Cycloaddition Reactions Initiated by Photochemically Excited Pyrylium Salts

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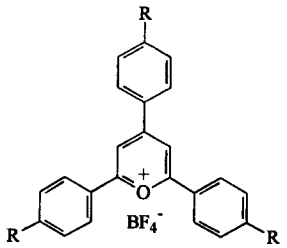
Several pyrylium, thiapyrylium, and pyridinium salts have been synthesized and used as sensitizers for photochemically induced electron-transfer (PET) reactions. The salts have been tested in the mixed cycloaddition reactions of styrenes **9** with 1,3-cyclohexadiene (**8**) or 1,1'-dicyclohexenyl (**23**). In the case of the PET [4 + 2] cycloaddition of styrene (**9a**) to 1,3-cyclohexadiene (**8**), the reaction takes place via the cation radical of the diene. When chloroform instead of dichloromethane is used as the solvent, only [2 + 2] cycloaddition products are obtained. In contrast, if 1,3-cyclohexadiene (**8**) is replaced by 1,1'-dicyclohexenyl (**23**), the key step of the reaction seems to be the oxidation of styrene (**9**). The product ratios depend on the sensitizers used. If solvent-separated ion pairs are formed, styrene reacts as a diene to give 1-cyclohexenyloctahydrophenanthrene derivatives **28**; cycloaddition via contact ion pairs leads to the Diels-Alder product with styrene acting as the dienophile.

2,4,6-Triarylpyrylium salts **1** are easily excited photochemically by visible light. The excitation of one electron from the doubly occupied highest molecular orbital (HOMO) to the lowest unoccupied one (LUMO) results in the formation of an electron hole in the HOMO. Therefore, the excited pyrylium ion can act as an oxidizing agent as well as a Lewis acid. For this reason catalysis of the following reactions by photoexcited pyrylium ions can be observed: Lewis acid catalyzed reactions[1], oxidation and oxygenation reactions[2,3], cleavage of double bonds[3], electron-transfer-catalyzed cycloadditions[16–21], cycloreversions[14–16], and dimerizations, Cope rearrangements[7,8], and *cis/trans* isomerizations[9–13].



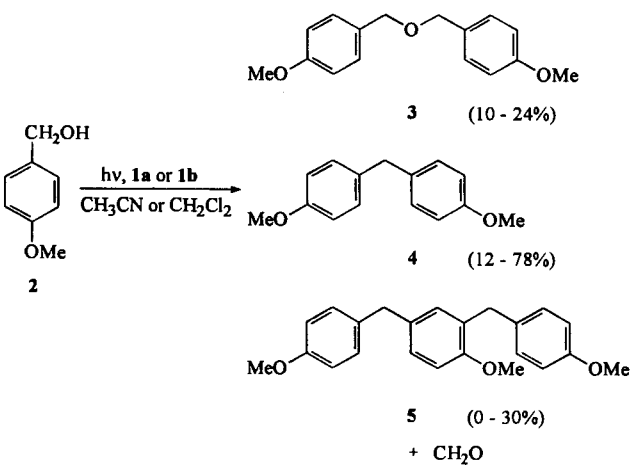
	R
a	H
b	OMe
c	Me
d	Br
e	Cl
f	F
g	Ph

1

For example, irradiation of 2,4,6-triphenyl- or 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (**1a** and **1b**) in the presence of 4-methoxybenzyl alcohol (**2**) leads to the formation of bis(4-methoxybenzyl) ether (**3**) (10–24%), bis(4-methoxyphenyl)methane (**4**) (12–78%), [4-methoxy-3-(4-methoxybenzyl)phenyl](4-methoxyphenyl)methane (**5**) (up to 30%), and formaldehyde (Scheme 1)[1]. The sensitizer can be recovered. Even in the presence of air or oxygen, no oxidation products of the easily oxidizable 4-methoxybenzyl alcohol can be observed.

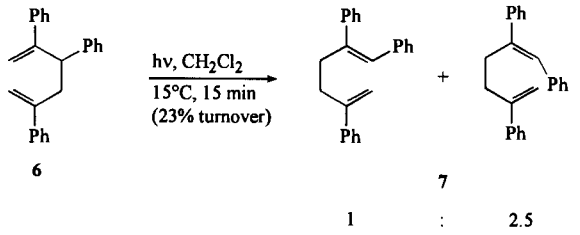
This reaction can best be explained by the intermediate formation of the anisyl cation under the influence of the excited pyrylium ion as a very active Lewis acid catalyst. The dianisylmethane then is formed by *ipso* attack of the anisyl cation on the 4-methoxybenzyl alcohol with liberation of formaldehyde. In contrast, benzyl or 3-chlorobenzyl alcohols with considerably higher oxidation potentials, are oxidized under the influence of excited **1a** or **1b** to give the corresponding benzaldehydes in good yields together with small amounts of the benzoic acid[1]. Similarly, tetraline is oxidized to tetralone (60%). For the regeneration of the active catalyst (10 mol-%) the presence of oxygen is necessary. Otherwise, the pyrylium salt has to be applied in stoichiometric amounts. The different behavior of 4-methoxybenzyl alcohol and benzyl or 4-chlorobenzyl alcohol can be explained by the faster deprotonation of the intermediate cation radicals of electron-poor benzyl alcohols to give the easily oxidizable benzylic radicals. On the other hand, the benzylic cations of electron-poor benzyl alcohols generated by the Lewis acid activity of the excited pyrylium ions are less stable than in the case of 4-methoxybenzyl alcohol.

Scheme 1



If oxygen is excluded, 1,1-diphenylethylene is cyclodimerized to give 1,1,4-triphenyltetrahydronaphthaline as a [4 + 2] cycloadduct and 1,1,4-triphenyl-1,2-dihydronaphthaline as an oxidative dehydrodimer in a 3:1 ratio together with small amounts of the [2 + 2] cycloadduct 1,1,2,2-tetraphenylbutane. The catalyst may be recovered almost totally[1]. Accordingly, the reaction takes place with styrene in the absence of oxygen. In the presence of air or oxygen, 3,3,6,6-tetraphenyl-1,2-dioxane[2] and benzophenone are formed as oxygenation products. Benzophenone may be formed by oxygenation of the olefinic double bond, catalyzed by the photoexcited pyrylium ion. This reaction can be described as a cycloaddition of oxygen to the intermediate olefin cation radical followed by electron back transfer from 1,1-diphenylethylene. The thus formed dioxetane derivative is cleaved to benzophenone under the reaction conditions. This is a typical reaction of higher substituted alkenes[3]. Similarly, 1,3-cyclodienes are oxygenated to give endoperoxides. In this way, α-terpinene is almost quantitatively converted into ascaridol[4] if **1a** is used as photosensitizer. In some cases, the excited pyrylium salt catalyzed formation of cation radicals leads to dehydrogenated products[5] or is followed by Wagner-Meerwein rearrangement[6]. Also Cope rearrangements can be initiated via the intermediate cation radical[7]. For example, 2,3,5-triphenyl-1,5-hexadiene (**6**) under the catalysis of photoexcited **1a** effectively rearranges to a mixture of (*E*)- and (*Z*)-1,2,5-triphenyl-1,5-hexadiene (**7**)[8] (Scheme 2) in a ratio of 1:2.5, while the thermal reaction at 250°C leads to a 1:1 mixture of the isomers.

Scheme 2



Electron-transfer-catalyzed *cis/trans* isomerizations[9–13] and cycloreversions[14–16] have been reported to be catalyzed by photoexcited pyrylium salts.

Photoexcited pyrylium ions are especially effective catalysts for the electron-transfer-initiated Diels-Alder reactions. If **1a** is used as catalyst, 1,3-cyclohexadiene (**8**) dimerizes within a few minutes at room temperature almost quantitatively. The thermally initiated dimerization, however, only takes place at elevated temperature and pressure in low yield[17]. Mixed photoinitiated pyrylium salt catalyzed Diels-Alder reactions with 1,3-cyclohexadienes have been reported for styrenes[18], enol ethers[19], 1,4-dioxane[20], indole[21], and 2-vinyl indole[22].

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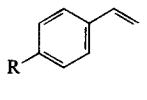
To gain more insight into the underlying rules we have studied the photoexcited pyrylium salt catalyzed cycloaddition reactions in greater detail by variation of the reaction conditions and the structure of the sensitizer.

Properties of the Pyrylium Salt Sensitizers

The product distributions and the yields of photoelectron-transfer-catalyzed cycloaddition reactions using 2,4,6-triarylpyrylium salts are often influenced by the substitution pattern of the aryl groups. For example, in the cross Diels-Alder reaction of styrene (**9a**) with 1,3-cyclohexadiene (**8**) using **1a** as sensitizer in acetonitrile only small amounts of the cross Diels-Alder product are formed. If 2,4,6-trianisylpyrylium tetrafluoroborate (**1b**) is applied as a sensitizer high yields of this product can be obtained.



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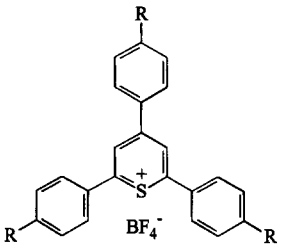
	R
a	H
b	Cl
c	Me
d	OMe

The substituents at the phenyl rings influence the oxidation potentials of the excited pyrylium salts. As a working hypothesis, the value of the oxidation potential will be a major factor for the product yields and product distributions. By exchanging sulfur or nitrogen for the oxygen in the heterocycle **10a**, **10b** and **11** with good sensitizer properties are obtained.



