53. Selectivity and Charge Transfer in Photoreactions of α,α,α-Trifluorotoluene with Olefins[1])

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In photoreactions of α,α,α-trifluorotoluene with olefins, the mode of reaction strongly depends on the charge transfer between the starting materials. Substitution of an F-atom is preferred if the electron transfer becomes exergonic, *i.e.* if $\Delta G < 0$ according to the *Rehm-Weller* equation. In all other systems of $\Delta G > 0$, the olefins undergo cycloaddition onto the arene ring. In the transition area of $\Delta G \approx 0$ eV, both the electron transfer and the reaction mode can be controlled by varying the solvent polarity. For instance, 1 and 9 mainly form cycloaddition products in dioxane ($\Delta G = +0.11$ eV), whereas in solvents with $\varepsilon > 3$ ($\Delta G < 0$), substitution is the only observed photoreaction. Moreover, in systems of endergonic electron-transfer processes, the degree and the direction of charge transfer influence both the regio- and the stereochemistry of the cycloaddition.

1. Introduction. – The photoreactions of olefins with aromatic compounds have been investigated for a long time [3]. Different mechanisms have been proposed at least for the *meta*-cycloaddition [3–10], but only the 'exciplex-mechanism' provides a rationalization which fits all the experimental evidence [2]. In addition to the exciplex, dipolar intermediates ('zwitterions') have been proposed on various occasions [1] [9–14] in order to explain the high regioselectivities of photocycloadditions with donor- and acceptor-substituted benzenes. We have recently shown that charge transfer may influence the selectivity of product formation in various bimolecular photoreactions [2] [8] [15–18]. In extension of these investigations, we have studied the photoreactions of α,α,α-trifluorotoluene (1) with olefins, and we have found striking changes, not only in the mode of reaction but also in the regio- and stereoselectivity of the cycloadditions. The mode of reaction has already been rationalized on the basis of thermodynamics of electron transfer in a preliminary communication [18] *(Scheme 1)*: Substitution of an F-atom under formation

Scheme 1. *Mode of Reaction and Free Enthalpy of Electron Transfer in Photoreactions of α,α,α-Trifluorotoluene with Olefins*
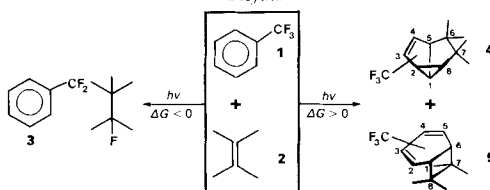
of **3** is preferred if $\Delta G < 0$ according to the *Rehm-Weller* equation [19]. In this contribution, we describe both the substitution and the cycloaddition reactions of **1** with 1,3-dioxoles **6–9** and vinylene carbonates **10–11**.

2. Results. – 2.1. *Products.* The preparative irradiations ($\lambda = 254$ nm) of solutions containing α,α,α-trifluorotoluene (**1**, 1M) and one of the olefins **6–11** (0.5M) in dioxane resulted in formation of the products **12–24**. The yields and product ratios are listed in *Table 1*. Almost all products were isolated by HPLC and identified spectroscopically by ¹H- and ¹³C-NMR data and by their elemental analysis. Only **12** and **13** were analysed directly in the reaction mixture since the separation by HPLC led to elimination resulting in the formation of **25** from **12**. The yields and product ratios changed with the irradiation time because several of the photoproducts are photo- and thermolabile. Therefore, high yields of the *ortho*-adducts **16** and **17** were only obtained at low conversions *(Table 1)*.

Nearly all olefins showed a preference for only one mode of reaction. Substitution of an F-atom under formation of **12–14** was the only process with the alkyl-substituted 1,3-dioxoles **6–8**, respectively. The vinylene carbonates **10** and **11** mainly formed *meta*-cycloadducts. However, 1,3-dioxole **9** did not show any preference for one reaction mode: substitution under formation of **15a/15b** was observed as well as *ortho*- and *meta*-cycloadditions yielding **16–19**.

High selectivities were also observed concerning the stereochemistry of the formation of *meta*-cycloadducts: whereas 1,3-dioxole **9** only yielded '*exo*'-configurated adducts, vinylene carbonate **11** exclusively formed the '*endo*'-isomers. Again, **9** did not show any
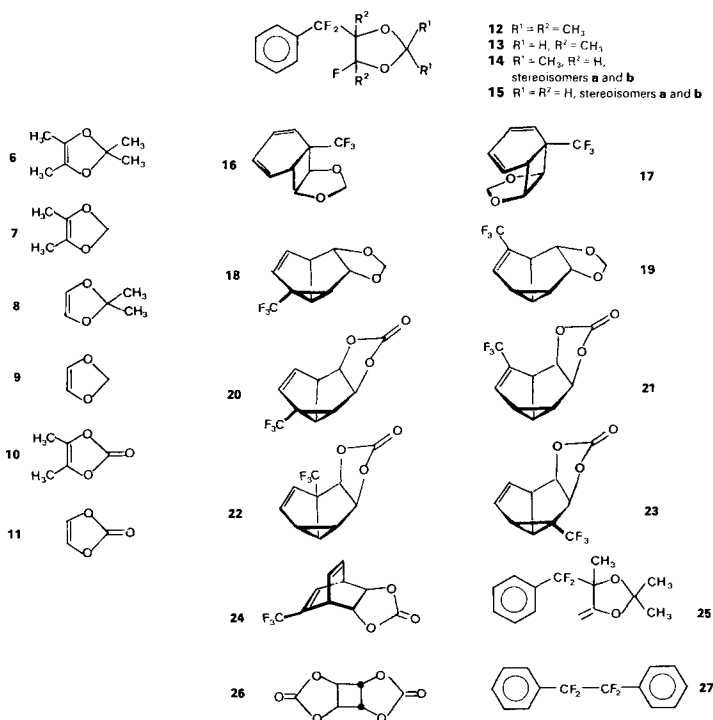

12 $R^1 = R^2 = CH_3$
13 $R^1 = H$, $R^2 = CH_3$
14 $R^1 = CH_3$, $R^2 = H$,
   stereoisomers **a** and **b**
15 $R^1 = R^2 = H$, stereoisomers **a** and **b**

Table 1. *Yields and Ratios of the Photoproducts* **12–24** *in Dioxane*

Olefin	Products (Ratio[a]))	Yield [%][b])
6	**12**[c])	60
7	**13**[c])	60
8	**14a,14b**[d])	72
9	**18,19,16/17**[e]),**15a/15b**[d]) (ratio 1.0:0.7:0.8:0.3[f])	55
10	*meta*-adducts[g])	
11	**20,21,22,23,24** (ratio 1.0:0.6:0.7:0.5:0.1)[h])	50

