Pyrylium Salts as Photosensitizers in Homogeneous and Heterogeneous Electron-Transfer Catalysis. – A Comparison with Cyano Arenes[1)]

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Two new triphenylpyrylium salts, both being fixed to a polymeric backbone, have been synthesized. They are sensitizers for photochemically induced electron-transfer reactions, offering the possibility of heterogeneous charge transfer. Their usability in electron-transfer-catalyzed dimerizations and mixed cycloadditions of 1,3-cyclohexadiene and phenyl vinyl ether has been tested in comparison to other common photosensitizers such as 9,10-dicyanoanthracene and 1,4-dicyanonaphthalene. In addition, 2,4,6-triphenylpyrylium tetrafluoroborate was shown to operate as an efficient sensitizer for the dimerization and the photooxygenation of 1,1-diphenylethene. Diverse selectivities in the product formation indicate different mechanisms and are discussed in view of earlier results reported in the literature.

Pyrylium-Salze als Photosensibilisatoren in homogener und heterogener Elektronentransfer-Katalyse. – Ein Vergleich mit Cyanoaromaten

Zwei neue Polymer-gebundene Pyrylium-Salze wurden synthetisiert. Sie wirken als Sensibilisatoren in photochemisch induzierten Elektronentransfer-Reaktionen und ermöglichen so heterogenen Ladungstransfer. In vergleichenden Studien mit anderen gebräuchlichen Photosensibilisatoren, wie 9,10-Dicyanoanthracen und 1,4-Dicyanonaphthalin wurde ihre Verwendbarkeit bei Elektronentransfer-katalysierten Dimerisierungen und der gemischten Cycloaddition zwischen 1,3-Cyclohexadien und Phenylvinylether untersucht. Darüber hinaus erwies sich auch 2,4,6-Triphenylpyrylium-tetrafluoroborat als effizienter Sensibilisator für die Dimerisierung und Photooxygenierung von 1,1-Diphenylethen. Die unterschiedlichen Selektivitäten der Produktbildung weisen darauf hin, daß hier verschiedenartige Mechanismen wirken. Die Ergebnisse werden im Zusammenhang mit früheren Literaturergebnissen diskutiert.

Polymer-supported reagents are available today for a lot of synthetic purposes[3)]. Their greatest advantage compared to homogeneous catalysts is the ease of removal from the products after the reaction is finished. The best known example for this type of reagent is Merrifield's resin (**1**)[4)]. Its development was an important step towards modern peptide synthesis as it is known today. In photochemistry, there are only few examples of polymer-bound catalysts. Neckers[5)] used Rose Bengale that was fixed to an insoluble matrix in order to produce singlet oxygen. The same author revealed that Leermakers'[6)] polymer-fixed sensitizer (polyvinyl phenyl ketone) did not work as a heterogeneous triplet sensitizer, the rather good yields of photoproducts were produced by small amounts of impurities of the polymer that were soluble in the reaction mixture and functioned as homogeneous energy-transfer sensitizers.


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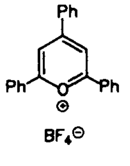
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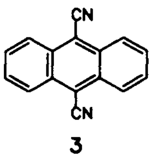
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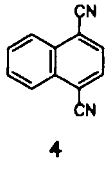
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This paper deals with photochemically induced electron transfer[7,8)] that should be rendered possible with heterogeneous sensitizers, as an example of which we chose polymer-bound pyrylium salts[9)]. The homogeneous alternative is 2,4,6-triphenylpyrylium tetrafluoroborate (**2**) which has been used for this type of reaction since 1973[10–12)]. Other very common electron acceptors in their singlet-excited states are cyano arenes such as 9,10-dicyanoanthracene (**3**) and 1,4-dicyanonaphthalene (**4**)[7,8)].

All these sensitizers are excited by ultraviolet or even visible light (λ > 300–450 nm). Their singlet-excited states are effective electron acceptors and, in polar media, they produce radical cations of olefins or dienes, which operate as electron donors. With the pyrylium salt **2**, Steckhan[12)] postulated a chain-reaction mechanism for the dimerization of 1,3-cyclohexadiene as donor (D) (eq. 1–4).

$$\mathbf{2}^{+} \longrightarrow \mathbf{2}^{+*} \tag{1}$$

$$\mathbf{2}^{+*} + \mathrm{D} \longrightarrow \mathbf{2}^{\bullet} + \mathrm{D}^{+\bullet} \tag{2}$$

$$\mathrm{D}^{+\bullet} + \mathrm{D} \longrightarrow \mathrm{D}_2^{+\bullet} \tag{3}$$

$$\mathrm{D}_2^{+\bullet} + \mathrm{D} \longrightarrow \mathrm{D}_2 + \mathrm{D}^{+\bullet} \tag{4}$$

$$\mathbf{2}^{\bullet} + \mathrm{D}_2^{+\bullet} \longrightarrow \mathbf{2}^{+} + \mathrm{D}_2 \tag{5}$$

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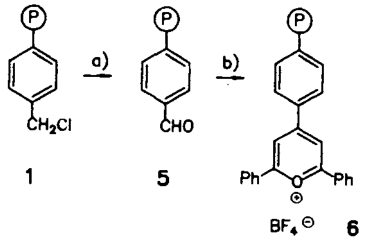
If the secondary electron transfer proceeds according to eq. 5, a conventional catalytic mechanism operates, which may be called electron-transfer sensitization[7,8,13]. In this context one should note that even the Diels-Alder dimerization of cyclohexadiene, catalyzed by aminium salts, eventually operates through a conventional catalytic process[14] rather than a chain mechanism[15]. To what extent a chain mechanism is involved in photochemical dimerizations of dienes, sensitized by typical sensitizers such as **2**–**4**, is presently not clear[7,8]. Terminating processes may be caused by the dimerization of the pyrylium radical **2•**[16,17].