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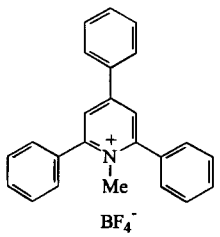


11

	R
a	H
b	OMe

The oxidation potentials of the excited pyrylium ions, E_{Ox} [$Py^{*+}/Py^{\cdot}$], can be calculated according to Eq. 1.

$$E_{Ox}[Py^{*+}/Py^{\cdot}] = E_{Red}[Py^{+}/Py^{\cdot}] + \Delta E_{excit}[Py^{+}/Py^{*+}] \quad (1)$$

The reduction potential, $E_{Red}[Py^{+}/Py^{\cdot}]$, can be measured by cyclic voltammetry, and the excitation energy, ΔE_{excit} [Py^{+}/Py^{*+}], can be obtained from fluorescence spectra. The oxidation potentials of the synthesized salts in their excited state are in the range from 1.98 to 2.59 V vs. NHE (Table 1).

Dimerization of 1,3-Cyclohexadiene

1,3-Cyclohexadiene (**8**) is often used as a model compound for electron-transfer-catalyzed Diels-Alder reactions[18–27].

Table 1. Potentials and spectroscopic properties of triarylpyrylium, triarylthiapyrylium, and *N*-methyltriphenylpyridinium tetrafluoroborates

Sensitizer	UV[a] λ_{max} [nm]	E_{red}[b] [V] vs NHE	Fluorescence[c] λ_{max} [nm] ([eV])	$E_{calcd.}$[d] [V] vs NHE
1a	280,368,416	-0.13	465 (2.66)	2.53
1b	275,310,422,470	-0.36	529 (2.34)	1.98
1d	225,397,435	-0.03	492 (2.52)	2.49
1e	301,394,442	-0.05	485 (2.55)	2.09
1f	234,283,372,415	-0.10	470 (2.63)	2.53
1c	256,300,394,444	-0.28	485 (2.55)	2.27
1g	236,289,443	-0.18	550 (2.25)	2.07
10a	252,273,379,414	-0.05	468 (2.64)	2.59
10b	233,262,296,455	-0.19	556 (2.23)	2.04
11	304	-0.84	432 (2.86)	2.02

[a] Excitation wavelength is underlined. — [b] Reversible reduction potentials ($Py^+/Py^\bullet$) of the pyrylium salts measured by cyclic voltammetry. — [c] Longest wavelength fluorescence (Py^+/Py^{*+}). — [d] Oxidation potentials of the excited pyrylium salts ($Py^{*+}/Py^\bullet$) calculated according to Eq. 1.

We have also used this extensively studied reaction to test the substituted triarylpyrylium salts **1a–1g**, the thiapyrylium salts **10a** and **10b**, and the pyridinium salt **11** for their efficiency and stereoselectivity in catalyzing this reaction (Scheme 3, Table 2).

Scheme 3

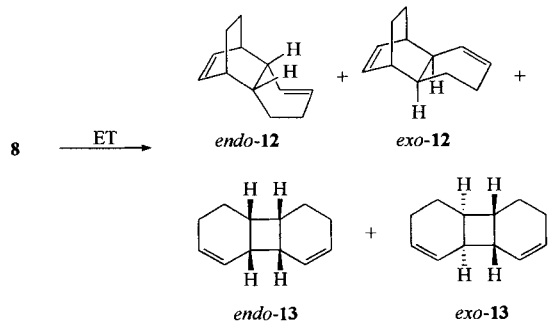


Table 2. Dimerization of **8** in CH_2Cl_2 in the presence of different sensitizers (2 mol-%)

Solvent	ε	*t* [min]	12+13 [%]	*endo*-12/(*exo*-12+*endo*-13)/*exo*-13
Toluene	2.4	90	Traces	-
$CHCl_3$	4.9	90	24.1	1:13.2:2.5
$CHCl_3$[a]	4.9	300	12.2	-: 4.7:1
CH_2Cl_2	9.1	10	100.0	[b]
CH_2Cl_2[a]	9.1	1080	24.0	1:25.5:4.3
CH_3CN	37.5	45	42.5	[c]

[a] Quantification by GLC.

In dichloromethane, all sensitizers are able to catalyze the dimerization of **8** in good yields. With **1a–1g** the Diels-Alder dimer **12** is formed almost quantitatively. When **10a**, **10b**, and especially **11** are used, the yields are smaller. In no case, the [2 + 2] dimers **13** are formed. The *endo* selectivity varies between 4:1 and 9.5:1 being highest with **10a** and **10b**, and lowest with **11**. In contrast to the initial proposal, the oxidation potential of the excited sensitizers cannot be correlated with the *endo/exo* ratios. Excited **1b**, **10b**, and **11** have all similar oxidation potentials of 1.98, 2.04, and 2.07 V, respectively.The *endo/exo* ratios, however, show values of 7.5:1 (**1b**), 9.5:1 (**10b**), and 4:1 (**11**). Therefore, other or additional factors have to be responsible for this observation.

The efficiency of the cycloaddition reaction and the product distribution are strongly affected by the solvent (Table 3). While in dichloromethane the formation of the [4 + 2] adducts is quantitative, in solvents of higher (acetonitrile) or lower (chloroform, toluene) dielectric constant the efficiency of the cyclodimerization is smaller. In addition, while in acetonitrile only [4 + 2] dimers with the highest *endo* selectivity are formed, in the less polar chloroform [2 + 2] dimers are generated almost exclusively. In toluene, electron-transfer-catalyzed processes are suppressed. In the absence of a sensitizer, long-time irradiation in dichloromethane or chloroform leads to the formation of the [2 + 2] adducts, presumably by energy-transfer processes.

Table 3. Dimerization of **8** in different solvents using **1a** as PET catalyst (2 mol-%)

Sensitizer	12 [%][a]	*endo/exo*	*t* [min]
1d	100.0	6.1:1	5
1e	100.0	6.8:1	10
1f	100.0	6.0:1	10
1a	100.0	7.1:1	10
1b	99.0	7.5:1	10
1c	91.7	8.3:1	10
1g	100.0	6.8:1	20
10a	79.3	9.0:1	10
10b	82.2	9.5:1	10
11	64.4	4.0:1	45

[a] Photolysis without **1a**. — [b] *endo*-**12**/*exo*-**12** = 7.1:1. — [c] *endo*-**12**/*exo*-**12** = 26.3:1.

The well-known Weller equation (Eq. 2) is frequently used to estimate the degree and the direction of charge transfer, even in systems of incomplete electron transfer[28,29].

$$\Delta G_{ET}(A^{\bullet-}D^{\bullet+}) = E^{Ox}_{1/2}(D) - E^{Red}_{1/2}(A) - \Delta E_{excit} + \Delta E_{coul}\ [eV] \quad (2)$$

$E^{Ox}_{1/2}(D)$ = Oxidation potential of donor [V]
$E^{Red}_{1/2}(A)$ = Reduction potential of acceptor [V]
ΔE_{excit} = Excitation energy [eV]
ΔE_{coul} = Coulombic interaction term

The influence of the solvent is expressed by the coulombic interaction term, ΔE_{coul}, containing the dielectric constant of the given solvent. However, in the case of a charged acceptor and a neutral donor the influence of the solvent polarity should be small due to the fact that the number of charged species does not change during the electron transfer. Small differences are possible because the amount of charge sep-

aration or localization in the excited state as compared with the ground state may either be smaller or larger depending on the system.

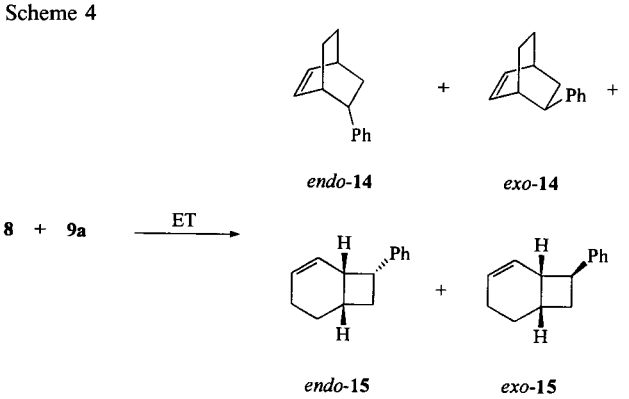
The calculation of the free enthalpy of formation of **1a**/**8**$^{\bullet+}$ from **1**$^{+}$/**8** using the singlet excitation energy of 2.66 eV for **1a**$^{+}$ and ignoring the solvent-dependent coulombic term results in a value of −0.84 eV. This is sufficiently negative to favor the electron transfer under formation of either a contact-ion pair (CIP), solvent-separated ion pair (SSIP), or free radical ions. In our case, the higher polarity of acetonitrile may result in a higher *endo* selectivity because the solvatization of **8**$^{\bullet+}$ and thereby the formation of the SSIP or the free radical cation may be favored. The lower yields as compared with the results in dichloromethane may be due to side reactions of the free radical cation as compared to a reaction via the SSIP.

In unpolar solvents like toluene, the formation of solvent-separated ion pairs (SSIP) is unfavorable and therefore electron back transfer from the CIP is dominating. The almost exclusive formation of the [2 + 2] cycloadduct **13** in chloroform must be due to a different pathway. In contrast to the more polar solvents which seem to favor the reaction via the singlet of the excited pyrylium salt, a triplet-sensitized reaction might dominate in this solvent. However, an energy-transfer process which mainly would lead to **13**[20] or a triplex mechanism[30] cannot be excluded.

Cross Cycloaddition Reaction of 1,3-Cyclohexadiene (8) with Styrene (9a) or Other Aryl Olefins

Because the reaction of **8** with styrene (**9a**) proceeds at a slower rate as compared with the dimerization of **8**, the variation of the sensitizer influences the product distribution even stronger. Besides the mixed and symmetrical [4 + 2] products also mixed [2 + 2] products are formed if halogen-substituted triarylpyrylium salts are used as sensitizers. Reaction parameters are the concentration of the olefins, the sensitizer concentration, the solvent, and the type of the sensitizer (Scheme 4).