[a])   At 10% conversion.
[b])   At max. 30% conversion.
[c])   Only mixtures of the stereoisomeric products **12** and **13**, respectively, were obtained (see text). The product ratio is 1.0:0.95 (for **12**) and 0.6:1.0 (for **13**), both arranged according to increasing GC-retention times. Yields were determined both by GC and NMR.
[d])   Although all NMR data are known, a structural assignment is not possible due to the complex coupling pattern (see text). The ratio of the substitution products is 1.0:0.6 (1.0:0.5) for **14** (for **15**).
[e])   **16/17** = *ca.* 1:1.
[f])   *Ca.* 25% of unidentified products (mixture of at least three compounds in 4:4:1 ratio). One of these minor products has been tentatively assigned the structure of 8-trifluoromethylsubstituted '*exo*'-*meta*-adduct on the basis of the NMR data.
[g])   At least four products in low quantum and chemical yield, probably *meta*-adducts according to NMR measurements of the reaction mixture.
[h])   *Ca.* 20% of unidentified products (mixture of at least two compounds).

selectivity for one of the stereoisomeric *ortho*-adducts **16** and **17**. Referring to the regioselectivity, only 2- and 4-substituted *meta*-adducts were formed with **9**. However, mixtures of various regioisomers were formed with **11**[5]). The dimerization of the olefins was only important in the photoreaction with vinylene carbonate **11**. There, **26** was formed in 20% yield and identified as the *anti*-isomer [21]. Similar dimerization products of the 1,3-dioxoles **6–9** were not detected. The tetrafluorodibenzyl derivative **27** was only formed in photoreactions with 1,3-dioxoles in yields < 5%[6]).

2.2. *Solvent Dependence of Product Formation*. All photoreactions of **1** with the olefins **6–11** can also be classified into two types according to their solvent dependences: Those olefins which form substitution products show a pronounced decrease of product formation in polar solvents, whereas the others do not. Two examples are presented in *Fig. 1*. Moreover, the absolute decrease of the product quantum yields depends on the donor abilities of the olefins *(Table 2)*. Whereas the factor ϕ (cyclohexane)/ϕ (acetonitrile) is relatively small for the strongest donor **6**, 1,3-dioxole **9** shows a factor of 10.

Again, as seen before, **1** and **9** form a special system: Whereas the solvent dependence for all products is similar to those of the other 1,3-dioxoles **6–8** *(Fig. 2* and *Table 2)*, the reaction modes change dramatically when varying the solvent polarity. As seen in *Fig. 2*, cycloaddition is completely suppressed while substitution is almost not affected.

Such a solvent effect on the quantum yields of all products has not been observed in the corresponding photoreactions with vinylene carbonates (in dioxane, i-PrOH, THF, and MeCN). However, the regioselectivity changes in favour of the 2- and 4-substituted *meta*-adducts **20** and **21** in polar solvents *(Table 3)*.

[5])   *Cornelisse* and *Osselton* have independently studied the photoreaction of **1** and **11** with the same results [20].
[6])   Evidence for the formation of another derivative of **1**, α,α-difluorotoluene (*ca.* 1%), was obtained by GC/MS analysis (see *Exper. Part*).
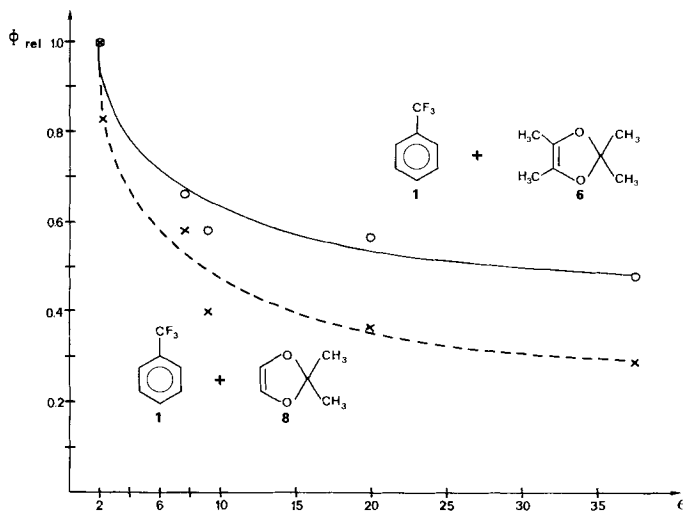
Fig. 1. *Dependence of the quantum yields of product formation on solvent polarity in photoreactions of* α,α,α-*trifluoro-toluene* (**1**) *with tetramethyl- and 2,2-dimethyl-1,3-dioxole* (**6** *and* **8**, *resp.*)
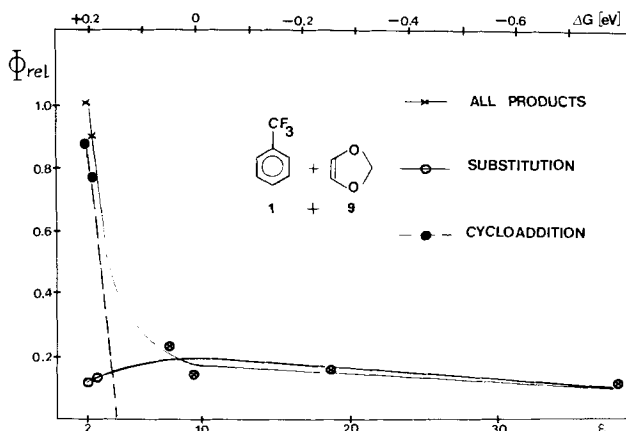

Fig. 2. *Dependence of the product quantum yields or solvent polarity for both substitution and cycloaddition in the photoreaction of* α,α,α-*trifluorotoluene* **1** *with 1,3-dioxole* **9**

Table 2. *Solvent Dependence of Product Formation in Photoreactions of* **1** *with 1,3-Dioxoles* **6–9**
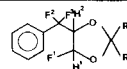
Olefin	$E_{1/2}^{ox}$ [V][a]	Φ(Cyclohexane)/Φ(MeCN)[b]
6	0.42	2.1
7	0.48	2.5
8	0.69	3.5
9	0.76	10.0

[a])   Electrochemical redox potentials (*vs.* Ag/AgNO₃ electrode) were measured by cyclic voltammetry (see *Exper. Part*).

[b]) Φ = Quantum yield of all products.