Synthesis of Polymer-Bound Pyrylium Salts

Starting point for the two-step synthesis of **6** is the commercially available Merrifield resin (**1**), which is cross-linked chloromethylated polystyrene. Its content of chlorine runs up to 4–5%, which is about 23% of the maximum theoretical amount.

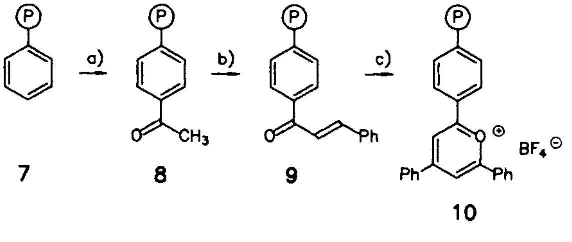


a) $NaHCO_3$, DMSO.– b) BF_3OEt_2, $PhCOCH_3$.

The first step is the oxidation of the chloromethyl group with dimethyl sulfoxide[18]. Elemental analysis and calculations from the isolated yield show that polymer **5** contains 2.5% oxygen, which is 20.6% of the theoretical amount at 100% hypothetical functionalization of the polymer.

This polymeric aldehyde is finally converted to poly[2,6-diphenyl-4-(4′-vinylphenyl)pyrylium tetrafluoroborate] (**6**) by a procedure of Lombard and Stéphan[19]. Elemental analysis and calculations from the isolated yield of polymer **6** show that every ninth to 12th ring bears a pyrylium unit, which is 8.5–11.5% of the theoretical value.

Another isomeric polymer-bound pyrylium salt was synthesized from polystyrene **7**. The crucial step of this synthesis is the aldol condensation of poly(vinylacetophenone)[20] (**8**) with benzaldehyde to yield **9**, which tends to cross-link in the presence of acids[21] or light[22,23]. This fact brings about that **10** is a cross-linked macromolecule and thus insoluble in organic solvents.

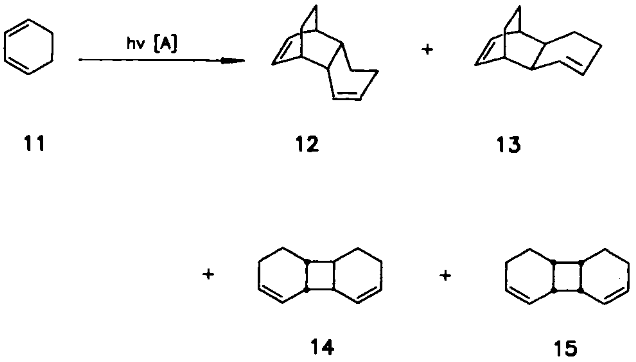


In order to remove impurities of low molecular weight, the polymers **6** and **10** were washed successively with water, acetonitrile, acetone, dichloromethane, and ether. This procedure ensured heterogeneous reaction conditions in the following photoreactions.

Photoreactions

Dimerization of 1,3-Cyclohexadiene (11)

This reaction has been reviewed by several groups since the 1960s (overviews are given in ref.[2,7,8,24]). The ordinary thermal Diels-Alder reaction yields the dimers **12** (*endo*) and **13** (*exo*) in a 4:1 ratio[25,26], whereas the cyclobutane dimers **14** (*anti*) and **15** (*syn*) are only minor products, besides at least one different dimer[26].



Changing to triplet-photosensitized reaction conditions, the main products become **13**, **14**, and **15** in a ratio of about 1:3:1[2,24–27]. Electron transfer (thermally or photochemically induced), however, yields, as unsensitized thermal conditions do, the dimers **12** and **13**[2,7,8,12,24,28]. In Table 1, various sensitizers are compared, including the new polymer-bound pyrylium salts **6** and **10**.

Table 1. Dimerization of 1,3-cyclohexadiene (**11**)[a]

sensitizer	12	yields[b] (%) 13	14	15	total	12:13
3	41.1	1.8	–	–	42.9	22.4
2[c]	1.5	–	–	–	1.5	–
2[d]	30.4	1.2	–	–	31.6	25.2
6	14.4	1.2	0.2	0.1	15.9	11.9
10	1.6	0.3	0.3	0.1	2.3	5.9

[a] Irradiation time 7 h (photo reactor), wavelength λ > 400 nm (filter solution: 6.9 g $NaNO_2$, 4.5 g $CuSO_4 \times 5H_2O$ in 1 l 2.7 M NH_3)[30], solvent: CH_3CN, concentrations: **11** 0.05 M, sensitizer 0.02 M (polymers 100% loading assumed). – [b] Yields determined by GLC. – [c] Products were obviously destroyed after 45 min irradiation time due to the high concentration of **2**. – [d] Concentration: 0.0017 M.

