# SELECTIVITY AND CHARGE TRANSFER IN PHOTOREACTIONS OF ARENES WITH OLEFINS\* 1. SUBSTITUTION VERSUS CYCLOADDITION

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<u>Abstract</u>: In photoreactions of arenes with olefins the mode of reaction strongly depends on the charge transfer between the starting materials. Substitution is preferred if the electron transfer becomes exergonic, i.e. if  $\Delta G < 0$  according to the Rehm-Weller equation. In some special systems substitution is avoided by electron transfer-triplet formation. Various photoreactions which already have been described in the literature are dicussed in view of this  $\Delta G$ -correlation besides own experimental results.

## INTRODUCTION

Recent results from this laboratory clearly showed that charge transfer may influence the selectivity of product formation in various bimolecular photoreactions of olefins with carbonyl compounds and arenes 1-6. The often observed trend of donor-acceptor pairs with extreme CT-character to form substitution products <sup>7</sup>) rather than cycloadducts were sufficiently rationalized by a mechanism which involves electron transfer under formation of radical cation-anion pairs. The final products are formed from these intermediates in a consecutive reaction sequence first by transfer of an ionic group and then by coupling of the radical pairs. The reactions of  $\alpha, \alpha, \alpha$ -trifluorotoluene  $\underline{1}$  with 1.3-dioxoles  $\underline{2}$  may exemplify this mechanism <sup>4</sup>) (Scheme 1). Further examples are given by the photoreactions of ketones <sup>8</sup>) and diketones <sup>1,8</sup>) with electron-rich olefins. In all





<sup>\*</sup> Part 6 of "Selectivity and Charge Transfer in Photoreactions of Donor-Acceptor Systems". For part 5 see ref. 4b.

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systems which we have been studying this mechanism is in accordance with the observed solvent dependences of product formation 1,2,4,8. Furthermore we were able to observe radical ion intermediates such as contact ion pairs (CIP) and solvent separated ion pairs (SSIP) by conventional 9 and laser flash spectroscopy 8. Starting from these results we wish to present a rule which can rationalize the selectivities of substitution versus cycloaddition in photoreactions of arenes with olefins. This rule bases on

- (i) the exciplex mechanism of these photoreactions 4-6, 10, 11;
- (ii) the Weller-theory of electron transfer  $^{13)}$ .

## 2 RESULTS AND DISCUSSION

Benzonitrile 7

#### 2.1 General Remarks

The free enthalpies of electron transfer  $\Delta G$  can be easily calculated by means of the Rehm-Weller-equation (1) <sup>13</sup>:

$$\Delta G = F \left[ E_{1/2}^{Ox}(D) - E_{1/2}^{Red}(A) \right] - \Delta E_{excit} + \frac{e^2 N}{4\pi \varepsilon_o a} \left[ \frac{1}{\varepsilon} - \frac{2}{37.5} \right]$$
(1)

with  $E_{1/2}^{0}(D)$  ( $E_{1/2}^{\text{Red}}(A)$ ) = oxidation (reduction) potential of the donor (acceptor) molecule in acetonitrile,  $\Delta E_{\text{excit}}$  = excitation energy, F = 96490 C, e = 1.602 x 10<sup>-19</sup> C,  $\varepsilon_{0}$  = 8.854 x 10<sup>-12</sup> Fm<sup>-1</sup>,  $\varepsilon$  = dielectric constant of the solvent,  $\varepsilon$  of acetonitrile = 37.5, N = 6.023 x 10<sup>23</sup> mol<sup>-1</sup>, a = encounter distance 7 Å. A simplified version of (1) for 1.4-dioxane (dielectric constant  $\varepsilon$  = 2.2) as solvent is given as follows

$$\Delta G[eV] = E_{1/2}^{Ox}(0) - E_{1/2}^{Red}(A) - \Delta E_{excit} + 0.82$$
(2)

We have chosen 1,4-dioxane, since (i) this corresponds to the polarity which is normally used in photoreactions of arenes with olefins; (ii) the potential curves of exciplex and SSIP cross in an  $\varepsilon$ -region of  $\leq 10^{-14}$ , and (iii) the formation of CIP (= exciplex with full electron transfer  $^{13}$  is spectroscopically observable even in non-polar solvents such as cyclohexane  $^{9}$ .