Table 3. *Product Quantum Yields of the Photoreaction between α,α,α-Trifluorotoluene* (**1**) *and Vinylene Carbonate* **11** *in Various Solvents*

Solvent	ε	ϕ (20–24)	ϕ (20 + 21)/ϕ (22 + 23)
Dioxane	2.21	1.0	1.3
i-PrOH	19.92	1.1	2.0
THF	7.58	1.0	1.9
MeCN	37.5	1.0	2.3

Table 4. *¹H- and ¹⁹F-NMR Data*[a]) (CDCl₃; δ in ppm, J in Hz) *of the Substitution Products* **14** *and* **15**

	14a	14b	15a	15b
H¹	6.04 (*dd*, J(H¹,F¹) = 67.4, J(H¹,H²) = 1.0, 1 H)	5.64 (*dd*, J(H¹,F¹) = 65.6, J(H¹,H²) = 2.8, 1 H)	6.08 (*dd*, J(H¹,F¹) = 66.2, J(H¹,H²) = 0.9, 1 H)	5.85 (*dd*, J(H¹,F¹) = 64.2, J(H¹,H²) = 3.1, 1 H)
H²	4.65 (*dddd*, J(H²,F¹) = 17.0, J(H²,F²) = 16.9, J(H²,F³) = 6.2, 1H)	4.47 (*dddd*, J(H²,F¹) = 23.3, J(H²,F²) = 11.5, J(H²,F³) = 9.3, 1H)	4.46 (*dddd*, J(H²,F¹) = 17.2, J(H²,F²) = 16.3, J(H²,F³) = 6.0, 1H)	4.40 (*m*, Σ J = 46.8[b]), 1 H)
R¹	1.43 (*s*, 3 H) 1.47 (*s*, 3 H)	1.42 (*s*, 3 H) 1.52 (*s*, 3 H)	5.25 (br. *s*, 1 H) 5.30 (*d*, J = 2.0, 1 H)	5.23 (br. *s*, 1 H) 5.33 (br. *s*, 1 H)
C₆H₅	7.3–7.5 (*m*, 5 H)	7.3–7.6 (*m*, 5 H)	7.4–7.5 (*m*, 5 H)	7.4–7.6 (*m*, 5 H)
F¹	−112.2 (*dddd*, J(F¹,F²) = 1.2, J(F¹,F³) = 1.4, 1 F)	−127.3 (*dddd*, J(F¹,F²) = 18.4, J(F¹,F³) = 15.4, 1 F)		
F²	−112.1 (*ddd*, J(F²,F³) = 258.6, 1 F)	−105.0 (*ddd*, J(F²,F³) = 259.0, 1 F)		
F³	−103.6 (*ddd*, for *J*, see F¹, 1 F)	−101.3 (*ddd*, for *J*, see F¹, 1 F)		

[a]) ¹H-NMR: 90 MHz, standard Me₄Si; ¹⁹F-NMR: 75.4 MHz, standard CFCl₃.
[b]) Resonances of *m* coincide with that of an impurity, individual coupling constants have not been determined.

Table 5. *¹H- and ¹³C-NMR Data* (CDCl₃; δ in ppm, J in Hz) *of the* ortho-*Adducts* **16** *and* **17**

	¹H-NMR			¹³C-NMR	
	16	17		16	17
			C(1)	44.37 (J(C,F) = 28.0)	49.30 (J(C,F) = 26.8)
H−C(2)	5.60 (*dq*, J(2,3) = 9.6, J(2,5) = 0.9, 1H)	5.42 (*dm*, J(2,3) = 9.6, 1H)	C(2)	118.37 (J(C,F) = 2.6)	116.60 (J(C,F) = 3.0)
H−C(3)	6.19 (*ddm*, J(3,4) = 5.1, 1H)	6.08 (*ddm*, J(3,4) = 5.4, 1H)	C(3)	127.52	127.93
H−C(4)	5.97 (*ddd*, J(4,5) = 9.0, 1H)	5.87 (*ddm*, J(4,5) = 9.6, 1H)	C(4)	123.13	123.25
H−C(5)	5.78 (*ddm*, J(5,6) = 5.4, 1H)	5.54 (*m*, J(5,6) = 5.4, 1H)	C(5)	122.07	121.43
H−C(6)	3.29 (*m*, J(6,7) + J(6,8) = 3.6, 1H)	3.50 (*m*, J(6,7) + J(6,8) = 9.0, 1H)[a])	C(6)	37.56 (J(C,F) = 2.8)	38.00 (J(C,F) = 2.5)
H−C(7)	4.55 (*m*, J(7,8) = 5.2, 1H)	4.88, 4.92 (*m*, J(7,8) = 5.4, 2H)	C(7)	81.96	80.72
H−C(8)	4.51 (*m*, 1H)	4.88, 4.92 (*m*, J(7,8) = 5.4, 2H)	C(8) CF₃	84.85 (J(C,F) = 1.2) 124.97 (J(C,F) = 280.2)	83.24 (J(C,F) = 3.4) 126.43 (J(C,F) = 279.5)
OCH₂O	5.23 (*s*, 1H) 5.28 (*s*, 1H)	5.25 (*s*, 1H) 5.54 (*s*, 1H)	OCH₂O	96.29 (J(C,F) = 1.9)	99.49

[a]) In C₆D₆, 4.41 and 4.75 ppm, J(6,7) = 6.6 and J(6,8) = 2.1 Hz.

2.3. *Structure of the Products*. The constitutions of the substitution products **12–15** have been proven spectroscopically by ^{1}H- and ^{19}F-NMR. However, it was not possible to perform a complete configurational assignment. Even in case of the isolated stereo-isomers **a** and **b** of each **14** and **15**, the *cis/trans* assignment was complicated by the flexible and unknown conformation of both the dioxolane ring and the difluorobenzyl side chain. Nevertheless, the configuration of **14a** and **15a** must be the same due to their similar NMR data *(Table 4)*. The same holds for **14b** and **15b**.

The most photolabile products of the reaction between **1** and 1,3-dioxole **9** were identified as the stereoisomeric *ortho*-adducts **16** and **17** on the basis of the NMR data *(Table 5)*. The signals at 3.29 and 3.50 ppm result from only one proton at C(6) of **16** and **17**, respectively. Furthermore, C(1) of **16** and **17** is shifted downfield and shows typical ^2J(C,F) coupling constants. These effects only correspond with the structures **16** and **17** having CF$_3$ at C(1). In particular, the isomer with the smaller (higher) retention time (according to HPLC) was assigned *'exo'* (*'endo'*) on the basis of the following arguments: (*i*) One expects for the *'endo'*-adduct a larger coupling constant J(6,7) because of the smaller dihedral angle as for the *'exo'*-isomer [1] [10] [22]. Therefore, the isomer with J(6,7) = 6.6 Hz must be *'endo'* (**17**) and the isomer with J(6,7) < 3.6 Hz *'exo'* (**16**) (see *Table 5*). (*ii*) The cyclobutane protons H–C(7) and H–C(8) of **16** have smaller chemical-shift values due to the anisotropy effect of the diene group. The corresponding signals of **17** are shifted downfield. Similar effects have been observed in anisole adducts [1].

The remaining products **18–23** shows the typical NMR spectra as expected for *meta*-adducts [1] [9] [10] [12–14] [22] (see *Table 6* and *7*). Both the substitution pattern and the configuration have been determined: (*i*) The ^{13}C-NMR data of the C-atoms which bear the CF$_3$ group as indicated by the C,F-coupling constant of *ca.* 30 Hz are generally shifted downfield by *ca.* 5–15 ppm *(Table 7)*. (*ii*) High coupling constants between H–C(5) and H–C(6) and between H–C(7) and H–C(8) (both *ca.* 6 Hz), respectively, characterize the *'endo'*-configuration of **20–23** [13]. The *'exo'*-adducts **18** and **19** are characterized by coupling constants for these protons smaller than 1 Hz [1] [10].