2,4,6-Triphenylpyrylium tetrafluoroborate (**2**) is the only sensitizer we used that is completely soluble in acetonitrile at a concentration of 0.02 M. This concentration (40 mole-%), compared to that of 1,3-cyclohexadiene (**11**) is obviously too high, because decay of the photoproducts started after 45 minutes of irradiation. 9,10-Dicyanoanthracene (**3**) is less soluble, and the polymers **6** and **10** are finally completely insoluble in acetonitrile. For this reason we set up a reaction with 8.5% of the original concentration of **2**, which should correspond to the concentration of active groups on our polymer **6**. The difference in yields between these two experiments is most likely due to the heterogeneous reaction conditions in the case of the polymer-bound pyrylium salts. The product ratio of the electron-transfer-catalyzed dimerization of **11** is very sensitive to the reaction conditions, e.g. solvent[2,12,24,29], concentration of **11**[2,24,31], wavelength[24,27], and sensitizer[24]. The results obtained with the acceptors used here are summarized in Tables 2–4 and reveal the following conclusions:

a) The typical product formed by electron-transfer catalysis[24], i.e. the *endo* Diels-Alder adduct **12**, is preferentially formed in polar solvents. In solvents of lower polarity (according to the dielectric constant ε), triplet-energy transfer causes increasing formation of **13**–**15** (Table 2).

b) As already shown for **2**, **4**, and *p*-chloranil[24], the concentration dependence in acetonitrile indicates the involvement of differently solvated radical-ion pairs for the polymeric acceptor **6**, too, i.e. the *endo* isomer **12** is favored with decreasing concentration of **11** (Table 3).

c) At λ < 400 nm, triplet-energy transfer has to be considered, resulting in increasing formation of the products **13**–**15**. In the case of **6**, this is mostly caused by the unreacted carbonyl units of **6**, whereas the Merrifield resin (**1**) only inefficiently works as triplet sensitizer (cf. control experiment with **5** and **1**, Table 4).

The influence of high pressure on the electron-transfer-catalyzed dimerization of **11** has been studied by Turro and Mattay[2,32] confirming these findings. Moreover, their investigations provide a method for controlling the diastereoselectivity in cycloadditions of this type for the first time. For an example of pressure-induced diastereoselectivity in *hetero* Diels-Alder reactions, see works by Tietze and Buback[33].

Table 2. Dimerization of **11**, sensitized with 1,4-dicyanonaphthalene: solvent dependence of the yields and the ratio of **12**:**13**[a]

solvent	ε (20°C)	**12**	yields[b] (%) **13**	**14**	**15**	total	**12**:**13**
CH_3CN	37.5	6.7	0.7	1.6	0.5	10.5	9.6
CH_2Cl_2	9.1	8.7	4.1	5.8	1.7	20.3	2.1
THF	7.4	0.1	0.9	2.2	0.7	3.9	0.1
benzene	2.28	1.7	2.1	3.3	0.8	7.9	0.8
1,4-dioxane	2.20	0.8	2.3	5.5	1.8	10.4	0.3

[a] Irradiation time 22 h (merry-go-round apparatus), wavelength λ > 300 nm (pyrex), sensitizer: 1,4-dicyanonaphthalene (**4**) 0.02 M. – [b] Yields determined by GLC.

Table 3. Dimerization of **11** in acetonitrile: dependence of the yields and the ratio of **12**:**13** on the concentration of **11**

conc. of **11** [M]	sensitizer	λ [nm]	time [h]	**12**	yields[a] (%) **13**	**14**	**15**	total	**12**:**13**
0.4	**4**[b]	>300	22	3.1	0.5	0.3	0.1	4.0	6.2
0.05	**4**[b]	>300	22	6.7	0.7	1.6	0.5	9.5	9.6
0.4	**6**[c]	>400	0.75	1.4	0.3	0.1	0.1	1.7	5.5
0.05	**6**[c]	>400	0.75	3.2	0.2	–	–	3.5	13.3

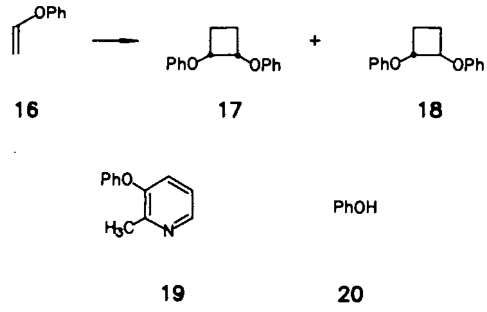
[a] Yields determined by GLC, solvent: acetonitrile. – [b] Concentration: 0.02 M, merry-go-round apparatus. – [c] Concentration: 0.42 g/50 ml, photo reactor.

Table 4. Dimerization of **11** in acetonitrile; dependence of the yields and the ratio of **12**:**13** on the wavelength

sensitizer	λ [nm]	**12**	yields[a] (%) **13**	**14**	**15**	total	**12**:**13**
6	>300[b]	3.3	1.0	1.9	0.6	6.8	3.4
	>350[c]	2.5	0.3	0.3	0.1	3.2	7.7
	>400[d]	3.2	0.2	–	–	3.5	13.3
5	>300[b]	0.1	2.8	7.3	2.5	12.7	0.02
	>400[d]	trace	–	–	–	–	–
1	>300[b]	0.1	1.2	3.4	1.1	5.9	0.1
	>400[d]	trace	–	–	–	–	

[a] Yields determined by GLC, solvent: acetonitrile. – [b] Pyrex glass. – [c] Edge filter, wavelength λ > 350 nm. – [d] Filter solution[30].