Scheme 4



a) Influence of the Diene/Dienophile Ratio

Using **1a** as sensitizer under standard conditions, we have obtained 7.2% of the cross [4 + 2] product **14**, 1.6% of the mixed [2 + 2] product **15**, and 41% of the symmetrical dimer **12**. Higher yields of the cross Diels-Alder product (up to 38%) can be obtained if the catalyst, dissolved in dichloromethane, is added dropwise during the irradiation in such a way that a weak fluorescence is retained throughout the whole reaction time[24].

Surprisingly, the use of an excess of **9a** with respect to the diene does not increase the yield of the cross Diels-Alder product **14**. Only the cross [2 + 2] product **15** is formed in a higher yield while the dimer **8** is quenched to a large extent (Table 4).

b) Influence of the Solvent

Similar to the case of the dimerization of **8**, cross [4 + 2] cycloaddition product **14** is only obtained in reasonable yields in dichloromethane as solvent. With all other solvents only small amounts of **14** are obtained while the yield of **15** is increased (Table 5).

In toluene, only minor amounts of cycloaddition products are formed after 90 minutes. After 12 hours, the yield of the [2 + 2] product **15** has increased to 2.9%, and some **13** is also detected. A similar behavior is observed in chloroform after 3 hours of irradiation with somewhat higher yields of **15** and **13**. The highest yields of mixed and symmetrical [2 + 2] cycloadducts are obtained in tetrahydrofuran. In acetonitrile the formation of both mixed cycloadducts **14** and **15** is almost completely suppressed by using **1a** as sensitizer. Only dicyclohexadiene (**12**) is formed in ca. 14% yield. However, when **1b** is employed as sensitizer the mixed [2 + 2] adduct **15** is obtained in 12% yield. Because of the long irradiation times, energy-transfer processes leading to **15** cannot totally be excluded as shown by the experiment in the absence of a sensitizer. The results demonstrate that with **1a** as sensitizer the highest yields are obtained in dichloromethane, while with **1b** acetonitrile as solvent is superior. With 9,10-dicyanoanthracene (**16**) as sensitizer in acetonitrile the yields are low, while the *endo* selectivity of **12** is high. If $LiClO_4$ is added by using dichloromethane as solvent an effect can be seen in the formation of **14** and **15**.

Table 4. Mixed cycloaddition reaction of **8** with **9a** in the presence of **1a** as PET catalyst (2 mol-%) in CH_2Cl_2; variation of the styrene concentration

8	9a	12 [%]	t [min]	*endo*-12/*exo*-12	14 [%]	t [min]	*endo*-14/*exo*-14	15 [%]	t [min]	*endo*-15/*exo*-15
0.1m	0.1m	41.0	(60)	3.8:1	7.2	(90)	9.0:1	1.6	(90)	2.4:1
0.1m	0.2m	22.8	(90)	2.7:1	7.0	(90)	10.6:1	2.3	(90)	2.3:1
0.1m	0.5m	11.4	(90)	1.6:1	9.9	(90)	18.5:1	8.6	(90)	2.5:1
0.1m	1.0m	5.4	(90)	1.4:1	9.0	(90)	14.6:1	8.6	(90)	2.3:1

Table 5. Mixed cycloaddition reaction of **8** with **9a** in the presence of **1a** (2 mol-%) in various solvents

Solvent	12+13 [%]	t [h]	*endo*-12/(*exo*-12+ *endo*-13)/*exo*-13	14 [%]	t [h]	*endo*-14/*exo*-14	15 [%]	t [h]	*endo*-15/*exo*-15
Toluene	4.6	(4)	1:7.4:1	0.3	(4)	2.4:1	2.9	(12)	1:2.7
$CHCl_3$	10.8	(3)	1:8.0:1,3	0.9	(3)	4.4:1	8.6	(3)	1:2.4
THF	23.6	(10)	-:5.3:1	-			17.6	(10)	1:2.5
CH_2Cl_2	41.0	(1)	[e]	7.2	(1,5)	9.0:1	1.6	(1,5)	1:2.4
CH_2Cl_2[a]	36.3	(1)	[f]	6.9	(1,5)	14.8:1	0.8	(1,5)	1:2.2
CH_2Cl_2[b]	10.7	(18)	-:4.7:1	-			7.2	(18)	1:2.5
CH_3CN	14.2	(1)	[g]	0.6	(0,5)	6.6:1	0.3	(1,5)	1:1.5
CH_3CN[c]	23.7	(2,5)	9.0:6.1:1	1.3	(5)	7.1:1	12.0	(5)	1:2.3
CH_3CN[a,c]	24.0	(9)	12.8:5.6:1	1.1	(9)	8.8:1	13.9	(9)	1:2.3
CH_3CN[d]	17.5	(12)	33.1:8.0:1	2.3	(19)	6.8:1	5.2	(19)	1:1.8

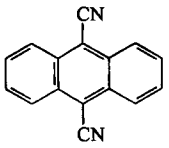
[a] Addition of 6 mol-% $LiClO_4$. — [b] Photolysis without a catalyst. — [c] **1b** as the catalyst. — [d] **16** as the catalyst. — [e] *endo*-**12**/*exo*-**12** = 3.8:1. — [f] *endo*-**12**/*exo*-*12* = 4.5:1. — [g] *endo*-**12**/*exo*-**12** = 11.8:1.

Table 6. Reaction of **8** with **9a** in CH_2Cl_2 in the presence of different catalysts (2 mol-%)

Sensitizer	12 [%]	t [min]	*endo*-12/*exo*-12	14 [%]	t [min]	*endo*-14/*exo*-14	15 [%]	t [min]	*endo*-15/*exo*-15
1a	41.0	(60)	3.8:1	7.2	(90)	9.0:1	1.6	(90)	1:2.4
1b	51.8	(45)	5.3:1	10.2	(90)	24.3:1	-		-
1c	42.2	(90)	4.5:1	8.3	(90)	14.0:1	0.8	(90)	1:2.2
1d	35.9	(45)	2.3:1	7.4	(90)	11.5:1	5.3	(90)	1:2.4
1e	39.6	(60)	3.0:1	5.1	(90)	16.0:1	3.6	(90)	1:2.4
1f	33.9	(60)	2.5:1	5.8	(90)	19.8:1	3.9	(90)	1:2.4
1g	45.1	(45)	2.5:1	7.2	(90)	8.8:1	4.9	(90)	1:2.0
10a	61.8	(60)	4.7:1	7.5	(60)	11.7:1	1.2	(90)	1:1,5
10b	37.0	(20)	4.5:1	8.2	(60)	15.1:1	1.1	(60)	1:2,2
11	28.5	(60)	4.5:1	5.8	(90)	11.1:1	1.7	(90)	1:2.1
17[a]	28.3	(30)	5.3:1	2.9	(30)	16.0:1	-		

[a] 25 mol-%, thermal electron transfer without irradiation.

The yield of **15** is reduced by 50% while the *endo* selectivity in **14** is strongly enhanced. This salt effect can be explained by the liberation of the solvated cation radicals from the contact ion pair ($\mathbf{1a}^{\bullet}/\mathbf{8}^{\bullet+}$) by formation of $\mathbf{1a}^{\bullet}/Li^{+}$ [20b,29]. In the more polar solvent acetonitrile no distinct effect has been observed. In summary, the formation of the cycloaddition products **14** and **15** is very sensitive to a change of the reaction conditions.



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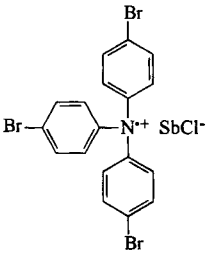
c) Influence of the Sensitizer

To study the influence of the sensitizer on the electron-transfer-catalyzed cycloaddition of **8** to **9a**, the photolyses have generally been performed in dichloromethane at wavelengths $\lambda \geqslant 354$ nm. Only with **5**, wavelengths $\lambda \geqslant 315$ nm have been used. The concentration of the sensitizer used is usually 2 mol-%. The progress of the reaction and the product quantification have been evaluated by GLC (Table 6).

All of the salts are effective as electron-transfer catalysts. However, the yields and product distributions differ with respect to their structure. With **1b**, only the symmetrical and mixed Diels-Alder products **12** and **14** are formed with high *endo* selectivity. With all other sensitizers, the cross [2 + 2] adducts **15** are formed additionally in variable yields. The use of halogenated pyrylium salts **1d**–**1f** and also **1g** furnishes the highest yields of **15**. The *endo*/*exo* ratio of ca. 1:2.4 for **15** does not vary while it is strongly influenced in the case of the Diels-Alder products ranging from 5.3:1 (**1b**) to 2.3:1 (**1d**) for the dimer **12** and from 24.3:1 (**1b**) to 8.8:1 (**1g**) for the mixed product **14**. Thermal electron transfer using tris(4-bromophenyl)aminium hexachloroantimonate (**17**) as the catalyst in high concentrations (25 mol-%) leads only to the [4 + 2] adducts with the dimer **12** as the major product. The product ratios are not correlated with the oxidation potentials of the excited sensitizers. The results may be correlated with the free enthalpies of formation of the radical ion pairs. More negative enthalpies for the electron transfer should favor the formation of the [4 + 2] adducts via the SSIP or the free radical cations[20] as compared with the [2 + 2] adducts. The results compiled in Table 7, do not give a consistent picture, though.



17

Table 7. Free enthalpies of formation according to Eq. 2 for **8** and **9a** in CH_2Cl_2 by using different PET catalysts

Sensitizer	ΔG_{ET} ($1^{\cdot}/8^{\cdot+}$)[a] [eV]	ΔG_{ET} ($1^{\cdot}/9a^{\cdot+}$)[a] [eV]
1b	-0.29	+0.13
1l	-0.33	+0.09
10b	-0.35	+0.07
1g	-0.38	+0.04
1c	-0.58	-0.16
1d	-0.80	-0.38
1e	-0.81	-0.39
1f	-0.84	-0.42
1a	-0.84	-0.42
10a	-0.90	-0.48

[a] Ignoring solvent effects.