One of the minor products of the photoreaction between **1** and **11** was identified as the *para*-adduct **24** on the basis of the signals at 4.3 ppm for H–C(1) and H–C(4). The analogous protons of an alternative *ortho*-structure should be shifted upfield (< 4 ppm). CF$_3$ is located at an olefinic C-atom as indicated by its high C,F-coupling constant.

3. Discussion. – 3.1. *Mode of Reaction*. In a preceding paper of this series, we have rationalized the selectivities between substitution and cycloaddition by means of the *Rehm-Weller* equation of electron transfer for photoreactions of arenes with olefins in general [2a]. A simplified version of this equation is given as follows

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

with $E_{\frac{1}{2}}^{ox}$(D) = oxidation potential of the donor (D), $E_{\frac{1}{2}}^{red}$(A) = reduction potential of the acceptor (A), both in MeCN, $\Delta E_{excit.}$ = excitation energy of the electronically excited species, and $\Delta E_{coul.}$ = *Coulomb* interaction energy in a given solvent. The advantage of *Weller's* semiempirical equation is that one can use redox potentials which are measured in MeCN and calculate ΔG for another solvent of choice[7]. A detailed derivation of *Eqn. 1* is described elsewhere [19].

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[7]   The dependence of ΔG and $\Delta E_{coul.}$ on the solvent polarity is also described by *Masuhara* and *Mataga* [23].

Table 6. ^{1}H-NMR Data (CDCl$_3$; δ in ppm, J in Hz) of the meta-Adducts **18–23**

Proton	18	19	20	21	22	22 in C$_6$D$_6$	23
H–C(1)	2.87 (dd, J(1,5) = 5.4, J(1,8) = 7.2, 1H)	2.90 (q, J(1,5) = 5.7, J(1,2) + J(1,8) = 12.3, 1H)	3.04 (dd, J(1,5) = 5.7, J(1,8) = 7.0, 1H)	3.17 (q, J(1,2) + J(1,8) = 12.5, 1H)	3.00 (m, 1H)	2.38 (t, J(1,2) = J(1,8) = 6.4, 1H)	3.10 (dd, J(1,2) = 7.2 J(1,5) = 5.4, 1H)
H–C(2)		2.05 (m, 1H)		2.23 (m, 1H)	2.30 (m, 1H)	1.58 (td, J(2,3) = 2.2, J(2,8) = 7.6, 1H)	2.72 (dd, J(2,3) = 2.3, 1H)
H–C(3)	5.70 (d, J(3,4) = 5.4, 1H)	6.20 (dq, J(3,2) = 2.0, J(3,F) = 2.0, 1H)	5.90 (d, J(3,4) = 5.4, 1H)	6.48 (d, J(3,2), ca. 2, 1H)	6.18 (m, 1H)	5.67 (dm, J(3,4) = 5.5, 1H)	5.67, 5.95 (dd, J(3,4) = 5.4, 2H)
H–C(4)	5.65 (m, 1H)		5.73 (ddm, J(4,5) = 2.4, 1H)		5.55 (m, 1H)	5.32 (dm, 1H)	5.67, 5.95 (dd, J(3,4) = 5.4, 2H)
H–C(5)	3.61 (m, 1H)	3.60 (dm, 1H)	3.68 (m, 1H)	3.75 (td, J(1,5) = 6.2, J(5,7) = 1.6, 1H)			3.72 (m, J(4,5) = 2.3, 1H)
H–C(6)	4.15 (d, J(6,7) = 3.7, 1H)	4.40 (d, J(6,7) = 8,6, 1H)	5.16 (dd, J(6,5) = 6.3, J(6,7) = 8.6, 1H)	5.25 (dd, J(6,5) = 6.2, J(6,7) = 9.0, 1H)	5.34 (m, 1H)	4.74 (d, J(6,7) = 9.0, 1H)	5.32 (dd, J(6,7) = 9.0, J(5,6) = 6.0, 1H)
H–C(7)	4.50 (d, 1H)	4.55 (d, 1H)	5.35 (ddm, J(7,8) = 6.1, 1H)	5.46 (dm, J(7,2) + J(7,8) = 6.4, J(7,5) = 1.6, 1H)	5.34 (m, 1H)	4.45 (dd, J(7,8) = 6.0, 1H)	5.55 (dd, J(5,7) = 1.2, 1H)
H–C(8)	2.39 (d, 1H)	2.05 (m, 1H)	2.51 (dd, 1H)	2.23 (m, 1H)	2.30 (m, 1H)	1.30 (q, 1H)	
OCH$_2$O	5.21 (s, 1H) 4.88 (s, 1H)	5.24 (s, 1H) 4.93 (s, 1H)					

Table 7. ^{13}C-NMR Data (CDCl$_3$; δ in ppm, J in Hz) of the meta-Adducts **18–22**

	18	**19**	**20**	**21**	**22**
C(1)	37.99[a])	35.15[b])	40.33[c])	41.74	38.09
	(J(C,F) = 2.1)	(J(C,F) = 1.3)	(J(C,F) = 2.3)		(J(C,F) = 2.7)
C(2)	42.95	29.51	45.00	32.30[d])	32.49[e])
	(J(C,F) = 36.0)		(J(C,F) = 36.0)	(J(C,F) = 1.4)	
C(3)	125.40, 133.72	135.70	128.27, 135.19	138.02	137.16, 127.07
	(J(C,F) = 1.7)	(J(C,F) = 5.0)	(J(C,F) = 1.0)	(J(C,F) = 5.2)	(J(C,F) = 2.0)
C(4)		133.28		137.03	
		(J(C,F) = 33.0)		(J(C,F) = 25.0)	
C(5)	53.06	51.40	52.08	51.29	67.26
				(J(C,F) = 1.3)	(J(C,F) = 29.5)
C(6)	89.89	90.11	87.71	87.40	87.94
					(J(C,F) = 2.0)
C(7)	80.54	80.70	83.03	83.98	83.04
C(8)	37.80[a])	38.65[b])	32.74[c])	32.39[d])	30.12[e])
	(J(C,F) = 2.7)	(J(C,F) = 1.3)	(J(C,F) = 3.0)		
CF$_3$	124.71	122.17	124.19	121.47	125.55
	(J(C,F) = 272.0)	(J(C,F) = 269.0)	(J(C,F) = 273.0)	(J(C,F) = 270.2)	(J(C,F) = 278.0)
OCO	96.16	95.89	155.13	154.61	154.95

[a]) The assignment may be interchanged. [b])–[c]) See *Footnote a*.

The results of such a calculation for **1** have already been reported in the preliminary communication [18]. They clearly demonstrate that substitution is preferred in systems of exergonic electron transfer, whereas in all other cases of $\Delta G > 0$ mainly cycloadditions are observed *(Scheme 1)*. Note that the rationalism also includes the photoreaction of **1** with cyclopentene [12].