Using the redox potentials and the excitation energies, which are collected in Table 1.  $\Delta G$  can now be calculated for arene-olefin systems for both the arene as acceptor and donor:

ARENE = ACCEPTOR

- Benzene  $\frac{4}{2}$   $\Delta G = E_{1/2}^{0x}(D) 0.07$  (3)
- $\alpha_{\star}\alpha_{\star}\alpha_{\star}$  -Trifluorotoluene  $\underline{1}$   $\Delta G = E_{1/2}^{Ox}(D) 0.65$  (4)
  - $\Delta G = E_{1/2}^{Ox}(D) 0.95$

(5)

## ARENE = DONOR

α,α,α-Trifluorotoluene <u>]</u>	$\Delta G = -E_{1/2}^{\text{Red}}(A) - 0.92$	(6)
	Pod	

Benzonitrile  $\underline{7}$   $\Delta G = -E_{1/2}^{\text{Red}}(A) - 0.93$  (7) Benzene  $\underline{4}$   $\Delta G = -E_{1/2}^{\text{Red}}(A) - 1.68$  (8)

Toluene 
$$\underline{6}$$
  $\Delta G = -E_{1/2}^{\text{Red}}(A) - 1.96$  (9)  
Anisole  $\underline{5}$   $\Delta G = -E_{1/2}^{\text{Red}}(A) - 2.30$  (10)

To decide whether the arene is the acceptor or the donor in a special system, one has to calculate  $\Delta G$  by means of equation (3) - (10) or an equation, which can be derived from (1) as shown before.

This procedure may also help to determine the direction of charge transfer in systems of incomplete electron transfer. For example in photoreactions of vinylene carbonate  $\frac{8}{2}$  ( $E_{1/2}^{0x}$  = 3.07 V, calculated

from IP = 10.08 eV  $^{20}$  according to Miller  $^{16}$ ;  $E_{1/2}^{\text{Red}} = -2.64$  V) with  $\alpha, \alpha, \alpha$ -trifluorotoluene or benzene 4, respectively, the olefin acts as acceptor, since in both cases  $\Delta G(\underline{1}, \underline{4} = D) < \Delta G(\underline{1}, \underline{4} = A)$ . These results may be transposed to formulae A and B as shown in Scheme 2. They have important consequences for the stereoselectivity of these photoreactions: Whereas 1.3-dioxoles 2 preferentially give exo-configurated cycloadducts  $^{4,6)}$ , vinylene carbonate 8 predominantly form the endo-stereoisomers  $^{4,21}$ . A more detailed discussion will be presented elsewhere  $^{22}$ .



Scheme 2: Direction of charge transfer in arene-olefin systems of incomplete electron transfer and consequences for the stereochemistry of both exciplex-intermediates and photoproducts (R = H: ref. 6,21; R = CF<sub>3</sub>: ref. 4).

#### 2.2 Substitution Reactions and Electron Transfer Triplet Formation

A schematic presentation of the meaning of equation (3) - (10) is shown in scheme 3. Only photoreactions of strong acceptor (A) arenes such as 1 and 7 may provide exergonic electron transfer processes with olefins like 1.3-dioxoles 2 (e.g.  $2\underline{a}-\underline{g}$ ). The same holds for donor arenes such as  $\underline{5}$  and  $\underline{6}$ , but only in reactions with strong acceptor olefins like benzoquinone  $\underline{20}$  and tetracyano-ethene  $\underline{21}$ .

It should be mentioned that dissociation of the photochemically formed CIP  $(A^{T}D^{\dagger})$  into free radical ions (FRI =  $A^{T} + D^{\dagger}$ ) may be a competitive reaction to the product formation 1-4,8,9) (for "exceptions" see below). This ionic photodissociation 23 is preferred in polar solvents:



Therefore the  $\Delta G$ -values of electron transfer and the solvent dependences of product formation may provide simple probes for the rationalization of the mode selectivities in arene-olefin systems of strong CT-character.