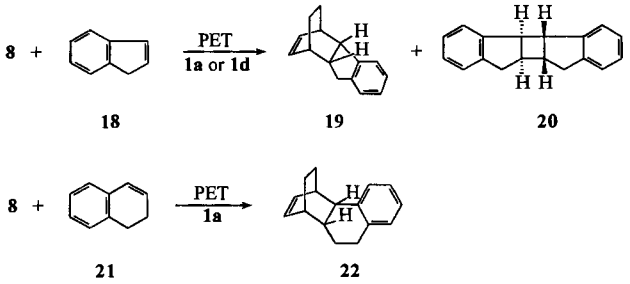
If this interpretation is assumed to be correct **1b** with the least negative value for ΔG_{ET} should give the highest yield of **15**. However, the opposite is true. The values for the halogenated pyrylium salts are all considerably negative independent of the primary formation of the diene cation radical or the dienophile cation radical. Therefore, the formation of **15** should have been unfavorable. It must be concluded that the sensitizer influence cannot simply be explained by the free enthalpies of formation as given by the Weller equation (Eq. 2).

d) Cross Diels-Alder Reaction of 1,3-Cyclohexadiene (8) with Other Aryl Olefins

While cross Diels-Alder products under standard conditions have not been obtained by reaction of **8** with 1,1-diphenylethene, (4,4-dimethoxy)-1,1-diphenylethene, stilbene, or 4,4′-dimethoxystilbene, the reactions have been successful with indene (**18**) and 1,2-dihydronaphthaline (**21**) (Scheme 5).

With **21** the cross Diels-Alder product **22** is formed in 10.2% yield with an *endo/exo* ratio of 4.5:1 by using **1a** as sensitizer. With indene (**18**) and **1a** as sensitizer, the cross Diels-Alder product **19** is formed in 27.5% yield exclusively in the *endo* configuration. The yield can be enhanced by using **1d** as sensitizer to give 40% of *endo*-**19**. As a by-product (4.2%), the [2 + 2] dimer of indene is formed. Of the four possible diastereoisomers only the *anti* head-to-head dimer **20** is observed. If 9,10-dicyanoanthracene is used as the sensitizer according to the results of Schuster[30] **19** is formed in 23% yield without total *endo* selectivity (*endo/exo* = 40:1). While under thermal electron-transfer conditions with **17** or tris(2,4-dibromophenyl)aminium hexachloroantimonate the yields of the cycloadducts are very low, the electrochemically induced electron transfer in acetonitrile/dichloromethane (1:1, 0.1 M $LiClO_4$; lutidine) at a potential of 1000 mV vs. the $Ag/AgClO_4$ reference electrode selectively leads to *endo*-**19** (40%). Similarly, **22** is formed from **8** and **21** in 11% yield (*endo/exo* = 8.1:1).

Scheme 5



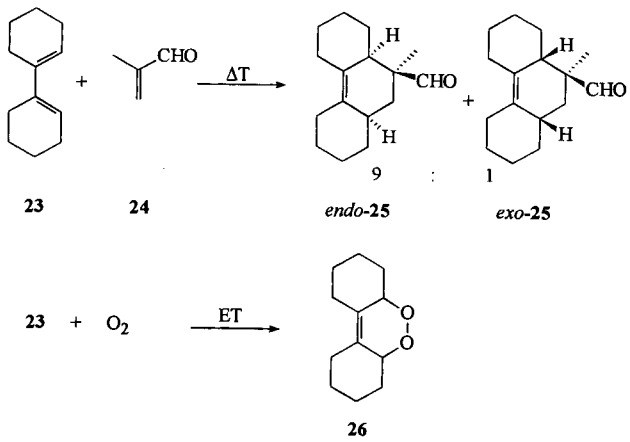
18 19 20

21 22

Application of 1,1′-Dicyclohexenyl (23) as Diene

1,1′-Dicyclohexenyl (**23**) is reactive towards electron-poor dienophiles like maleic anhydride or acrylic acid[31]. With methacroleine (**24**) Baldwin[32] obtained **25** as a 9:1 mixture of the *endo* and *exo* diastereomers (Scheme 6).

Scheme 6



23 24 *endo*-25 : 1 *exo*-25

26

In the presence of oxygen under thermal electron-transfer conditions using triarylamine cation radicals like **17** or the trityl cation as catalysts, Barton[33] obtained the endoperoxide **26** in ca. 70% yield (Scheme 6). Later, Nelsen[34,35] also studied this reaction using triarylamine cation radicals as catalysts and obtained **26** in 39% yield.

Using our pyrylium salts as sensitizers in dichloromethane we have been able to obtain cross Diels-Alder products of **23** and the electron-rich styrene derivatives **9a–9d** under photo-electron transfer conditions (Scheme 7).

Three types of products are obtained: 1. Mixed Diels-Alder products **27a–27d**, in which the styrenes act as dienophiles and **23** as diene. 2. Mixed Diels-Alder products **28**, in which the styrenes act as dienes and **23** as dienophile. 3. Diels-Alder dimers **29** of **23**. Using **1b** as sensitizer, we have

Scheme 7

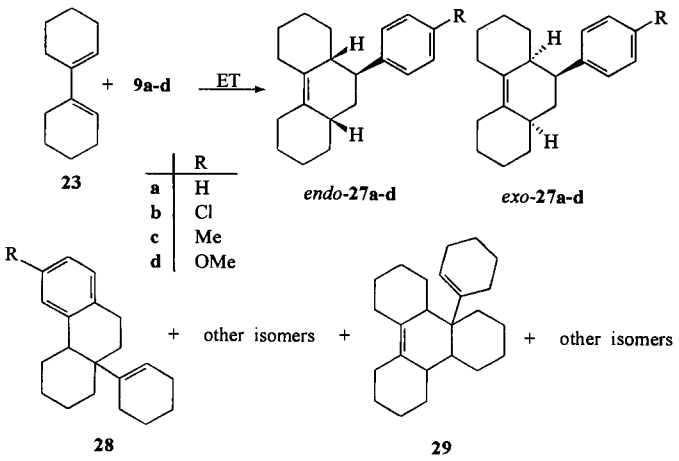
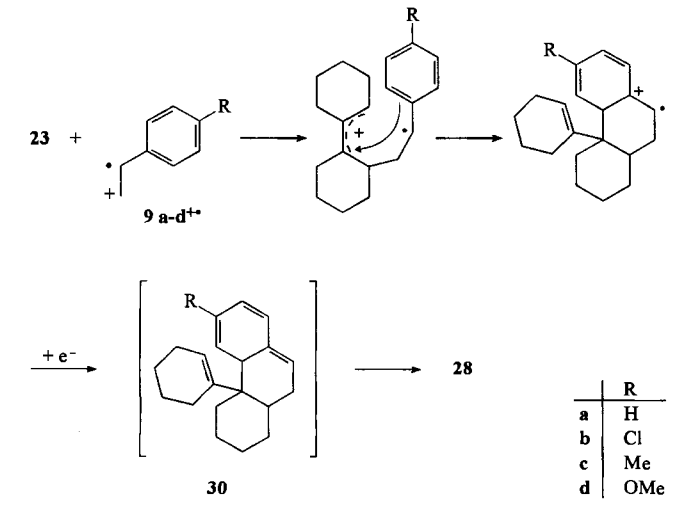


Table 8. Irradiation of **23** and styrene derivatives **9a–9d** using different pyrylium salts as PET catalysts (2 mol-%)

Sensitizer	Dienophile	**27** (*endo/exo*) [%]	**28** (Ratio of [%] isomers)	*t* [h]
1b	**9a**	33.6 (*1: 9.8*)	-	2
1a	**9a**	1.7 (*1: 9.3*)	-	4
1d	**9a**	5.8 (*1:10.1*)	-	4
1b	**9b**	48.3 (*1: 9.2*)	-	2
1a	**9b**	2.7 (*1: 7.0*)	3,5 (*11.1:1:1.1*)	3
1d	**9b**	2.1 (*1: 5.8*)	1.2 (*5.1:1:1.5*)	3
1b	**9c**	30.1 (*1: 8.9*)	-	4
1a	**9c**	10.0 (*1: 9.3*)	Traces	4
1d	**9c**	3.1 (*1: 8.5*)	1.5 (*1:1.4:3.8*)	4
1b	**9d**	52.8 (*1: 5.4*)	-	3
1a	**9d**	14.8 (*1: 5.3*)	Traces	3
1d	**9d**	58.3 (*1: 5.3*)	10.3 (*1:1.2:3.9*)	3

Scheme 8



obtained only the products **27a–27d** in good yield (Table 8). With the exception of **27d**, the *endo/exo* ratio is ca. 9:1 which is almost the same as in the thermal electron-transfer-catalyzed reaction of **23** with **24** (Scheme 6).

The yield of **27** is decreased drastically by using **1a** and **1d** as sensitizers, and at the same time several diastereomeric products of type **28** are formed. The intermediate **30**, produced by the reaction of the styrene cation radical acting as diene with **23** as dienophile, is converted into **28** by rearomatization (Schema 8).

An exception is the reaction with 4-methoxystyrene (**9d**) in which the yield of Diels-Alder product **27d** is not as drastically diminished if **1a** instead of **1b** is used as sensitizer. With **1d**, the yield of **27d** is even slightly enhanced to 58%. In this case also **28** is formed in 10% yield as a byproduct.