Dimerization of Phenyl Vinyl Ether (16)



Shigemitsu and co-workers[34] studied this system first. They used dimethyl terephthalate and other triplet photosensitizers as energy transmitters. Evans et al.[35] revised this reaction, and, using **3** as electron-transfer catalyst, could attain higher yields of the cyclodimers **17** and **18**. This group also identified 2-methyl-3-phenoxypyridine (**19**) and phenol (**20**) as byproducts when acetonitrile as solvent was used.

Table 5. Dimerization of phenyl vinyl ether (**16**); yields of **17** and **18**, depending on sensitizer and irradiation time[a]

sensitizer	irradiation time [h]	yields[b] (%) **17**	**18**	**17**:**18**
acetone	3	traces		≈1
	19	1.3	1.1	1.2
acetophenone	3	1.9	1.7	1.1
	19	7.0	5.9	1.2
3	3	19.4	22.8	0.85
	19	13.4	25.4	0.53
2	3	15.8	13.6	1.16
	19	11.9	24.5	0.49

[a] Solvent: acetonitrile, wavelength λ > 400 nm (merry-go-round apparatus), concentrations: **16** 0.2 M, sensitizer 0.02 M. – [b] Yields determined by GLC.

Interestingly, with **3** or **2** as sensitizer, the yield of **17** drops whereas that of **18** is enhanced with prolonged irradiation time[36]. This is an indicator of the proposed[35b] electron-transfer mechanism, because, with acetophenone as triplet photosensitizer, this effect does not appear (Table 5).

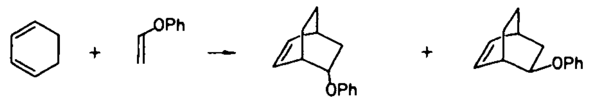
2,4,6-Triphenylpyrylium tetrafluoroborate (**2**) is nearly as efficient as 9,10-dicyanoanthracene (**3**) as an electron-transfer sensitizer for this reaction. The polymer-bound pyrylium salts do not work as well, as Table 6 shows. We found the same byproducts as Evans et al.[35] in varying yields.

Table 6. Dimerization of phenyl vinyl ether (**16**) under SET conditions[a]

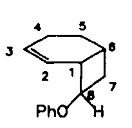
sensitizer	irradiation time	yields[b] (%) 17	18	19	20	17:18
3	50 min	14.1	9.7	7.9	5.9	1.45
	6 h	21.9	15.4	10.7	9.9	1.42
2	50 min	7.8	5.2	2.0	4.5	1.50
	6 h	18.6	12.4	7.1	9.4	1.50
6	50 min		traces		0.8	1.6
	6 h	1.4	0.8	0.2	1.9	1.45
10	50 min	0.6	0.4	0.1	0.7	1.5
	6 h	1.0	0.6	0.1	1.1	1.7

[a] Solvent: acetonitrile, wavelength $\lambda > 400$ nm[30], concentrations: **16** 0.2 M, sensitizer 0.02 M (100% hypothetical loading in case of **6** and **10** assumed). — [b] Determined by GLC.

Addition of Phenyl Vinyl Ether (16) to 1,3-Cyclohexadiene (11)



11 **16** **21** **22**



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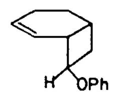

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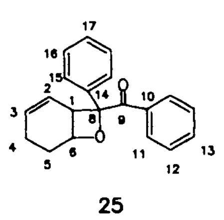

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This reaction has been described by Bauld et al.[37] who used tris(*p*-bromophenyl)aminium hexachloroantimonate as a thermal electron-transfer agent. They isolated 75% of a 1.3:1.0 product mixture of the *endo* and *exo* Diels-Alder adducts **21** and **22**, applying a ninefold excess of the olefin **16**. No information is given on the extent of cyclodimerization of both starting materials.

We have studied this reaction under photochemically induced electron-transfer conditions, testing whether other products such as **23** (*syn*) or **24** (*anti*) are formed and if the reaction of **11** and **16** with themselves is suppressed.

Control experiments in acetonitrile showed that energy transfer with typical triplet sensitizers such as acetone, acetophenone, and benzophenone is unfavorable for this reaction. Only the dimers **12**–**15** are formed in considerable yields. With benzophenone, fluorenone, and benzil, oxetanes are formed with 1,3-cyclohexadiene as byproducts, whereas in solvents like tetrahydrofuran, benzene, or diethyl ether no products arise. Only with benzil, fluorenone, anthracene, and 9,10-dibromoanthracene in acetonitrile, small amounts of **21** and **22** are formed. The relatively high ratio of **12**:**13** (benzil 0.3, fluorenone 1.4, anthracene 3.7, 9,10-dibromoanthracene 3.0) indicate the participation of electron-transfer pathways. For more details see work by Vondenhof[38].

Table 7 comprises the results in acetonitrile with typical electron-transfer sensitizers at long-wavelength irradiation.