The reactants **1** and **9** form a special system since ΔG is only slightly positive ($\Delta G = +0.11$ eV in 1,4-dioxane). As a consequence, this photoreaction does not show any significant selectivity for one mode of reaction. However, the electron transfer should become exergonic in more polar solvents according to the *Coulomb* interaction energy [2a]:

$$\Delta E_{\text{coul.}} = \frac{e^2 N}{4\pi \varepsilon_o a}\left[\frac{1}{\varepsilon} - \frac{2}{37.5}\right] \tag{2}$$

with $F = 96490$ C, $e = 1.602 \times 10^{-19}$ C, $\varepsilon_o = 8.854 \times 10^{-12}$ Fm^{-1}, ε = dielectric constant of the solvent (ε of MeCN = 37.5), $N = 6.023 \times 10^{23}$ mol^{-1}, and a = encounter distance 7 Å. This *Eqn. 2* is derived from the *Born* equation as shown by *Weller* [19]. Both the *Coulomb* attraction and the solvation enthalpy were taken into account. For example $\Delta E_{\text{coul.}} = 0.91, 0.82, 0.16$, and -0.055 eV in cyclohexane ($\varepsilon = 2.02$), 1,4-dioxane ($\varepsilon = 2.2$), THF ($\varepsilon = 7.58$), and MeCN ($\varepsilon = 37.5$), respectively[7]). Due to the sharp decrease of $\Delta E_{\text{coul.}}$ in solvents of small ε values, ΔG already becomes negative if $\varepsilon > 2.5$. As a consequence, **1** and **9** only form substitution products even in dibutyl ether ($\varepsilon = 3.08$, $\Delta E_{\text{coul.}} = 0.56$ eV, $\Delta G = -0.15$ eV). Therefore, the mode selectivity can now be controlled on the basis of *Weller*'s theory of electron transfer by using various solvents.

3.2. *Product Formation and Ionic Photodissociation*. All systems which form substitution products show a general type of solvent dependence. Two examples are presented in *Fig. 1* and *2*. These effects may be best rationalized in assuming a competition between product formation and ionic photodissociation, which we have studied in more detail in

Scheme 2. *Proposed Mechanism of Photoreactions of α,α,α-Trifluorotoluene with Olefins*
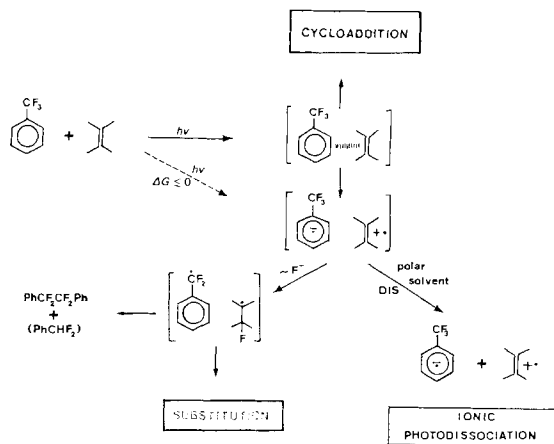
ketone/olefin systems [15–17] [24–26]. We conclude from these results a mechanism of product formation as shown in *Scheme 2*. The assumption of an exciplex intermediate seems reasonable, even in systems that exhibit exergonic electron transfer, since the rate constants of fluorescence quenching of 1 by olefins do not follow the theoretical curve of direct electron transfer reported by *Rehm* and *Weller* [18]. Note that the cycloaddition processes do not show such a solvent dependence. This again indicates that there is no complete electron transfer with olefins like cyclopentene and vinylene carbonates.

Most probably, the substitution process proceeds in a cage reaction *via* migration of an F-atom and recombination of the radical pair *(Scheme 2)*. Escape of difluorobenzyl radicals from this pair leads to the dibenzyl derivative **27** and α,α-difluorotoluene[6]), probably by H abstraction from the solvent. However, besides this common solvent dependence of all 1,3-dioxoles, the absolute decrease of product formation is different *(Table 2)*. That means that the ionic-dissociation yield decreases with the increase of the CT character of the 1/olefin systems [18]. Similar effects have been reported by *Mataga* for pyrene/acceptor systems [27]. The author explained these effects as being due to the faster nonradiative direct degradation to the ground state in the stronger complex which competes with ionic dissociation. In our systems, this degradation corresponds to product formation. Both processes proceed under back electron transfer. This increased back electron transfer process in systems of extreme ΔG values (according to *Eqn. 1*) have also been observed in rigid systems by *Miller* [28] and in fluid solution by *Farid* [29]. According to *Miller*, these effects are due to a '*Marcus*-type' relationship whose maximum rate constants of 10^{13} s^{-1} are cut off by the diffusion-control limit (for further details see [28]). Consequently, decreased rate constants of electron transfer are observed in systems of high exergonity.

3.3. *Stereoselectivity.* The '*endo*'-stereoselectivity which is observed in most *meta*-cycloadditions has been rationalized on the basis of secondary orbital interactions in the exciplex state by *Houk* [30]. There is no exception in the photoreaction of 1 with olefins such as cyclopentene [12] and vinylene carbonate **11**. In addition, the reaction with **11** proceeds almost totally stereoselective whereas the '*endo*'/'*exo*' ratio is only 8:1 with

cyclopentene [12]. This may be due to increased secondary interactions between the partly positive arene ring and the carbonate group in the exciplex state which is caused by a reversed charge transfer [18]: A calculation of the free enthalpy of electron transfer according to *Eqn. 1* results in $\Delta G = 1.72$ eV for **11** (= A (acceptor)) and $\Delta G = 2.42$ eV for **1** (= A), respectively[8]), which clearly confirms the above mentioned statement. On the contrary, all the other olefins which have been investigated cause a 'normal' charge transfer with **1** as acceptor [18]. As a consequence, the stereoselectivity turns to 'exo' in photoreactions with **9** due to repulsive effects between the O-atoms and the partly negative arene. Similar effects have also been observed in photoreactions with benzene [8] [10] and anisole [1] [9] [14]. These rationalizations are illustrated in more detail in *Scheme 2* of [2a].