Because the sensitizer strongly influences the product yield and product distribution in the reaction of **23**, a larger number of catalysts have been tested in the reaction of **23** with **9a** (Table 9). As in the case of the pyrylium salts, the use of thiapyrylium salt **10b** results in a high yield of **27a** (68%) while the application of **10a** only gives traces of the cycloadduct. In some cases, [4 + 2] or [2 + 2] dimers **29** of dicyclohexenyl **23** are formed as byproducts in very low yield. We have not succeeded in determining the exact structure because even after prolonged irradiation not enough material has been isolated.

Table 9. Irradiation of **23** and **9a** using different catalysts (2 mol-%)

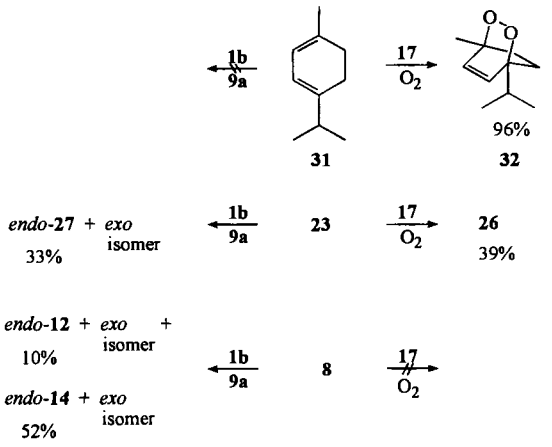
Sensitizer	**27a** (*endo/exo*) [%]	**28a** (Ratio of [%] isomers)	Dimeres of **23**	*t* [h]
1b	33.6 (*1: 9,8*)	-	-	2
1a	1.7 (*1: 9,3*)	Traces	-	4
1d	5.8 (*1:10,1*)	-	Small amounts	4
10b	68.1 (*1:11,0*)	-	Small amounts	2
10a	0.6 (*1:12,2*)	Traces	Small amounts	2
11	20.4 (*1:11,2*)	-	-	2
17[a]	7.9 (*1: 3,1*)	30.1 (*1:3.6:4.9*)	Byproduct	1

[a] 25 mol-%, thermal electron transfer without irradiation.

When the triarylamine cation radical salt **17** is used for the thermal catalysis of this reaction, only compounds of type **28a** are formed as main products while the Diels-Alder adduct **27a** is only a byproduct.

In contrast to the reactions of **8**, which dimerizes quantitatively and even yields considerable amounts of dimers during the cross-Diels-Alder reaction with **9a**, dimerization of **23** during photolysis occurs only to a minor extent. In the presence of **9a** almost exclusively cross Diels-Alder products are formed. The reason for this behavior could be the steric hindrance of the diene **23** by the alkyl substituents at the double bonds. This is supported by the fact that the sterically strongly hindered α-terpinene (**31**) neither dimerizes nor undergoes a cross-Diels-Alder reaction with **9a** when irradiated in the presence of **1b** as sensitizer. Interestingly, in the reaction of 1,3-dienes with oxygen catalyzed by triarylaminium salts, Nelsen[34] has found that the yields of endoperoxides are the higher the stronger the steric hindrance of the diene. At the same time, the tendency towards dimerization decreases (Scheme 9). With α-terpinene (**31**), the endoperoxide **32** is obtained in 96%, while with **23** the yield of the endoperoxide **26** is only 39%. Compound **8** dimerizes so fast that no endoperoxide at all has been obtained.

Scheme 9



The almost exclusive formation of the cross Diels-Alder products by the reaction of **23** with styrene derivatives during the photochemically initiated electron transfer indicates that this reaction proceeds via the cation radicals of the styrenes. With the exception of **9d**, the formation of the styrene cation radical is less favorable than that of the diene **23** (Table 10). However, the sterical hindrance of the diene seems to prevent the reaction from proceeding via the cation radical of **23**.

Table 10. Free enthalpies of formation according to Eq. 2 for **23** and different styrene derivatives **9a–9d** by using **1b** as sensitizer in CH_2Cl_2 [with $E_{red}(\mathbf{1b}^+/\mathbf{1b}^\bullet) = -0.36$ V; $E_{excit} = 2.34$ eV]

Electron donor	E_{ox} [V vs NHE]	ΔG_{ET} ($\mathbf{1b}^\bullet/\mathbf{D}^{\bullet+}$)[a] [eV]
23	1.63	-0.35
9a	2.11	+0.13
9c	1.91	-0.07
9b	2.13	+0.15
9d	1.54	-0.44

[a] Ignoring solvent effects.

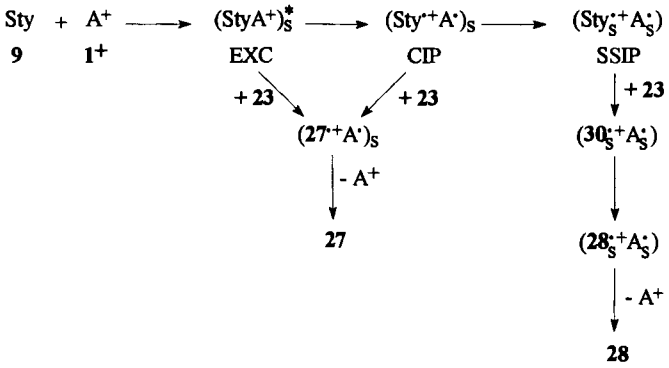
Table 11. Free enthalpies of formation for $\mathbf{23}^{\bullet+}$, $\mathbf{9a}^{\bullet+}$ and different sensitizers in CH_2Cl_2

Sensitizer	ΔG_{ET}(Sensitizer$^\bullet$/$\mathbf{23}^{\bullet+}$) [eV]	ΔG_{ET} (Sensitizer$^\bullet$/$\mathbf{9a}^{\bullet+}$) [eV][a]
1a	-0.90	-0.42
1b	-0.35	+0.13
1d	-0.86	-0.38
10a	-0.96	-0.48
10b	-0.41	+0.07
11	-0.39	+0.09

[a] Ignoring solvent effects.

The changing product distributions with different sensitizers seems to indicate that the reaction can proceed along several reaction paths. The reaction paths leading to the [4 + 2] adduct **27a** are only followed, if the free enthalpies of formation for the styrene cation radical ($\mathbf{9a}^{\bullet+}$) is very small (Table 11). However, for positive or small negative values of the free enthalpies of formation the electron transfer with the direct generation of solvent-separated ion pairs according to the Weller equation (Eq. 2) is unfavorable. In this case, the reaction may take place via exciplexes[20,29], and styrene acts as dienophile (Scheme 10). For negative values of the enthalpy of formation for $\mathbf{9a}^{\bullet+}$, surprisingly no Diels-Alder products **27** are generated. Instead, products of type **28** are obtained. Obviously, the styrene cation radical can act as diene, if the production of the solvent-separated ion pair is favored.

Scheme 10



With styrene derivative **9d**, for which the cation radical formation is exergonic, another reaction path must exist. This is supported by the preparative results which are not consistent with those of the other styrenes.

For PET-catalyzed cycloaddition reactions using pyrylium salts as sensitizers, several parallel reaction channels can be envisaged, for example energy transfer, electron transfer, and intermediate triplex formation[30]. Reaction parameters like concentration of the sensitizer, concentration ratios, type of sensitizer, and solvents are influencing the reaction channels differently. Since our observables (product distributions, yields, and *endo/exo* ratios) are the sum of several competing reaction paths, it is very difficult and sometimes impossible to separate the influences of the various reaction parameters.

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Experimental

^{1}H NMR: Bruker WH-90, Bruker AC-200, Bruker AM-400 (δ values, internal standard). – ^{13}C NMR: Bruker WH-90, Bruker AC-200, Bruker AM-400 (δ values, internal standard). – IR: Pye Unicam SP-1100. – UV: Varian Cary 219, Perkin-Elmer Modell spectrometer 554. – MS: Kratos MS 50 and MS 30. – Melting points (uncorrected): Kofler microheating plate (Reichert). – Preparative LC: Silica gel for flash chromatography 30–60 mm (Baker), silica gel SiliTech 63–200 μm (Woelm). – Gas chromatography: Carlo-Erba model FTV 4100 and 4180 (FID detector), Hewlett-Packard Integrator Mod. 3390 A; fused silica capillary glass column HP 1 (Hewlett-Packard) (12 m, ID 0.2 mm, film thickness 0.33 μm), carrier gas N_2. – GC-MS: Gaschromatograph HP 5890

(Hewlett-Packard) with fused silica capillary glass column HP 1 (Hewlett-Packard) (12 m, ID 0.2 mm, film thickness 0.33 μm), carrier gas He, detector MSD 5970 (Hewlett-Packard), data system HP 9133, HP 300 (Hewlett-Packard). – Cyclic voltammetry: 10^{-3} M solutions of the substrate in acetonitrile containing 0.1 M $LiClO_4$ as electrolyte were measured with a computer-controlled electroanalysis system model CYSY 1 (Cypress Systems Inc., Lawrence/Kansas) in combination with cell stand C1 A/B (Bioanalytical Systems Inc., West Lafayette/Indiana), a glassy carbon anode ($d = 1.6$ mm), a platinum wire cathode, and an $Ag/AgNO_3$ (0.1 M in acetonitrile; +570 mV vs. NHE) reference electrode. The reported potentials E_{red} and E_{ox} are obtained by extrapolation of the respective peak potentials at different scan rates to a scan rate of zero. – Photolyses: Irradiations were performed with a light-source system consisting of an Osram XBO 450 OFR 450-W xenon lamp, a Müller Elektronik LAX 1450 lamp housing, and an Oriel long-pass filter 5146 ($\lambda > 345$ nm) or 5145 ($\lambda > 315$ nm).

General Procedure for the Formation of Pyrylium Salts: According to a literature procedure[36] for the synthesis of 2,4,6-tripyrylium tetrafluoroborate (**1a**), $BF_3 \cdot OEt_2$ is slowly added to a mixture of the carbonyl compounds (if starting materials are solids, they are dissolved in a small amount of toluene). After heating for 2 h at 100°C the thus formed diethyl ether is evaporated and the oily product dissolved in acetone. Upon the addition of diethyl ether the product precipitates. Purfication is performed by multiple recrystallization from acetone.

