++} - \text{CF}_3$, 47.8), 199 (12.4), 195 (12.8), 185 (18.1), 163 (13.1), 162 (22.9), 162 (22.9), 159 (12.3), 115 (9.7), 93 (15.6), 82 (64.1), 81 (CCF_3^+ , 26.0), 79 (24.1), 67 (100), 55 (12.1), 54 (47.4), and 41 (38.5).

The reaction between compounds (2) + (4) gave the following products. 4-Cyano-7-trifluoromethyl-*endo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (14), m/z 239 (M^{++} , 9.0%), 212 ($M^{++} - \text{HCN}$, 1.2), 171 (NCPPhCF_3 , 2.3), 170 ($M^{++} - \text{CF}_3$, 6.8), 159 ($M^{++} - \text{CN}$, 13.3), 91 (8.0), 81 (CCF_3^+ , 100), 80 (33.5), 79 (29.6), 68 (6.3), 67 (19.7), 53 (7.5), and 41 (13.0); and 4-Cyano-7-trifluoromethyl-*exo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (15), m/z 239 (M^{++} , 6.8%), 212 ($M^{++} - \text{HCN}$, 1.1), 170 ($M^{++} - \text{CF}_3$, 6.5), 159 (11.0), 152 (NCPPhCF_2^+ , 1.8), 91 (8.1), 81 (CCF_3^+ , 100), 80 (42.8), 79 (31.4), 67 (21.1), 53 (8.1), and 41 (15.5).

The reaction between compounds (3) + (4) gave the following products. 6-Cyano-4-trifluoromethyl-*endo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (18), m/z 239 (M^{++} , 8.2%), 238 ($M^{++} - \text{H}$, 4.4), 198 (3.1), 170 ($M^{++} - \text{CF}_3$, 7.2), 159 (8.1), 106 (4.3), 82 (6.5), 81 (CCF_3^+ , 100), 80 (50.0), 79 (26.5), 67 (22.1), 53 (7.6), and 41 (13.3); and 4-cyano-6-trifluoromethyl-*endo*-tetracyclo[6.3.0.0^{2.4}.0^{3.7}]undec-5-ene (20), m/z 239 (M^{++} , 10.3%), 211 (5.5), 198 (6.1), 170 ($M^{++} - \text{CF}_3$, 28.3), 159 (14.1), 152 (9.3), 142 (11.4), 128 (5.8), 82 (7.0), 81 (CCF_3^+ , 100), 80 (78.8), 77 (12.1), 69 (CF_3^+ , 2.4), 68 (6.3), 67 (21.8), 63 (5.1), 53 (8.4), 51 (8.1), and 41 (14.9).

Acknowledgements

We are very grateful to the Deutsche Forschungsgemeinschaft for financial support. We also thank the Bayer AG for providing us with g.c. and h.p.l.c. materials, and Prof. H.-G. Thomas and Dr. Meltzow for providing the cyclic voltammetry and the preparative g.c. apparatus. M. Vondenhof is thanked for his experimental help as an undergraduate research participant and for his critical reading of the manuscript.

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* Here we have used the tetracycles as the basic structure for the *meta* adducts.