At first sight, the formation of both the 'exo'- and the 'endo'-ortho-adducts **16** and **17** is surprising, since the stereoselectivity is unique in all other cycloadditions. A photochemical or thermal rearrangement between **16** and **17** may be excluded for the following reasons: (*i*) the **16**/**17** ratio does not depend on the irradiation time; (*ii*) both stereoisomers are thermally stable up to 100° (> 100°: decomposition). Such a rearrangement has been observed in the anisole/1,3-dioxole systems [1]. As a consequence we assume a mechanism of the *ortho*-cycloaddition as shown in *Scheme 3*. An exciplex of the structure

Scheme 3. *Regio- and Stereoselectivities in Cycloadditions of 1,3-Dioxole to α,α,α-Trifluorotoluene*
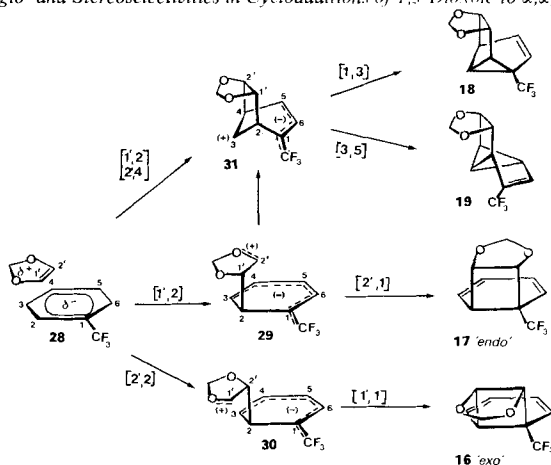

28 may be the common precursor of both the *ortho*- and *meta*-cycloadducts. Then the attack onto the *ortho*-position of the arene should yield a dipolar intermediate which is optimally stabilized by the CF_3 group ('zwitterions' **29** and **30**). The formation of the second C–C bond at position 1 of the arene leads to the 1-substituted *ortho*-adducts. An alternative bond formation in the *meta*-position of **29** seems to be less favourable. One reason may be a stabilization of the transition state by an interaction between the carboxonium ion and the negative arene part. The alternative zwitterion **30** forms the 'exo'-ortho-adduct **16**. Here a *meta*-bond formation would lead to a destabilization of the transition state due to a repulsion of the n-orbitals of the O-atom and the negative arene.

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[8]) $E^{ox}_{1/2}$ (**1**) = 2.91 V, $E^{red}_{1/2}$ (**1**) = − 3.18 V, $E^{red}_{1/2}$ (**11**) = − 2.64 V, $E^{ox}_{1/2}$ (**11**) = 3.07 V, and $\Delta E_{excit.}$ (**1**) = 4.65 eV.

3.4. *Regioselectivity*. The origin of the high regioselectivity of the *meta*-cycloaddition with 1,3-dioxole **9** can be easily understood by assuming a dipolar intermediate which, for convenience, could also be represented as a zwitterion **31** *(Scheme 3)*. The assumption of dipolar intermediates is in accordance with the exciplex mechanism, since we could show in our kinetic studies that an exciplex (here **28**) is a necessary, but not a direct precursor of the products [8]. CF_3 can stabilize a negative charge in position 1 of **31**. Formation of the cyclopropane either between C(3) and C(1) or between C(3) and C(5) leads to the regioisomers **18** or **19**, respectively. Almost similar effects have been observed by *Cornelisse* in the **1**/cyclopentene system [12]. Compared to that, vinylene carbonate **11** forms a mixture of 4 regioisomeric *meta*-adducts *(Scheme 4)*. Here, the charge separation is relatively weak ($\Delta G = 1.72$ eV compared to $\Delta G = 0.11$ eV in the **1**/**9** system [18]).

Scheme 4. meta-*Cycloaddition of Vinylene Carbonate to α,α,α-Trifluorotoluene*
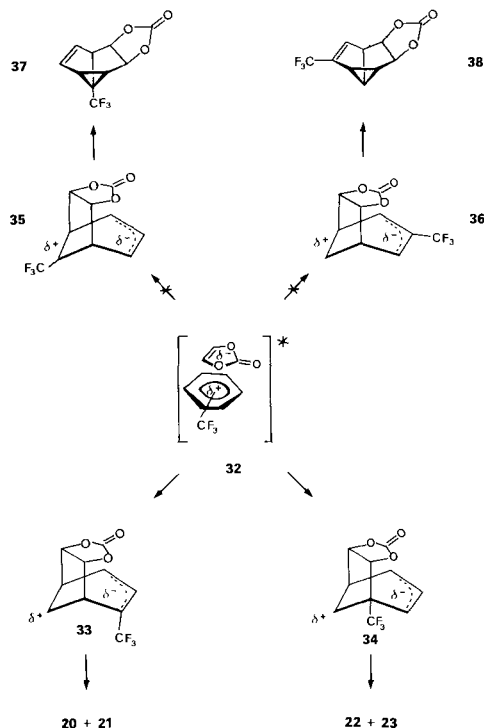
Therefore, an acceptor substituent cannot stabilize a negative charge to the same extent as in the former system. Consequently, there is no preference for a certain structure, *i.e.* for the exciplex **32** and/or the *meta*-bonded intermediates **33** and **34**. However, some charge separation seems to be involved even in this system: (*1*) An 1-substituted *meta*-adduct **37** is not formed. This would require the CF_3 group to be located at an unfavourable position (see **35**). (*2*) In polar solvents, the formation of **20** and **21** is favoured by a factor of 1.7 supporting our hypothesis of a charge separation at least in intermediates of the type **33**.

This dependence of the regioselectivity on the charge separation has also been observed in other systems: *e.g.* anisole and vinylene carbonate only form 1-substituted *meta*-adducts [13] ($\Delta G = 0.34$ eV [2]). Furthermore, the capability of charge stabilization by various substituents may also influence the regioselectivity: *e.g.* although benzonitrile and **1** do cause the same degree and direction of charge transfer upon irradiation (both ΔG *ca.* 1.7 eV for **11** (= A) [2]), the cyanoarene preferentially forms 2- and 4-substituted *meta*-adducts [13]. This may be caused by a higher efficiency in stabilizing negative charges by the CN group.

Experimental Part

1. *General.* α,α,α-Trifluorotoluene was purchased from *Janssen* and further purified by distillation over K_2CO_3. The olefins were synthesized according to methods described in the literature: **6** and **7** [31], **8** and **9** [32], **10** [33], and **11** [34]. Spectrophotometric-grade solvents (from *Fluka*) were used for quantitative measurements. For preparative procedures, the solvents were purified by standard methods. Especially peroxids were removed from ethers, and CH_2Cl_2 was distilled over K_2CO_3. GC: *Carlo Erba Fractovap 2101* using *OV 101* and *NPGS* glass columns, both 5% on *Chromosorb WAW DMCS* 80/100 mesh. Anal. and prep. HPLC: *Perkin Elmer Ser. 3-LC-65 T* and *Gilson-303* Chromatograph, respectively; *Chromosorb Si 60* columns, mixtures of max. 50% AcOEt in hexane. For details of the measurement of the electrochemical redox potentials, see [2a]. IR spectra: *Perkin-Elmer-377* spectrometer. ^{1}H- and ^{13}C-NMR spectra: *Varian EM 390* (90 MHz) and *Varian CFT 20* (20 MHz) spectrometer, respectively. The ^{19}F-NMR spectra of **14a** and **14b** were recorded on a *Bruker WP 80*. For NMR data, see *Tables 4–7*. After max. two chromatographic purifications, all isolated products were at least 95% pure and satisfactory microanalytical data were obtained: C ± 0.30%, H ± 0.15%.