2,4,6-Tris(4-methoxyphenyl)pyrylium Tetrafluoroborate (**1b**): According to the general procedure, 3.4 g (25 mmol) of 4-methoxybenzaldehyde and 7.5 g (50 mmol) of 4-methoxyacetophenone are allowed to react with 7.5 (60 mmol) of $BF_3 \cdot OEt_2$ to give 1.5 g (12%) of **1b**, m.p. 347°C (346–347°C[37]). – IR (KBr): $\tilde{\nu} = 2990$ cm^{-1} w (H–C), 1640 m (C=O$^+$–C), 1600 s (C=C), 1500 s (C=C), 1250 s, 1200 s (Ar–O–C), 1080 s (B–F), 850 w (Ar–H). – ^{1}H NMR (200 MHz, DMSO): $\delta = 3.90$ (s, 6H, 2 CH_3), 3.93 (s, 3H, CH_3), 7.14 (d, $J = 9$ Hz, 6H, aromat. 3′-, 5′-H), 8.10 (d, $J = 9$ Hz, 4H, aromat. 2′-, 6′-H), 8.40 (d, $J = 9$ Hz, 2H, aromat. 2′-, 6′-H), 8.55 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): $\delta = 55.94$ (2 CH_3), 56.07 (CH_3), 110.37 (C-3, -5), 115.23 (3 C-2′, 3 C-6′), 121.14 (2 C-1′), 124.23 (C-1′), 130.5 (2 C-3′, 2 C-5′), 132.35 (C-3′, -5′), 161.49 (C-4), 164.45 (2 C-4′), 165.25 (C-4′), 167.47 (C-2, -6). – MS (70 eV): m/z (%) = 401 (8) [M$^+$ + 2], 400 (40) [M$^+$ + 1], 399 (100) [M$^+$], 385 (15) [M$^+$ + 1 – CH_3], 384 (55) [M$^+$ – CH_3], 200 (16), 135 (42), 44 (97). – $C_{26}H_{23}O_4$ [M$^+$]: calcd. 399.1596; found 399.1615 (MS).

2,4,6-Tris(4-methylphenyl)pyrylium Tetrafluoroborate (**1c**): According to the general procedure, 3.0 g (25 mmol) of 4-methylbenzaldehyde and 6.8 g (50 mmol) of 4-methylacetophenone are allowed to react with 7.5 ml (60 mmol) of $BF_3 \cdot OEt_2$ to give 4.5 g (41%) of **1c**, m.p. 312°C (310–312°C[36]). – Fluorescence: excitation at $\lambda = 394$ nm; emission at $\lambda = 485$ nm in accordance with the literature[38]. – IR (KBr): $\tilde{\nu} = 1640$ cm^{-1} m (C=O$^+$–C), 1610 s (C=C), 1510 s (C=C), 1210 m, 1080 s (B–F), 830 w (Ar–H). – ^{1}H NMR (200 MHz, DMSO): $\delta = 2.48$ (s, 9H, 3 CH_3), 7.57 (d, $J = 8$ Hz, 6H, aromat. 3′-, 5′-H), 8.44 (d, $J = 8$ Hz, 4H, aromat. 2′-, 6′-H), 8.50 (d, $J = 8$ Hz, 2H, aromat. 2′-, 6′-H), 8.98 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): $\delta = 21.39$ (CH_3), 21.44 (2 CH_3), 113.10 (C-3, -5), 126.27 (2 C-1′), 128.51 (2 C-2′, 2 C-6′), 129.38 (C-1′), 129.96 (C-2′, -6′), 130.44 (3 C-3′, 3 C-5′), 146.12 (C-4′), 146.76 (2 C-4′), 163.76 (C-4), 167.47 (C-2, -6). – MS (70 eV): m/z (%) = 351 (100) [M$^+$], 261 (12), 233 (10), 175.5 (10) [M^{++}], 119 (42), 91 (30), 44 (97). – $C_{26}H_{23}O$ [M$^+$]: calcd. 351.1749; found 351.1765 (MS).

2,4,6-Tris(4-bromophenyl)pyrylium Tetrafluoroborate (**1d**): According to the general procedure, 1.8 g (10 mmol) of 4-brombenzaldehyde and 4.0 g (20 mmol) of 4-bromacetophenone are treated with 3.1 ml (25 mmol) of $BF_3 \cdot OEt_2$ to give 1.4 g (22%) of **1d**, m.p. 296°C. – IR (KBr): $\tilde{\nu} = 1640$ cm^{-1} m (C=C$^+$–C), 1600 s (C=C), 1500 s (C=C), 1250 s, 1080 s (B–F), 1020 s (Ar–Br), 840 w (Ar–H). – ^{1}H NMR (200 MHz, DMSO): $\delta = 8.02$ (d, $J = 7.8$ Hz, 4H, aromat. 3′-, 5′-H), 8.03 (d, $J = 7.8$ Hz, 2H, aromat. 3′-, 5′-H), 8.51 (d, $J = 7.8$ Hz, 4H, aromat. 2′-, 6′-H), 8.55 (d, $J = 7.8$ Hz, 2H, aromat. 2′-, 6′-H), 9.20 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): $\delta = 115.53$ (C-3, -5), 128.25 (2 C-1′), 130.23 (2 C-4′), 130.63 (C-1′), 130.91 (2 C-2′, 2 C-6′), 131.55 (C-4′), 131.88 (C-2′), 132.98 (3 C-3′, 3 C-5′), 164.05 (C-4), 169.42 (C-2, -6). – MS (70 eV): m/z (%) = 544/546/548/550 (8/24/24/8) [M$^+$ + 1], 543/545/547/549 (25/75/75/25) [M$^+$], 465/467/469 (14/38/10) [M$^+$ + 1 – Br], 464/466/468 (50/100/50) [M$^+$ – Br]. – $C_{23}H_{14}Br_3O$ [M$^+$]: calcd. 543.8672; found 543.8669 (MS).

2,4,6-Tris(4-chlorophenyl)pyrylium Tetrafluoroborate (**1e**): According to the general procedure, 3.5 mg (25 mmol) of 4-chlorbenzaldehyde and 7.7 g (50 mmol) of 4-chloracetophenone are treated with 7.5 ml (60 mmol) of $BF_3 \cdot OEt_2$ to give 2.3 g (19%) of **1e**, m.p. 306°C (308–310°C[36]). Fluorescence: excitation at $\lambda = 394$ nm; emission at $\lambda = 485$ nm in accordance with the literature[38]. – IR (KBr): $\tilde{\nu} = 1640$ cm^{-1} m (C=O$^+$–C), 1600 s (C=C), 1500 s (C=C), 1100 s (Ar–Cl), 1080 s (B–F), 1020 s, 840 w (Ar–H). – ^{1}H NMR (200 MHz, DMSO): $\delta = 7.78$ (d, $J = 9$ Hz, 4H, aromat. 3′-, 5′-H), 7.82 (d, $J = 9$ Hz, 2H, aromat. 3′-, 5′-H), 8.51 (d, $J = 9$ Hz, 4H, aromat. 2′-, 6′-H), 8.57 (d, $J = 9$ Hz, 2H, aromat. 2′-, 6′-H), 9.08 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): $\delta = 115.07$ (C-3, -5), 127.56 (2 C-1′), 130.04 (3 C-3′, 3 C-5′), 130.54 (2 C-2′, 2 C-6′), 130.76 (C-1′), 131.88 (C-2′, -6′), 140.55 (2 C-4′), 141.07 (C-4′), 163.68 (C-4), 169.94 (C-2, -6). – MS (70 eV): m/z (%) = 412/414/416/418 (30/28/9/1) [M$^+$ + 1], 411/413/415/417 (100/95/32/4) [M$^+$], 377/379/381 (10/7/1) [M$^+$ + 1 – Cl], 376/378/380 (40/25/4) [M$^+$ – Cl]. – $C_{23}H_{14}Cl_3O$ [M$^+$]: calcd. 411.0111; found 411.0093 (MS).

2,4,6-Tris(4-fluorphenyl)pyrylium Tetrafluoroborate (**1f**): According to the general procedure 3.1 g (25 mmol) of 4-fluorbenzaldehyde and 6.9 g (50 mmol) of 4-fluoracetophenone are allowed to react with 7.5 ml (60 mmol) of $BF_3 \cdot OEt_2$ to give 4.5 g (40%) of **1f**, m.p. 280°C (244–246°C[39]). – Fluorescence: excitation at $\lambda = 372$ nm; emission at $\lambda = 470$ nm in accordance with the literature[38]. – IR (KBr): $\tilde{\nu} = 1640$ cm^{-1} m (C=O$^+$–C), 1600 s (C=C), 1510 s (C=C), 1470 m, 1240 s (C–F), 1180 s, 1070 s (B–F), 850 w (Ar–H). – ^{1}H NMR (200 MHz, DMSO): $\delta = 7.60$–7.78 (m, 6H, aromat. 3′-, 5′-H), 8.62–8.75 (m, 6H, aromat. 2′-H, 6′-H), 9.11 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO, in accordance with the literature[39]): $\delta = 114.37$ (C-3, -5), 117.25 [3 C-3′, 3 C-6′, ^2J(C,F) = 22.4 Hz], 125.57 [2 C-1′, ^4J(C,F) = 2.4 Hz], 128.76 [C-1′, ^4J(C,F) = 2.4 Hz], 132.00 [2 C-2′, 2 C-6′, ^3J(C,F) = 9.5 Hz], 133.34 [C-2′, -6′, ^3J(C,F) = 9.5 Hz], 163.64 (C-4), 166.66 [3 C-4′, ^1J(C,F) = 254.8 Hz], 168.82 (C-2, -6). – MS (70 eV): m/z (%) = 365 (15) [M$^+$ + 2], 364 (80) [M$^+$ + 1], 363 (100) [M$^+$], 269 (30), 123 (73), 95 (28), 44 (28). – $C_{23}H_{14}F_3O$ [M$^+$]: calcd. 363.0997; found 363.1001 (MS).