Table 7. Addition of phenyl vinyl ether (**16**) to 1,3-cyclohexadiene (**11**) under SET conditions[a]

sensitizer	yields[b] (%) 12–15	17, 18	21	22	23, 24	12:13
3	15.6	3.8	20.4	9.0	0.5	7.4
4[c]	11.3	5.2	20.3	7.1	0.3	5.4
2	12.4	2.6	14.2	5.5	0.2	7.4
6	5.9	0.1	1.2	0.5	traces	1.7
10	3.0	0.1	0.4	0.1	0.1	5.2
benzil[d]	77.8	–	0.3	0.2	6.9	–

[a] Solvent: acetonitrile, concentrations: **11** 0.11 M, **16** 1.0 M, sensitizer 0.02 M, polymers 0.42 g/50 ml (= 0.02 M at 100% theoretical loading), irradiation time 5 h (wavelength $\lambda > 400$ nm). — [b] Yields determined by GLC. — [c] Wavelength $\lambda > 300$, irradiation time 24 h. — [d] 14% of 8-phenacyl-8-phenyl-7-oxa-bicyclo[4.2.0]oct-2-ene (**25**) is formed (see Experimental).

Polymers **6** and especially **10** give only low yields of the Diels-Alder products **21** and **22**, whereas with the cyano arenes **3** and **4** or the homogeneous pyrylium salt **2** the cycloadducts are formed in yields up to 29.4%.

Compared to the triplet reactions, the dimerization of **11** is significantly diminished and the [2 + 2] cycloadducts **23** and **24** are formed in trace amounts only. As in the dimerization of phenyl vinyl ether (**16**), phenol (**20**) and the pyridine **19** are formed as byproducts.

The influence of the solvent on this reaction has been investigated with **4** as electron acceptor. The results are shown in Table 8 and allow the following conclusions: Only in polar solvents such as acetonitrile or dichloromethane the mixed Diels-Alder adducts **21** and **22** as well as the phenyl vinyl ether dimerization products **17** and **18** are formed in relatively high yields indicating electron-transfer processes. In solvents of lower polarity the portion of triplet-energy transfer increases, and the dimers **12**–**15** are formed predominantly. This rationalization corresponds to the *endo*/*exo* ratio of **12**:**13** which is high (low) in polar (non polar) solvents (see above).

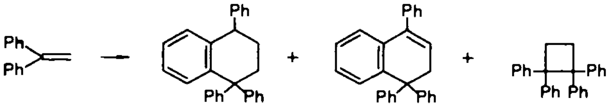
Tab. 8. Addition of phenyl vinyl ether (**16**) to 1,3-cyclohexadiene (**11**); solvent dependence[a]

solvent	yields[b] (%) **12**–**15**	**17**,**18**	**21**	**22**	**23**,**24**	**21**:**22**	**12**:**13**
CH_3CN[c]	8.2	5.5	20.3	7.2	0.4	2.8	5.8
CH_2Cl_2[d]	5.0	1.1	15.2	3.6	3.2	4.2	2.5
THF[d]	1.8	0.5	0.6	0.3	1.0	2.0	0.3
Et_2O[d]	7.0	1.5	2.2	1.1	3.3	2.0	0.3
benzene[d]	10.2	3.9	3.1	1.8	5.3	1.7	0.4

[a] Sensitizer: 1,4-dicyanonaphthalene (**4**) 0.02 M, **11** 0.11 M, **16** 1.0 M, merry-go-round apparatus (Pyrex). — [b] Yields determined by GLC. — [c] Irradiation time 18 h. — [d] Irradiation time 24 h.

Dimerization and Photooxygenation of 1,1-Diphenylethene (26)

The dimerization of 1,1-diphenylethene (**26**) under electron-transfer conditions was first reported by Neunteufel and Arnold[39]. Later, Mattes and Farid[40] showed that different radical-ion pairs are involved in case of **3** as electron-transfer sensitizer yielding either **29** [via the geminate pair which we have called the contact ion pair (CIP) in another context[2,7,8,24]] or preferentially **27** and **28** (by cage separation). The same authors also investigated the photooxygenation of **26** catalyzed by **3** or 2,6,9,10-tetracyanoanthracene which results in the formation of benzophenone (**30**) and the 1,2-dioxane **33** besides **29**. Neither yields nor informations about the formation of other oxygenation products such as the oxirane **31** and the tetrahydrofuran **32** are reported although other authors have identified them earlier[41–43].



26 **27** **28** **29**

Ph_2CO

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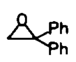

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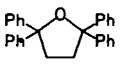

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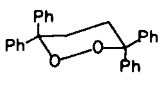

33

We have investigated both the dimerization and the photooxygenation of **26** using the pyrylium salt **2** as sensitizer and have compared its efficiency with the common acceptors **3** and **4**. In view of recent results reported by Akaba and Tokumaru[44] who claim pyrylium salts not to produce superoxide anions ($O_2^{-\bullet}$), **2** eventually should show different selectivities at least for the photooxygenation.

The result of the dimerization of **26** under electron-transfer conditions with **2**, **3**, and **4** as sensitizers are summarized in Table 9. Interestingly, the measured ratio of **29**:(**27** + **28**) in the dimerization catalyzed by **3**, which corresponds to the cage/escape portion, is in the same order of magnitude as predicted by Mattes and Farid[45] using their empirical equation for the concentration we have used (0.2 M). In case of the pyrylium salt **2** as sensitizer, this ratio decreases to nearly zero[46] indicating mostly separation of the CIP. This seems reasonable since $\mathbf{2}^+$ is reduced to $\mathbf{2}^\bullet$ after the initial electron transfer (cf. eq. 2) leaving no Coulombic attraction. Compared to **3**, the pyrylium salt is nearly doubly efficient, although some polymeric material is formed in the latter case. The high selectivity of **4** which corresponds to an almost exclusive escape process is not yet clear.