2. *Irradiation Conditions.* The preparative irradiations were carried out in a photoreactor from *Gräntzel* (160-W low-pressure mercury lamp, quartz filter) containing 100 ml of a soln. of 1M α,α,α-trifluorotoluene and 0.5M olefin under N_2. K_2CO_3 (*ca.* 2 g) was added to all solns. which contain 1,3-dioxoles in order to prevent acid-catalyzed decompositions of the products. In some cases, a photoreactor fitted with a quartz-immersion well and a low-pressure mercury lamp *TNN* 15 W (from *Heraeus*) was used as well. The reaction mixture was checked by anal. GC. After *ca.* 10–15 h (160-W lamp) or *ca.* 2–3 d (15-W lamp), the reaction was stopped (*ca.* 50% conversion) for workup.

Irradiations for anal. purposes were performed in a 'merry-go-round' apparatus (from *H. Mangels*, Bornheim-Roisdorf) which was fitted with a *TNN*-15-W lamp. K_2CO_3 was added to the dioxole solns. as well (see above). The concentrations of the starting materials and the products were determined by GC (internal standard method; *NPGS* column for reactions with 1,3-dioxoles, *OV-101* column for the other reactions). Anal. HPLC measurements were performed to check the peak assignment and to exclude thermal consecutive reactions of the products (see text for a discussion of the thermal rearrangement of **16** and **17**).

3. *Product Isolation.* After removal of the solvents by distillation at r.t., only the mixtures from the photoreactions of **8** and **9** could be distilled at *ca.* 60–70°/0.1 Torr without excessive decomposition. However, a separation into the components was not possible by this method. Therefore, most of the mixtures were first filtered over silica gel (*Woelm*, 32–100 mesh) in order to remove polymeric materials and then separated by semi-prep. HPLC *(Si 60)*. In general, the dioxole products were separated using mixtures containing max. 5% of AcOEt, more polar solvents (50% AcOEt) were required for the products from **1**/**11**.

In case of the products from **6** and **7**, all these methods failed since **12** and **13** decomposed even under HPLC conditions. A separation attempt by liquid chromatography over basic alumina (*Super I* from *Woelm*) with AcOEt/hexane 1:99 resulted in the isolation of the elimination product **25**.

4. *Products from* **6** *and* **7**. All attempts to isolate the products from **6** by distillation or chromatographic methods failed due to their lability. Instead the elimination product **25** was separated using HPLC (see above). *4-(α,α-Difluorobenzyl)-2,2,4-trimethyl-5-methylene-1,3-dioxolane* (**25**): colourless oil. ^{1}H-NMR (CDCl$_3$): 1.15 (*s*, CH$_3$); 1.37 (*s*, CH$_3$); 1.54 (*t*, *J*(H,F) = 1.5, CH$_3$); 4.23 (*dt*, *J*(H,H) = 2.5, *J*(H,F) = 1.0, 1H, =CH$_2$); 4.51 (*dt*,

$J(H,H) = 2.5$, $J(H,F) = 0.6$, 1H, $=CH_2$); 7.3–7.6 (m, Ph). MS: 254 (23.8, M^+), 239 (2.2, $M^+ - CH_3$), 127 (100, $PhCF_2^+$), 109 (12.6), 91 (2.5), 85 (32.9), 77 (10.6), 67 (29.8), 59 (18.7), 43 (51.2).

The products from **7** were identified as *4-(α,α-difluorobenzyl)-5-fluoro-4,5-dimethyl-1,3-dioxolane* (**13**; two isomers) due to their GC/MS data. Isomer with the smaller retention time: MS: 226 (3.9, $M^+ - HF$), 127 (4.3, $PhCF_2^+$), 100 (6.3), 99 (100, **7**$^+ - 1$), 77 (3.0), 71 (2.8), 53 (21.2), 51 (2.2), 43 (15.8). Isomer with the higher retention time: MS: 226 (21.9, $M^+ - HF$), 133 (2.2), 127 (11.3, $PhCF_2^+$), 100 (6.2), 99 (100, **7**$^+ - 1$), 77 (5.1), 69 (15.8), 51 (2.8), 43 (18.9).

5. *Products from* **8**. *4-(α,α-Difluorobenzyl)-5-fluoro-2,2-dimethyl-1,3-dioxolane* (**14**). *Isomer* **14a**: smaller GC-retention time; colourless oil. MS: 231 (15.3, $M^+ - CH_3$), 171 (6.1), 149 (2.4), 138 (3.9), 127 (14.5, $PhCF_2^+$), 119 (32.2, $M^+ - PhCF_2$), 109 (2.4), 101 (2.8), 91 (2.4), 77 (5.5), 61 (2.9), 59 (2.8), 57 (2.3), 51 (3.6), 43 (100).

Isomer **14b**: higher GC-retention time; colourless oil. MS: 246 (0.3, M^+), 231 (5.6, $M^+ - CH_3$), 171 (4.7), 138 (4.0), 127 (18.4, $PhCF_2^+$), 119 (37.1, $M^+ - PhCF_2$), 109 (3.0), 101 (3.7), 100 (9.4, **8**$^+$), 91 (2.5), 85 (4.3, **8**$^+ - CH_3$), 77 (6.6), 61 (4.6), 59 (4.2), 57 (2.7), 51 (4.2), 43 (100).

6. *Products from* **9**. Beside the 1:1 adducts **15**–**19**, a compound with small retention time (HPLC) was isolated and identified as *1,1,2,2-tetrafluoro-1,2-diphenylethane* (**27**). ^{1}H-NMR (CDCl$_3$): 7.43 (br. s, Ph). ^{13}C-NMR (CDCl$_3$): 126.76, 126.98, 127.18 (t, $J(CF) = 4$, $o - C$); 128.09 (s, $m - C$); 129.06 (br. s, $p - C$). MS: 255 (2.1, $M^+ + 1$), 254 (14.0, M^+), 127 (100, $PhCF_2^+$), 77 (14.3, $C_6H_5^+$), 51 (4.1).

A low-boiling product (rel. GC-retention time with regard to **15**: 0.2) may be identified as *α,α-difluorotoluene*. MS: 128 (12.3, M^+), 127 (100, $M^+ - 1$), 109 (3.1, $M^+ - F$), 88 (7.2), 84 (8.7), 77 (29.5, $C_6H_5^+$), 51 (15.1).

4-(α,α-Difluorobenzyl)-5-fluoro-1,3-dioxolane (**15**). *Isomer* **15a**: smaller GC-retention time; colourless oil. MS: 218 (2.7, M^+), 173 (2.3), 172 (24.8), 141 (2.3), 127 (100, $PhCF_2^+$), 101 (2.2), 91 (6.0, $M^+ - PhCF_2$), 78 (2.6), 77 (9.7), 72 (11.5, **9**$^+$), 71 (1.1), 63 (3.8), 62 (2.3), 51 (4.5).

Isomer **15b**: higher GC-retention time; colourless oil. MS: 218 (3.8, M^+), 173 (1.1), 172 (11.5), 141 (2.1), 127 (100, $PhCF_2^+$), 101 (2.3), 91 (6.1, $M^+ - PhCF_2$), 78 (1.7), 77 (10.9), 72 (42.2, **9**$^+$), 71 (3.0), 63 (3.3), 62 (2.7), 51 (5.4).