2,4,6-Tris(1,1′-biphenyl-4-yl)pyrylium Tetrafluoroborate (**1g**): According to the general procedure, 1.8 g (10 mmol) of 4-phenylbenzaldehyde and 3.9 g (20 mmol) of 4-phenylacetophenone are treated with 3.1 ml (25 mmol) of $BF_3 \cdot OEt_2$ to give 1.4 g (23%) of **1g** with an impurity of 1,3,5-Tris(1,1′-biphenyl-4-yl)benzene, m.p. 161–165°C. – IR (KBr): $\tilde{\nu} = 1640$ cm^{-1} m (C=O$^+$–C), 1610 s (C=C), 1500 s (C=C), 1250 s, 1080 s (B–F), 1020 s (Ar–Br), 850 m (Ar–H), 780 m (Ar–H), 705 m (Ar–H). – ^{1}H NMR (200 MHz, DMSO): $\delta = 7.40$–8.00 (m, aromat. CH), 8.08 (d, 6H, aromat. 3′-,

5′-H), 8.66 (d, 4H, aromat. 2′-, 6′-H), 8.73 (d, 2H, aromat. 2′-, 6′-H), 9.18 (s, 2H, 3-, 5-H). – $C_{41}H_{30}O$ [M^+]: calcd. 538.2297; found 538.2299 (MS).

General Procedure for the Formation of the Thiapyrylium Salts: According to a literature procedure[40] for the synthesis of 2,4,6-triphenylthiapyrylium tetrafluoroborate (**10a**), 7.5 ml (10.0 mmol) of an aqueous Na_2S (4.9%) solution is slowly added with stirring to 1.0 g (2.5 mmol) of **1a**. The color of the solution changes to red during stirring at room temperature for 1 h. After the reaction mixture has been added to a solution of 15 ml of HBF_4 in 25 ml of H_2O, stirring is continued for another hour. The yellow precipitate (0.4 g, 39% yield) is washed with diethyl ether and recrystallized from acetone/diethyl ether (1:1), m.p. 192°C (195–196°C[36]). – IR (KBr): $\tilde{\nu} = 1640\ cm^{-1}$ m, 1590 s, 1490 m, 1440 s, 1080 s (B–F), 770 m (Ar–H), 700 w (Ar–H). – ^1H NMR (200 MHz, DMSO): δ = 7.80 (br., 6H, aromat. 3′-, 5′-H), 8.30 (br., 4H, aromat. 2′-, 6′-H), 8.46 (br., 2H, aroamt. 2′-, 6′-H), 9.30 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): br. signals. – MS (70 eV): *m/z* (%) = 327 (8) [M^+ + 2], 326 (35) [M^+ + 1], 325 (100) [M^+], 247 (8), 162.5 (3) [M^{++}], 121 (8). – $C_{23}H_{17}S$ [M^+]: calcd. 325.1051; found 325.1041 (MS).

2,4,6-Tris(4-methoxyphenyl)thiapyrylium Tetrafluoroborate (**10b**): According to the general procedure 0.9 g (2.0 mmol) of **1b** is converted into 0.4 g (40%) of **10b**, m.p. 285°C. – UV λ_{max} (CH_2Cl_2) = 455 nm (448 nm in acetic acid[41]). – IR (KBr): $\tilde{\nu} = 2980\ cm^{-1}$ w (H–C), 1620 m, 1580 s, 1450 s, 1260 s, 1200 s (Ar–O–C), 1080 s (B–F), 850 w (Ar–H). – ^1H NMR (200 MHz, DMSO): δ = 3.95 (s, 9H, 3 CH_3), 7.27 (br., 6H, aromat. 3′-, 5′-H), 8.25 (br., 4H, aromat. 2′-, 6′-H), 8.43 (br., 2H, aromat. 2′-, 6′-H), 8.95 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): br. signals. – MS (70 eV): *m/z* (%) = 417 (8) [M^+ + 2], 416 (35) [M^+ + 1], 415 (100) [M^+], 400 (18) [M^+ – CH_3], 372 (12), 207.5 (8) [M^{++}]. – $C_{26}H_{23}O_3S$ [M^+]: calcd. 415.1368; found 415.1394 (MS).

N-Methyl-2,4,6-triphenylpyridinium Tetrafluoroborate (**11**)[42]: 1.23 g (3.50 mmol) of pyrylium salt **1a** is dissolved in 100 ml of hot ethanol; subsequently, 18 ml of a solution of methyl amine (30%) in ethanol is added to the obtained solution. The mixture is heated in a water bath for 1 h, and water is added. The white precipitate is washed and recrystallized from ethanol to give 0.33 g (26%) of **11**, m.p. 224–226°C (217–218°C[43]). – IR (KBr): $\tilde{\nu} = 1620\ cm^{-1}$ s, 1580 m (C=C), 1265 w, 1200 w, 1080 s (B–F), 900 w, 790 m (Ar–H), 710 s (Ar–H). – ^1H NMR (200 MHz, DMSO): δ = 3.78 (s, 3H, CH_3), 7.68 (m, 9H, 3 3′-H, 3 4′-H, 3 5′-H), 7.87 (m, 4H, 2 2′-H, 2 6′-H), 8.24 (m, 2H, 2′-, 6′-H), 8.47 (s, 2H, 3-, 5-H). – ^{13}C NMR (50 MHz, DMSO): δ = 45.73 (NCH_3), 125.14 (C-3, -5), 128.61 (C-2′, -6′), 129.10 (2 C-2′, C-6′), 129.52 (2 C-3′, 2 C-5′), 129.58 (C-3′, -5′), 131.09 (2 C-4′), 132.18 (C-4′), 133.08 (2 C-1′), 133.45 (C-1′), 154.14 (C-4), 156.52 (C-2, -6). – MS (70 eV): *m/z* (%) = 323 (2) [M^+ + 1], 322 (3) [M^+], 308 (28) [M^+ + 1 – CH_3], 307 (100) [M^+ – CH_3], 306 (50), 246 (10), 230 (20), 202 (10). – $C_{24}H_{20}N$ [M^+]: calcd. 322.1596; found 322.1594 (MS).

General Procedure for the Photolysis: 1 mmol each of the diene and dienophile is dissolved in 10 ml of CH_2Cl_2. The solution is transferred to a 25-ml Schlenk tube, and the solid pyrylium salt is added. The Schlenk tube is placed in a water bath (15°C) and irradiated. The reaction is monitored by GC analysis.

Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (**12**): 497 mg (6.20 mmol) of 1,3-cyclohexadiene (**8**) is dissolved in 50 ml of CH_2Cl_2, and the solution is irradiated in a 100-ml Schlenk tube for 20 min. Then, 8 ml of a 0.01 M solution of **1a** is slowly added, and a weak fluorescence of the mixture remains during the reaction. Salt **1a** is removed by filtration on silica gel. Kugelrohr distillation (70°C/1.5 Torr) gives 336 mg (68%) of **12** (*endo/exo* = 7:1). – GC-MS: *m/z* (%) = 161 (0.6) [M + 1]$^+$, 160 (4) [M^+], 80 (100) [$C_6H_8^+$], 79 (44); in accordance with literature data[20b].

5-Phenylbicyclo[2.2.2]oct-2-ene (**14**): 160 mg (2.00 mmol) of **8** and 210 mg (2.00 mmol) of **9a** are dissolved in 40 ml of CH_2Cl_2, and 16.0 mg (0.04 mmol) of **1a** is added to the solution. After irradiation for 2 h, salt **1a** is removed by filtration on silica gel, and the solvent is removed. Purification of the residue and separation from the dimers **12** by LC (*n*-heptane) give 96.0 mg (26%) of **14** (*endo/exo* = 10.8:1). – *endo*-**14**: ^1H NMR (200 MHz, $CDCl_3$): δ = 1.39 (m, 2H, 7′-, 8′-H), 1.43–1.85 (m, 3H, 4-H_{endo}, 7-, 8-H), 2.17 (ddd, 1H, 4-H_{exo}), 2.71 (m, 2H, 3-, 6-H), 3.03 (m, 1H, 5-H_{exo}), 6.28 (t, 1H, 1-H), 6.48 (m, 1H, 2-H), 7.16–7.38 (m, 5H, aromat. H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.17, 27.50, 36.48 (CH_2, C-4, -7, -8), 30.42, 36.99, 43.64 (CH, C-3, -5, -6), 125.64 (CH, aromat. C-4), 127.78, 128.03 (CH, aromat. C-2, -3, -5, -6), 132.32, 135.02 (CH, C-1, -2), 148.35 (C, aromat. C-1). – GC-MS: *m/z* (%) = 185 (4) [M + 1]$^+$, 184 (15) [M^+], 104 (12) [$C_8H_8^+$], 80 (100) [$C_6H_8^+$], 79 (35). – $C_{14}H_{16}$ (184.3): calcd. C 91.25, H 8.75; found C 91.29, H 8.86.