## Substitution Reactions with Acceptor-Arenes

This type of substitution has been observed only occasionally simply because it is restricted to extremly electron-rich olefins. One example which we mentioned before and which is discussed elsewhere in more detail  $^{(4)}$  is the photoreaction of  $\alpha, \alpha, \alpha$ -trifluorotoluene <u>1</u> with 1, 3-dioxoles <u>2</u> (Scheme 1). Further examples were reported by McCullough for naphthonitrile-tetramethylethene  $^{(32)}$ , by Pac for 1-naphthonitrile-indene  $^{(33)}$ , by Lewis for 9-cyanophenanthrene-tetramethylethene  $^{(34)}$  and by Arnold for dicyanobenzene (naphthalene)-tetramethylethene  $^{(35)}$ . All these systems have in common that the calculated  $\Delta G$ -values are around zero or even negative, which promote electron transfer



processes. The situations are somewhat different from that mentioned above, since the photolyses in polar solvents lead to free radical ions and only these latter intermediates form substitution products. However, all examples exhibit exergonic electron transfer in the primary process according to the Rehm-Weller equation (1).

## Substitution Reactions with Donor-Arenes

Donor-arenes and acceptor-olefins also form substitution products upon photolysis provided that  $\Delta G < 0$  or that  $\Delta G$  is at least only slightly positive. Most of the known examples were reported for toluene and anisole systems. Ohashi and coworkers studied the photoreactions of methoxybenzenes with acrylonitrile and they found that substitution occurs rather than cycloaddition to the aromatic

ring, if  $\Delta G$  becomes more negative <sup>36)</sup>. These observations were also confirmed by varying the olefin from acrylonitrile to its methyl derivatives <sup>36)</sup>. However, Gilbert reinvestigated these photoreactions and stated that substitution products were only formed in methanol <sup>37)</sup> (Scheme 4). Up to this state there are still open questions concerning this mechanism: i.e. only further studies of the solvent dependence of both the cyloaddition and substitution mode should provide more detailed informations; e.g. about the problem, whether <u>24</u> is formed via free radical ions or via contact ion pairs (exciplex with full electron transfer).



<u>Scheme 4</u>: Cycloaddition to the ortho-adduct  $\underline{23}$  and substitution to  $\underline{24}$  in anisole-acrylonitrile systems (from ref. 36, 37).

Ohashi also reported the 1,2-addition of toluene  $\underline{6}$  to tetracyanoethene  $\underline{21}^{38}$ . In this case  $\underline{25}$  is also formed in non-polar solvents, which accounts for a mechanism via an exciplex-intermediate followed by electron- and proton-transfer:



It should be mentioned, that the reaction rate was greatly increased in the presence of methanol. This at least points at methanol as a proton mediator. Whether free radical ions may be involved under these conditions is not known up to this state. Similar observations were described by McCullough for naphthalene (indene)-acrylonitrile systems <sup>39</sup>). Substitution is also observed in reactions with benzene itself, e.g. with p-quinone  $\underline{20}^{40}$ . In this case the excited species is  $\underline{20}$ . The strong reduction potential of  $\underline{20}$  compensates the smaller excitation energy and therefore  $\Delta G < 0$  (see equation 8).

## Electron Transfer-Triplet Formation

The kinetics of triplet formation from the radical ion pairs (SSIP) or the preceding exciplex have been studied in detail by Weller <sup>41)</sup>. The photoreaction of benzonitrile  $\underline{7}$  with 2,2-dimethyl-1,3-dioxole  $\underline{2e}$ , which only yields the dimer  $\underline{27}$  may be rationalized in terms of such a mechanism (Scheme 5). Besides back electron transfer two competing reactions proceed from the initially formed exciplex: tripet formation and ionic photodissociation. Only the former pathway leads to the dimer  $\underline{28}$ , the latter one is preferred only in polar solvents. A mechanism via energy transfer can be

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excluded because of the solvent dependence of product formation, i.e.  $\underline{28}$  is formed 5-fold less when changing the solvent from cyclohexane to acetonitrile. The same argument rules out triplet formation by recombination of free radical ions, which has been observed by Farid in the dimerization of 1.2-diphenylcyclopropene-3-carboxylate <sup>42</sup>.

Photoreactions of arenes with olefins via an electron transfer-triplet mechanism may be restricted to systems of exergonic electron transfer ( $\Delta G < 0$ ) As a consequence, benzonitrile and the weaker donor olefin  $\underline{2g}$  additionally form the azetine  $\underline{26}$  besides the dimer  $\underline{29}$  in a 1:5 ratio ( $\underline{26}$  was isolated as its derivative  $\underline{27}$  by means of HPLC <sup>50)</sup>. Similar photochemical additions of olefins to the nitrile triple bond have already been reported by Cantrell <sup>43)</sup>. All these benzonitrile-olefin systems described by this author provide positive  $\Delta G$ -values of electron transfer.