7,8-Methylenedioxy-1-(trifluoromethyl)bicyclo[4.2.0]octa-2,4-diene (= *1-Trifluoromethyl-3,5-dioxotricyclo[5.4.0.0^{2,6}]undeca-8,10-diene*; **16/17**)[9]. MS: 127 (5.1, $PhCF_2^+$), 109 (4.0), 91 (4.2), 72 (100, **9**$^+$), 71 (37.6), 51 (5.3), 43 (12.9).

6,7-'exo'-Methylenedioxy-2-(trifluoromethyl)tricyclo[3.3.0.0^{2,8}]oct-3-ene (= *4-Trifluoromethyl-9,11-dioxatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-ene*; **18**): colourless oil. MS: 218 (4.1, M^+), 127 (5.5, $PhCF_2^+$), 77 (3.8), 72 (3.6, **9**$^+$), 71 (100, **9**$^+ - 1$), 51 (2.7), 43 (3.8).

6,7-'exo'-Methylenedioxy-4-(trifluoromethyl)tricyclo[3.3.0.0^{2,8}]oct-3-ene (= *6-Trifluoromethyl-9,11-dioxatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-ene*; **19**): colourless oil. MS: 218 (3.2, M^+), 127 (9.6, $PhCF_2^+$), 77 (10.7), 72 (100, **9**$^+$), 71 (38.2, **9**$^+ - 1$), 51 (14.1), 43 (13.9).

7. *Products from* **11**. One product already precipitated during the photolysis in 20% yield and was identified as cis-anti-cis-*1,2:3,4-bis (carbonyldioxy)cyclobutane* (= *3,5,8,10-tetraoxatricyclo[5.3.0.0^{2,6}]decane-4,9-dione*; **26**) [21].

6,7-'endo'-Carbonyldioxy-2-(trifluoromethyl)tricyclo[3.3.0.0^{2,8}]oct-3-ene (= *4-Trifluoromethyl-9,11-dioxatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-en-10-one*; **20**): viscous oil. MS: 232 (9.8, M^+), 188 (3.7, $M^+ - CO_2$), 187 (5.6), 159 ($M^+ - CO_2 - CHO$), 147 (9.9), 146 (84.8, **1**$^+$), 145 (13.3), 140 (16.0, 159 – F), 127 (13.3, $PhCF_2$), 119 (44.1), 109 (23.0), 96 (11.7), 91 (100), 86 (84.0, **11**$^+$), 77 (11.9), 65 (18.9), 63 (15.0), 55 (21.1), 51 (19.7).

6,7-'endo'-Carbonyldioxy-4-(trifluoromethyl)tricyclo[3.3.0.0^{2,8}]oct-3-ene (= *6-Trifluoromethyl-9,11-dioxatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-en-2-one*; **21**): m.p. 119–22°. MS: 232 (5.0, M^+), 188 (4.9, $M^+ - CO_2$), 187 (5.7), 159 (27.7, $M^+ - CO_2 - CHO$), 147 (7.7), 146 (85.7, **1**$^+$), 145 (17.0), 140 (14.3, 159 – F), 127 (17.1, $PhCF_2^+$), 119 (42.9), 109 (24.8), 96 (16.9), 91 (100), 86 (81.5, **11**$^+$), 83 (12.8), 77 (13.8), 75 (11.2), 65 (22.2), 63 (18.1), 57 (10.3), 55 (26.9), 51 (22.4), 50 (11.8), 44 (20.7).

6,7-'endo'-Carbonyldioxy-5-(trifluoromethyl)tricyclo[3.3.0.0^{2,8}]oct-3-ene (= *7-Trifluoromethyl-9,11-dioxatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-en-10-one*; **22**): viscous oil. MS: 232 (10.4, M^+), 188 (3.2, $M^+ - CO_2$), 187 (5.3), 159 (24.0, $M^+ - CO_2 - CHO$), 147 (8.9), 146 (100, **1**$^+$), 145 (20.4), 140 (15.9), 127 (21.3, $PhCF_2^+$) 119 (47.1), 109 (24.5), 107 (10.6), 96 (18.4), 91 (91.9), 86 (100, **11**$^+$), 77 (11.6), 65 (21.6), 63 (17.5), 57 (10.2), 55 (20.6), 51 (21.2), 50 (12.1), 44 (13.4), 42 (11.8).

6,7-'endo'-Carbonyldioxy-8-(trifluoromethyl)tricyclo[3.3.0.0^{2,8}]oct-3-ene (= *13-Trifluoromethyl-9,11-dioxatetracyclo[6.3.0.0^{2,4}.0^{3,7}]undec-5-en-10-one*; **23**); viscous oil. MS: 232 (5.1, M^+), 188 (5.8, $M^+ - CO_2$), 187 (6.7), 159 (29.9, $M^+ - CO_2 - CHO$), 147 (9.9), 146 (89.3, **1**$^+$), 109 (29.0), 107 (16.4), 96 (16.8), 91 (100), 86 (67.4, **11**$^+$), 77 (14.4), 65 (23.9), 63 (20.7), 57 (12.0), 55 (14.0), 51 (24.2), 50 (15.3), 44 (22.0), 42 (19.7).

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[9] **16** and **17** rearrange thermally into each other under GC-conditions (*ca.* 200°). As a consequence, an assignment of the GC/MS data to one isomer or the other was not possible. For a similar example, see [1].

7,8-Carbonyldioxy-2-(trifluoromethyl)bicyclo[2.2.2]octa-2,5-diene (= 8-(Trifluoromethyl)tricyclo[5.2.2.0²·⁶]-undeca-8,10-dien-4-one; **24**): viscous oil. ^{1}H-NMR (CDCl$_3$): 4.3 (*m,* $\Sigma J = 11$, H–C(1), H–C(4)); 4.64 (*m,* $\Sigma J = 3.6$, H–C(7), H–C(8)); 6.4 (*m,* $\Sigma J = 7.4$, $^3J = 3.7$, H–C(5), H–C(6)); 6.9 (*d$_q$, J*(H,H) = 6.3, *J*(H,F) = 2.0, H–C(3)). ^{13}C-NMR (CDCl$_3$): 39.76 (*J*(C,F) = 1.5, C(1)); 40.63 (C(4)); 74.99, 75.23 (C(7) and/or C(8)), 122.25 (*J*(C,F) = 270.4, CF$_3$); 132.09, 132.77 (C(5) and/or C(6)); 134.78 (*J*(C,F) = 35.2, C(2)); 134.97 (*J*(C,F) = 5.4, C(3)); 171.30 (C=O). MS: 232 (0.1, *M* $^+$), 188 (0.2, *M* $^+$ – CO$_2$), 159 (13.5, *M* $^+$ – CO$_2$ – CHO), 147 (8.1), 146 (100, **1** $^+$), 145 (18.5), 127 (18.7, PhCF$_2^+$), 109 (10.0), 96 (18.3), 86 (91.3, **11** $^+$), 51 (8.7), 42 (13.7).

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