Table 9. Dimerization of 1,1-diphenylethene (**26**)[a]

sensitizer	time [h]	product ratios[b] **26**	**27**	**28**	**29**	polymer (%)	**29**: (**27** + **28**)
3	7	80.9	4.2	7.4	7.5	–	0.65
	15	50.3	9.8	24.0	15.9	–	0.63
4[c]	7	8.0	84.8	6.4	trace	–	0
2	7	44.4	23.3	30.1	2.2	13	0.04
	15	12.9	32.6	54.5	trace	19	

[a] Solvent: acetonitrile, sensitizer 0.02 M, **26** 0.2 M, wavelength $\lambda > 400$ nm[30]. — [b] Soluble products, determined by NMR. — [c] Wavelength $\lambda > 300$ nm (pyrex).

The different behavior of **3** on the one side and **2** on the other is reflected in the photooxygenation, too. Like Farid, we observe the formation of the 1,2-dioxane **33** and benzophenone (**30**) in the **3**-catalysis. However, in our experiment the formation of the cage product (**29**) is affected by O_2 to nearly the same extent as the escape reaction (leading to **27** and **28**). In comparison to that, benzophenone (**30**) is only an insignificant byproduct in the catalysis with **2**. This seems reasonable in view of other literature reports, since (a) **30** is assumed to be formed via $\mathbf{26}^{+\bullet}$ and $O_2^{-\bullet}$, yielding the corresponding 1,2-dioxetane followed by the common cleavage process as stated by Foote[41] and Gollnick[43] and (b) much less $O_2^{-\bullet}$ should be formed with **2** compared to **3**[44]. Farid assumed that benzophenone may be formed by reaction of O_2 with the dimeric radical cation (from the escape process). However, our results with **2** do not support this hypothesis. As for the dimerization of **26** in the absence of O_2, 1,4-dicyanonaphthalene (**4**) behaves quite differently, indicating another working mechanism (Table 10).

Table 10. Photooxygenation of 1,1-diphenylethene (**26**) under SET conditions[a]

sensitizer	yields[b] (%) **30**	**33**	product ratios[c] **26**	**27**	**28**	**29**	polymer (%)
3	15	30	–		traces		–
4[d]	–	–	1.5	88.4	7.0	3.1	–
2	5	68	32.2	28.8	39.0	–	≈10

[a] Solvent: acetonitrile, sensitizer 0.02 M, **26** 0.2 M, wavelength $\lambda > 400$ nm[30], irradiation time 3 h. — [b] Isolated. — [c] Soluble products, determined by NMR. — [d] Wavelength $\lambda > 300$ nm (pyrex).

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Experimental

Acetonitrile (Baker) was purified by boiling over CaH_2, distillation, and filtration over Al_2O_3 (activity I) and stored under argon. 1,3-Cyclohexadiene (**11**)[47], phenyl vinyl ether (**17**)[48], 1,1-diphenylethene[49] and the sensitizers 9,10-dicyanoanthracene (**3**)[50], 1,4-dicyanonaphthalene (**4**)[51], and 2,4,6-triphenylpyrylium tetrafluoroborate (**2**)[19] were prepared according to published procedures.

Yields of photoproducts were determined by GLC [Siemens Sichromat 3, FID capillary column by Hewlett-Packard (Ultra 2), 25 m, pressure 1.6 atm N_2] using naphthalene as an internal standard. GLC factors were 1.00 for dimers of 1,3-cyclohexadiene (**12**−**15**), 1.44 for dimers of phenyl vinyl ether (**17**, **18**), 1.40 for 2-methyl-3-phenoxypyridine (**19**), 1.53 for phenol (**20**), and 1.31 for adducts between 1,3-cyclohexadiene and phenyl vinyl ether. NMR analyses were performed with a Varian VXR 300 spectrometer, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are downfield to TMS. HPLC analyses were carried out with a Gilson 803.

For GC-MS, a Varian 3700 gas chromatograph with a 15 m OV 101 capillary column was used, which was connected to a Varian MAT 212 (70 eV) mass spectrometer.

Polymer **6**[18]: Merrifield resin (Merck) (5.057 g) is mixed with $NaHCO_3$ (7 g) and dry dimethyl sulfoxide (DMSO) (100 ml). After heating to 155°C for 6 h, the polymer is filtered and washed successively with hot DMSO, hot water, acetone, dichloromethane, and dry ether. Then the product is dried until its weight remains constant. Yield of poly(*p*-formylstyrene) **5** is 4.917 g, which implies a content of functionalized phenyl rings of 20.6% of the theoretical amount. − IR (KBr): $\tilde{\nu}$ = 2720 cm^{-1} ($\tilde{\nu}_{Fermi}$), 1700 (C=O).

$(C_9H_8O)_n$ $(132.16)_n$
Calcd. C 81.79 H 6.10 O 12.10
(100% functionalization of the polymer assumed)
Found C 88.1 H 7.4 O 4.1

According to the elemental analysis, 33.8% of the phenyl rings of polymer **5** are functionalized with a carbaldehyde group.