<u>Scheme 5</u>: Photoreactions of benzonitrile  $\underline{7}$  with 1,3-dioxoles  $\underline{2\underline{e}}$  and  $\underline{2\underline{g}}$ . 2.3 Photoreactions of Chloro-, Bromo-, and Iodobenzenes: An Exeption?





The reactions of halogenated arenes such as chloro-, bromo-, and iodobenzene mainly form substitution products with cyclopentene <sup>44)</sup> (Scheme 6), although  $\Delta G > 0$  at least for chloro- and bromobenzene. A similar substitution, but in a reversed direction, is observed in the photoreaction of benzene itself with 1.2-dichloroethene <u>13</u> <sup>45)</sup>. All these arene-olefin systems exhibit positive,

but relatively small  $\Delta G$ 's, indicating polar exciplex intermediates with the negative charge at the halogenated species (Table 4). Migration of  $X^{(-)}$  should lead to the substitution products. Such a mechanism may count for systems with X = Cl, Br, J, since their carbon-halogen bonds are relatively weak. Indeed, photoreactions of the corresponding fluoronated arene-olefin systems preferentially yield cycloadducts <sup>44)</sup> (Scheme 6), since the C-F bond strengths are of the same order of magnitude as C-H bonds.

Therefore these systems do not seem to be exceptions of this  $\Delta G$ -correlation, since competing reactions may occur depending on the polarity of the exciplex-intermediates and on the bond strengths of the migrating substituents.

### 3 CONCLUSION

In conclusion, the photoreactions of arenes with olefins, which exhibit extremely strong CTcharacter can be rationalized on the basis of the exciplex-mechanism. We have shown that substitution is preferred if  $\Delta G$  of electron transfer is negative or nearly zero. These  $\Delta G$ -values can be easily calculated by means of the Rehm-Weller equation from the electrochemical redox-potentials of the starting materials and from the excitation energy of the electrochemical excited species. In the proceeding paper of this series we will show that a similar  $\Delta G$ -correlation may provide a useful guide for the rationalization of the modes of cycloaddition and even for the stereoselectivities of these photoreactions.

#### 4 EXPERIMENTAL

<u>Materials</u>: If not otherwise stated the arenes and olefins were purchased and purified by destillation or recrystallization, respectively. The 1.3-dioxoles were synthesized according to a method developed in this laboratory or according to Field . The solvents were used as available from Fluka (spectrophotometric grage). Acetonitrile was further purified by adsorptive filtration over activated aluminium oxide (Woelm) before it was used for electrochemical measurements. Tetra-n-butylammonium-tetra-fluoroborate (Fluka) was used as supporting electrolyte and was further purified by repeated recrystallization from ethyl acetate.

<u>Synthetic and Analytical Equipment</u>: Low pressure mercury lamps (TNN 15/32 from Heraeus and an immersion lamp 70 W from A. Gräntzel, respectively) were used as light sources for the photoreactions. Preparative irradiations were performed in quartz photoreactors; a "merry-go-round" apparatus was used for the measurements of relative quantum yields. - A Perkin-Elmer-Ser. 3-LC-65 T and a Gilson-303-Chromatograph were used for analytic and preparative chromatographic seperations, respectively. In both cases Chromosorb Si 60 columns and ethyl acetate-hexane mixtures were used as eluates. - Gaschromatographic analyses were performed on a Carlo Erba Fractovap 2101 using OV 17 and OV 101 columns. - H-NMR- and 'C-NMR-spectra were measured by means of a Varian EM 390 (90 MHz) and a Varian CFT 20 (20 MHz)-Spectrometer, respectively. Infrared- and UV-spectra were recorded on a 377- and 320-Spectrometer, both from Perkin-Elmer. - Cyclic Voltammetry: Voltage Scan Generator (Mod. VSG 72) and Labor-Potentiostat LB 81H, both from G. Blank Elektronik.

<u>Electrochemical Measurements</u>: Half-wave potentials were obtained by cyclic voltammetry at a platinum electrode versus a Ag/AgNO<sub>3</sub> electrode in acetonitrile at c = 1 mM. The supporting electrolyte was 0.1 M tetra-n-butyl<sup>3</sup> ammonium tetrafluoroborate, the scan speed was 100 mV/s.

<u>Preparative Photoreactions</u>: A solution of benzonitrile  $\underline{7}$  (4 g) and 1,3-dioxole  $\underline{2g}$  (10 g) or 2,2-dimethyl-1,3-dioxole  $\underline{2e}$  (10 g), respectively, in 200 ml cyclohexane were irradiated under nitrogen atmosphere using the 70 W-low pressure mercury lamp. After 5 h the conversion was ca. 30 % (GCanalysis). There was no change in the product formation by varying the light intensity. The solvent was removed under reduced pressure at room temperature and the reaction mixture was separated by HPLC.

Irradiation of 7 with 2g: Two products were isolated and identified spectroscopically.

 $\begin{array}{l} & \begin{array}{c} 2-Pheny1-3-oxg-1-azetine \ 27: \ oi1; \end{array} ^{1} H-NMR (CDC1_3) \ \delta \ 7.2-7.5 \ (m, 3H, m-H, p-H), \ 7.7-7.9 \ (m, 2H, \ o-H), \ 7.9 \ (s, 2H, CH_2); \end{array} ^{2} C-NMR (CDC1_3) \ \delta \ 125.66 \ (o-C \ of \ Ph), \ 128.26 \ (p-C \ of \ Ph), \ 128.83 \ (m-C \ of \ Ph), \ 133.73, \ 146.51, 151.34; \ MS \ (70 \ eV)^{3} m/e \ 146 \ (10.3, M+1), \ 145 \ (100, M), \ 117 \ (46.2, M-C0), \ 90 \ (51.9 \ (C_7H_6), \ 89 \ (44.3, C_7H_5), \ 63 \ (18.5, C_5H_3). \end{array}$ 

<u>exo-Bis-methylendioxy-cyclobutan 29: 29</u> was isolated as the component with the longer retention time. It is identical with the exo-dimer ("anti" in ref. 49), which is formed from  $\underline{2g}$  by sensitized photoreaction (ref. 49).

Irradiation of 7 with 2e: Only the formation of one product was observed by means of GC and HPLC. After HPLC-isolation this product was identified as exo-Bis-isopropyliden-cyclobutan  $\frac{28}{28}$  (ref. 49).

<u>Measurements of Relative Quantum Yields in Various Solvents</u>: Solutions (10 ml) of 7 (0.1 g) and  $\underline{2e}$  (0.5 ml) in cyclohexane, tetrahydrofuran, acetonitrile and methanol, respectively, were

irradiated in a "merry-go-round" apparatus by means of a TNN 15/32-lamp. The analyses were performed by GC using biphenyl as internal standard. The relative quantum yields of formation of <u>28</u> decrese with increasing solvent polarity: 1 (cyclohexane), 0.4 (tetrahydrofuran), 0.2 (acetonitrile), 0.01 (methanol).

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Arene	E <sup>0x</sup> [v] a)	$E_{1/2}^{\text{Red}}[v]^{a}$	ΔE <sub>exit</sub> d) [eV]
£ 🔘	2.11	-3.72 <sup>b)</sup>	4.61
	H <sub>3</sub> 1.34		4.46
5 CH3	1.83		4.61
2 0 CN	2.74 <sup>c)</sup>	-2.76	4.51
1 O CF3	2.91 <sup>c)</sup>	-3.18	4.65
3 <u>3</u> 0 co	ОСН <sub>3</sub> 2.40 <sup>с)</sup>	-2.62	4.44
<u>30</u> F	2.25 <sup>c)</sup>		4.64
40 -F.		-2.29	4.88

## Table 1: Electrochemical Redox-Potentials and Excitation Energies of some Benzene Derivatives

- a) If not otherwise stated the redox-potentials (Ag/AgNO3-electrode) were measured by cyclic voltametry (Pt-working electrode) in acetonitrile.
- b) In DME at -60 °C (ref. 15).
- c) Calculated from the ionization potentials according to Miller's formula (ref. 16):  $IP(\underline{7}) = 9.72$ eV (ref. 17),  $IP(\underline{1}) = 9.90$  eV (ref. 18),  $IP(\underline{39}) = 9.35$  (ref. 51),  $IP(\underline{30}) = 9.19$  eV (ref. 52).
- d) Taken from the UV absorption (0-0 transition); see also ref. 19.