4.802 g of **5** is mixed with acetic acid (15 ml) and Et_2O-BF_3 (12.8 ml) and heated to 100°C. The mixture is stirred, and 9.6 g of acetophenone (previously distilled) in 8 ml of acetic acid is added dropwise. After 3 h at 100°C, the product is collected on a Büchner funnel and washed with acetic acid, water, ether, and dichloromethane. After drying to constant weight, the yield is 5.698 g of **6**, which implies a content of boron of 0.2% (8.5% of the theoretical amount). − IR (KBr): $\tilde{\nu}$ = 1680 cm^{-1} (C=O), 1630 (C=O, pyrylium[52]).

$(C_{25}H_{19}OBF_4)_n$ $(422.23)_n$
Calcd. C 71.1 H 4.5 O 3.8 B 2.6
(at 100% functionalization of the polymer)
Found C 84.6 H 6.8 O 2.5 B 0.3

According to the elemental analysis, 11.5% of the phenyl rings of polymer **6** are functionalized with a pyrylium unit.

Synthesis of Polymer **10** started from polystyrene, which was prepared according to Braun[53]. Polyvinyl acetophenone, and polyvinyl benzylideneacetophenone were synthesized as described by Merrill[20] and Unruh[23]. Cyclization to the pyrylium system was performed as follows: 4.7 g of polyvinyl benzylidene acetophenone (**9**) was mixed with acetophenone (2.43 ml) and dry ether (15 ml). Et_2O-BF_3 (3.8 ml) is added, and the mixture is stirred at room temp. for ca. 12 h. The polymer **10** is collected, washed with ether, acetone, and dichloromethane and dried i.vac. − IR (KBr): $\tilde{\nu}$ = 1665 cm^{-1}, 1640, 1120−1030 ($\tilde{\nu}_{B-F}$).

Dimerization of 1,3-Cyclohexadiene (**11**) *and Phenyl Vinyl Ether* (**16**): In a typical procedure, a solution of 25 µl of 1,3-cyclohexadiene (0.05 M) in 50 ml of solvent was irradiated with a HPK 125-W lamp (Philips) through a pyrex immersion pit. The lamp was cooled with a solution of $NaNO_2$ (6.9 g) and $CuSO_4 \times 5H_2O$ (4.5 g) in 2.7 M NH_3 (1 l). Yields are summarized in Tables 1−6. For analytical purposes, some irradiations were performed in a merry-go-round apparatus (Hans Mangels, Bornheim) under pyrex-filter conditions.

Addition of Phenyl Vinyl Ether (**16**) *to 1,3-Cyclohexadiene* (**11**): All experiments were performed with a molecular ratio of **16**:**11** = 9:1. We used concentrations of 1.0 M of **17** and 0.11 M of **5**. Irradiation conditions were identical to those described above. Products were separated by HPLC, using a 10% ethyl acetate/hexane mixture as eluent. The yields are summarized in Tables 7 and 8.

Dimerization and Photooxygenation of 1,1-Diphenylethene (**26**): All irradiations were performed with a concentration of **26** of 0.2 M and 10 mole-% of sensitizer. The reaction conditions were as those described above. Photooxidations of the olefin were performed in an identical manner, but oxygen was bubbled through the solution during the irradiation. After the solvent was evaporated, dimers and photoproducts were separated from unreacted sensitizers by flash chromatography on silica gel 60 (Macherey & Nagel 0.04−0.063 mm) using ethyl acetate/hexane (40:60, v:v) as eluent. 2,2,6,6-Tetraphenyl-1,2-dioxan (**33**) precipitated during the irradiation and was identified according to Farid[40]. Product ratios were determined by NMR analysis (see Tables 9 and 10).

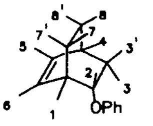
Spectral Data

Dimers of 1,3-cyclohexadiene (**11**) were characterized by their retention times at GLC analyses and comparison to independently synthesized samples. Dimers of phenyl vinyl ether (**16**) could be characterized by their retention times, too. The *trans* isomer is eluted first. Additionally, they were separated by HPLC (20% ethyl acetate in hexane).

cis-1,2-Diphenoxycyclobutane (**17**): The ^1H-NMR spectra of this compound and that of the *trans* isomer (**18**) were identical to the published ones[34]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.43 (CH_2), 73.93 (CH), 115.52 ($4C_{ortho}$), 121.01 ($2C_{para}$), 129.32 ($4C_{meta}$), 157.81 ($2C_{ipso}$). − MS: *m/z* (%) = 240 (4.7) [M^+], 120 (100), 91 (25.5), 77 (12.6), 65 (5.2), 51 (8.9).

trans-1,2-Diphenoxycyclobutane (**18**): ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.69 (CH_2), 76.84 (CH), 115.31 ($4C_{ortho}$), 121.11 ($2C_{para}$), 129.49 ($4C_{meta}$), 157.43 ($2C_{ipso}$). − MS: *m/z* (%) = 240 (4.9) [M^-], 120 (100), 91 (22.8), 77 (9.2), 65 (2.9), 51 (5.1).

endo-2-Phenoxybicyclo[2.2.2]oct-5-ene (**21**): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 (tddd, 7-H), 1.27 (tdt, 8-H), 1.35 (ddd, 3′-H), 1.67 (ddd, d, 8′-H), 1.89 (ddt, 3-H), 2.14 (dddd, 7′-H), 2.56 (m, 4-H), 2.83 (m, 1-H), 4.24 (dt, d, 2-H), 6.20 (ddd, 6-H), 6.34 (ddd, 5-H), 6.85 (m, $2H_{ortho}$), 6.89 (m, H_{para}), 7.24 (m, $2H_{meta}$). − ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.95 (C-7), 25.46 (C-8), 29.94 (C-4), 33.56 (C-3), 34.26 (C-1), 74.36 (C-2), 115.67 ($2C_{ortho}$), 120.29 (C_{para}), 129.36 ($2C_{meta}$), 131.32 (C-6), 136.31 (C-5), 158.10 (C_{ipso}). The assignments were made with COSY and HETCOR programs. − MS: *m/z* (%) = 200 (13.2) [M^+], 120 (12.3), 107 (89.5), 94 (23.4), 91 (15.4), 80 (65.4), 79 (100), 77 (20.0).



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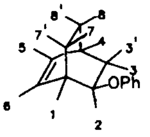
The numbers in the formula designate H atoms and not CH$_3$ groups.

exo-2-Phenoxybicyclo[2.2.2]oct-5-ene (**22**): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.1 – 1.4 (m, 5H), 2.0 (ddd, 1H, 3'-H), 2.57 (m, 4-H), 2.89 (m, 1-H), 4.41 (dtd, 2-H), 6.16 (m, 6-H), 6.39 (ddd, 5-H), 6.82 (m, 2H$_{ortho}$), 6.87 (m, H$_{para}$), 7.20 (m, 2H$_{meta}$). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 21.97 (C-7), 23.99 (C-8), 29.80 (C-4), 34.12 (C-1), 36.43 (C-3), 76.13 (C-2), 115.75 (2C$_{ortho}$), 120.30 (C$_{para}$), 129.28 (2C$_{meta}$), 130.37 (C-6), 134.81 (C-5), 157.63 (C$_{ipso}$). – MS: m/z (%) = 200 (12.6) [M$^+$], 120 (6.5), 107 (81.2), 94 (25.1), 91 (16.3), 80 (41.1), 79 (100), 77 (20.0).



22

The numbers in the formula designate H atoms and not CH$_3$ groups.

8-Phenoxybicyclo[4.2.0]oct-2-ene (**23** or **24**): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.56 (m, 1H), 1.80 (m, 1H), 2.07 (m, 2H), 2.22 (m, 2H), 2.61 (m, 1H), 2.86 (m, 1H), 4.43 (ddd, 1H), 5.97 (m, 2H), 6.83 (m, 2H$_{ortho}$), 6.93 (m, H$_{para}$), 7.26 (m, 2H$_{meta}$). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 22.29 (C-4), 26.11 (C-5), 26.40 (C-6), 31.77 (C-7), 40.92 (C-1), 77.80 (C-8), 115.07 (2C$_{ortho}$), 120.58 (C$_{para}$), 127.08 (C-2), 129.44 (2C$_{meta}$), 129.71 (C-3), 158.90 (C$_{ipso}$). – 2D-NMR spectra (COSY and HETCOR) made the assignments possible. – MS (major isomer): m/z (%) = 200 (2.4) [M$^+$], 120 (17.9), 107 (33.9), 94 (5.7), 91 (13.4), 80 (100), 79 (38.6), 77 (11.2); (minor isomer): m/z (%) = 200 (7.1) [M$^+$], 120 (15.8), 107 (32.2), 94 (5.8), 91 (15.5), 80 (100), 79 (38.3), 77 (12.3).

8-Phenacyl-8-phenyl-7-oxabicyclo[4.2.0]oct-2-ene (**25**): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.34 (m, 1H), 2.04 (m, 1H), 2.08 (m, 1H), 2.30 (m, 1H), 4.16 (dddd, 1-H), 5.16 (dddd, 6-H), 5.37 (dddd, 2-H), 5.83 (dddd, 3-H), 7.21 (m, 17-H), 7.30 (m, 4H, 2 15-H, 2 16-H), 7.40 (m, 3H, 2 12-H, 13-H), 7.96 (m, 2H, 2 11-H). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 20.12 (C-4), 25.32 (C-5), 41.35 (C-1), 76.10 (C-6), 95.25 (C-8), 124.00 (C-2), 124.61 (2C-15), 127.42 (C-17), 128.07 (2C-16), 128.25 (2C-12), 130.35 (2C-11), 130.87 (C-3), 132.83 (C-13), 133.87 (C-10), 138.24 (C-14), 200.09 (C-9). – Assignments were made with COSY and HETCOR spectra. – MS: m/z (%) = 212 (5.1) [M$^+$ – PhH], 185 (46.0) [M$^+$ – PhCO), 105 (100), 77 (30.5).

1,1,4-Triphenyl-1,2,3,4-tetrahydronaphthalene (**27**): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.68 (m, 1H), 1.99 (m, 1H), 2.67 (m, 2H), 4.22 (t, J = 7.5 Hz, 1H), 7.2 (m, 19H). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 29.66, 36.80, 46.22, 54.02, and diverse aromatic signals.

1,1,4-Triphenyl-1,2-dihydronaphthalene (**28**): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.28 (d, J = 4.7 Hz, 2H), 5.96 (t, J = 4.7 Hz, 1H), 7.2 (m, 19H). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 37.41, 52.82, and diverse aromatic signals.

1,1,2,2-Tetraphenylcyclobutane (**29**): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 3.20 (s, 4H), 7.3 (m, 20H). – ^{13}C NMR (75 MHz, CDCl$_3$): δ = 34.70, 61.60, 125.29, 127.23, 129.05, 147.29.

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