	Olefin	ε <sup>φ</sup> ∛2 [ν] <sup>α)</sup>	Ref.
<u>2a</u>	H <sub>3</sub> C CH <sub>3</sub>	0.42	24
<u>2b</u>	H <sub>3</sub> C 0' 'CH <sub>3</sub> H <sub>3</sub> C	<b>0.48</b>	24
<u>2c</u>		0.55	24
20	<u>_0,,CH³</u> H³C∕	<b>(</b> ) 0.60	24
<u>2e</u>		0.69	24
<u>2f</u>		<b>≻−сн</b> <sub>3 0.73</sub> <sup>b)</sup>	24
28	$\left( \left< \right>^{\circ} \right>$	0.76	24
2	∕∽oc₂h₅	1.44	24
<u>10</u>	ососн3	2.15	25
11	Г∕ н₃с	CH <sub>3</sub> 1.83	25
<u>12</u>	н₅с	сн3	24
<u>13</u>	CIHC == CHCI	2,67 <sup>c)</sup>	26

Table 2: Electrochemical Oxidation Potentials of Olefins

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a) See note (a) of Table 1.
b) Estimated from IP.
c) See note (c) of Table 1: IP (\underline{13}) = 9.64 eV (ref. 26).
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	Olefin	$E_{1/2}^{\text{Red}}[v]^{a}$	Ref.
<u>13</u>	CICH = CHCI	-2.29 (cis) < -3.1 (trans)	25
<u>14</u>	∽ <sub>CN</sub>	-2.7 -2.44	27, 28 29
<u>15</u>	CH₃ ← CN	-2.61	29
<u>16</u>	∕∽соосн₃	2.6 -2.2 -2.4	27, 28 30 29
<u>17</u>	сн₃ соосн₃	-2.3 -2.57	30 29
<u>18</u>		-2.63 -2.71	30 29
<u>19</u>		-2.21	29
<u>20</u>	o=<=o	0.64 0.78	31
<u>21</u>		-0.12 -1.38 b)	25

## Table 3: Electrochemical Reduction Potentials of Olefins

a) See note (a) of Table 1.

b) 2. reduction potential.

A	D	∆G [ev] ª)	S = Substitution <sup>c)</sup> C = Cycloaddition <sup>c)</sup>	Ref.
<u>31</u>	<u>11</u>	0.46 ± 0.24	S: > 60 <b>%</b> d) C: -	44
<u>32</u>	<u>11</u>	$0.34 \pm 0.43$	S: + <sup>d)</sup> C: -	44
<u>33</u>	<u>11</u>	0.4 ± 0.1	S: + <sup>d)</sup> C: -	44
<u>13</u>	<u>4</u>	0.61 <sup>b)</sup>	S: 60 <b>Z</b> <sup>e)</sup> C: 30 <b>Z</b>	45

<u>Table 4</u>: Free Enthalpies of Electron Transfer and Modes of Reactions in Halogenated Arene-Olefin Systems.

- a) If not otherwise stated calculated by means of equation (2).  $E_{1/2}^{\text{Red}}(\underline{31}) = -2.37 \pm 0.24 \text{ V}$  (in various solvents taken from ref. 31) and  $\Delta E_{\text{excit}} = 4.56 \text{ eV}$  (see note d of Table 1);  $E_{1/2}^{\text{Red}}(\underline{32}) = -2.25 \pm 0.43 \text{ V}$  (ref. 31) and  $\Delta E_{\text{excit}} = 4.56 \text{ eV}$  (see note d of Table 1);  $E_{1/2}^{\text{Red}}(\underline{33}) = -1.88 \pm 0.10 \text{ V}$  (ref. 31) and  $\Delta E_{\text{excit}} \sim 4.13 \text{ eV} = 300 \text{ nm}$  (taken from the broad UV-absorption band); for  $\underline{4}$  see table 1.
- b) Calculated by means of equation (8). A reversed electron transfer would yield  $\Delta G(4 = A, 13 = D) = 2.6 \text{ eV}.$
- c) + means formation of products without any details about yield; means no formation of products.
- d) Additional formation of halogenated biphenyls.
- e) In addition 10 % of <u>13</u>-dimers.