8-Phenylbicyclo[4.2.0]oct-2-ene (**15**): 0.80 g (10.0 mmol) of **8**, 1.04 g (10.0 mmol) of **9a** and 25.3 mg (0.06 mmol) of **1a** are dissolved in 30 ml of $CHCl_3$. After irradiation for 24 h, the catalyst is removed by filtration on silica gel and the solvent removed by evaporation. Separation of the 1,3-cyclohexadiene dimers by LC (*n*-heptane) gives 0.39 g (21%) of **15**. 1,2,4a,9,10,10a-hexahydrophenanthrene {GC/MS: *m/z* (%) = 184 (100) [M^+]} as a byproduct could not be separated (*endo*-**15**/*exo*-**15**/1,2,4a,9,10,10a*H*-phenanthrene = 3.4:9.4:1). The configuration and regiochemistry have been determined by 2D-NMR techniques and an NOE experiment. – *endo*-**15**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.50–1.85 (m, 2H, 7-H), 2.05–2.38 (m, 4H, 5-, 8-H), 2.80 (m, 1H, 6-H), 3.16 (m, 1H, 3-H), 3.90 (m, 1H, 4-H), 5.43 (m, 1H, 1- or 2-H), 5.91 (m, 1H, 1- or 2-H), 7.15–7.45 (m, 5H, aromat. H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.30 (C-8), 22.16 (C-7), 26.14 (C-5), 29.44 (C-6), 38.56 (C-3), 43.44 (C-4), 125.66, 127.72, 127.82, 128.98 (aromat. C), 127.54 (C-2), 128.30 (C-1). – GC-MS: *m/z* (%) = 185 (4) [M^+ + 1], 184 (15) [M^+], 104 (12) [$C_8H_8^+$], 80 (100) [$C_6H_8^+$], 79 (35). – *exo*-**15**: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.75–2.00 (m, 2H, 7-H), 2.05–2.38 (m, 4H, 5-, 8-H), 2.63 (m, 1H, 6-H), 2.97 (t, 1H, 3-H), 3.50 (dt, 1H, 4-H), 5.97 (m, 1H, 1- or 2-H), 6.00 (m, 1H, 1- or 2-H), 7.15–7.45 (m, 5H, aromat. H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.81 (C-8), 26.27 (C-7), 29.37 (C-6), 30.96 (C-5), 41.31 (C-3), 46.75 (C-4), 125.83, 126.52, 128.33, 128.85 (aromat. C), 128.29 (C-1), 129.73 (C-2). – GC-MS: *m/z* (%) = 185 (4) [M^+ + 1], 184 (15) [M^+], 104 (12) [$C_8H_8^+$], 80 (100) [$C_6H_8^+$], 79 (35). – $C_{14}H_{16}$ (184.3): calcd. C 91.25, H 8.75; found C 91.32, H 8.83.

1,4,4a,9,10,10a-Hexahydro-1,4-ethanophenanthrene (**22**): 87.5 mg (1.09 mmol) of **8**, 134 mg (1.03 mmol) of 1,2-dihydronaphthaline (**21**) and 4.00 mg (0.01 mmol) of **1a** are dissolved in 20 ml of dichloromethane. After irradiation for 1 h at λ ⩾ 345 nm, the catalyst is removed by filtration on silica gel and the solvent removed. Separation of the 1,3-cyclohexadiene dimers (49.0 mg; *endo/exo* = 10.2:1) by LC (*n*-heptane) gives 22.0 mg (10%) of **22** (*endo/exo* = 4.5:1). – ^1H NMR (200 MHz, $CDCl_3$): δ = 6.98–7.22 (m, 4H), 6.22 (t, 1H), 6.05 (t, 1H), 3.12 (m, 1H), 3.01 (m, 1H), 2.65 (m, 1H), 2.50 (m, 2H), 2.35 (m, 1H), 1.80 (m, 3H), 1.40 (m, 3H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.51, 139.58 (aromat. C); 134.60, 132.72, 127.98, 127.69, 125.95, 125.95, 124.89 (aromat. CH and olefin. CH); 42.37, 40.06, 37.20, 36.31, 29.21, 29.14, 26.82, 25.36 (CH, CH_2). – MS (70 eV): *m/z* (%) = 210 (3) [M^+], 148 (10), 130 (100), 129 (20), 119 (10), 80 (9), 79 (10). – $C_{16}H_{18}$ [M^+]: calcd. 210.1409; found 210.1409 (MS).

1,4,4a,9a-Tetrahydro-1,4-ethano-9H-fluorene (**19**): 164 mg (2.10 mmol) of **8**, 234 mg (2.00 mmol) of 1*H*-indene (**18**), and 4.00 ml (0.04 mmol) of a 0.01 M solution of **1d** in dichloromethane are dissolved in 50 ml of dichloromethane. After irradiation for 30 min at $\delta \geqslant 345$ nm, the catalyst is removed by filtration on silica gel and the solvent removed. Separation of the 1,3-cyclohexadiene dimers (45.0 mg; *endo/exo* = 10:1) by LC (*n*-heptane) gives 157 mg (40%) of **19** (only *endo*) as a colorless oil and 9.40 mg (4.1%) of **20** as a white solid. The ^{1}H-NMR spectrum of **19** was identical with the one reported in the literature[30]. The physical data of **20** were identical with the reported ones[44].

Formation of 1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydrophenanthrene Derivatives: 1,1'-Dicyclohexenyl (**23**), the styrene and 1 mol-% of catalyst **1b** are dissolved in 50 ml of CH_2Cl_2, and the resulting solution is irradiated for 2 h. After filtration on silica gel and evaporation of the solvent, purification of the crude product is performed by LC (*n*-heptane).

1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydro-9-phenylphenanthrene (**27a**): According to the general procedure 323 mg (2.00 mmol) of **23** and 210 mg (2.00 mmol) of styrene (**9a**) are converted into 112 mg (21%) of **27a**, m.p. 91°C. – ^{1}H NMR (90 MHz, $CDCl_3$): $\delta = 7.47-7.04$ (m, 5H), 3.20–2.64 (m, 3H), 2.27–0.78 (m, 18H). – *endo*-**27a**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.09$, 134.04, 129.76 (aromat. C and olefin. C); 128.01, 127.83 (2 aromat. CH); 125.65 (aromat. CH); 46.01, 42.44, 39.49 (CH); 36.48, 32.04, 31.36, 29.99, 29.29, 28.70, 27.80, 27.32, 26.47 (CH_2). – *exo*-**27a**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.10$, 130.09, 128.23 (aromat. C and olefin. C); 127.98, 127.79 (2 aromat. CH); 125.85 (aromat. CH); 45.33, 44.51, 38.80 (CH); 36.85, 35.33, 34.37, 30.51, 29.26, 29.17, 27.88, 27.29, 26.57 (CH_2). – MS (70 eV): *m/z* (%) = 266 (15) [M^+], 162 (100) [$C_{12}H_{18}^+$], 94 (19), 91 (14). – $C_{20}H_{28}$ [M^+]: calcd. 266.1954; found 266.2044 (MS).

9-(4-Chlorophenyl)-1,2,3,4,5,6,7,8,8a,9,10,10a-dodecahydrophenanthrene (**27b**): According to the general procedure 170 mg (1.00 mmol) of **23** and 140 mg (1.00 mmol) of 4-chlorostyrene (**9b**) are allowed to react to give 112 mg (37%) of **27b**, m.p. 76°C. – ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.33-6.96$ (m, 4H), 3.10–2.51 (m, 3H), 2.22–0.67 (m, 18H). – *endo*-**27b**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.57$, 133.81, 131.28, 129.80 (aromat. C and olefin. C); 129.13, 128.11 (2 aromat. CH); 45.86, 41.92, 39.39 (CH); 36.44, 32.01, 31.34, 29.92, 29.20, 28.67, 27.75, 27.27, 26.43 (CH_2). – *exo*-**27b**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 128.33$, 126.89, 125.83 (aromat. C and olefin. C); 129.11, 128.09 (2 aromat. CH); 44.66, 44.50, 36.77 (CH); 35.32, 34.52, 34.34, 30.45, 29.25, 29.10, 27.84, 26.54, 26.24 (CH_2). – MS (70 eV): *m/z* (%) = 300/302 (9/2) [M^+], 162 (100) [$C_{12}H_{18}^+$], 94 (19), 91 (14). – $C_{20}H_{25}Cl$ [M^+]: calcd. 300.1600; found 300.1650 (MS).

1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydro-9-(4-methylphenyl)phenanthrene (**27c**): According to the general procedure 173 mg (1.00 mmol) of **23** and 120 mg (1.00 mmol) of 4-methylstyrene (**9c**) are converted into 134 mg (49%) of **27c**, m.p. 91°C. – ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.15-7.01$ (m, 4H), 3.05–2.71 (m, 3H), 2.32 (s, 3H), 2.27–0.92 (m, 18H). – *endo*-**27c**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.03$, 135.00, 134.10, 129.72 (aromat. C and olefin. C); 128.71, 127.71 (2 aromat. CH); 46.02, 42.04, 39.52 (CH); 36.50, 32.18, 31.38, 30.02, 29.31, 28.71, 27.82, 27.36, 26.49 (CH_2); 21.09 (CH_3). – *exo*-**27c**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.25$, 132.60, 130.07, 129.05 (aromat. C and olefin. C); 128.94, 127.79 (2 aromat. CH); 44.87, 44.60, 38.87 (CH); 36.96, 35.35, 34.40, 30.53, 29.26, 29.20, 27.90, 27.31, 26.60 (CH_2); 21.09 (CH_3). – MS (70 eV): *m/z* (%) = 280 (12) [M^+], 162 (100) [$C_{12}H_{18}^+$], 94 (19), 91 (14). – $C_{21}H_{28}$ [M^+]: calcd. 280.2145; found 280.2195 (MS).

1,2,3,4,5,6,7,8,8a,9,10,10a-Dodecahydro-9-(4-methoxyphenyl)-phenanthrene (**27d**): According to the general procedure 164 mg (1.00 mmol) of **23** and 134 mg (1.00 mmol) of 4-methoxystyrene (**9d**) are allowed to react to give 126 mg (43%) of **27d**, m.p. 79°C. – ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.18-6.80$ (m, 4H), 3.80 (s, 3H), 3.05–2.69 (m, 3H), 2.25–0.85 (m, 18H). – *exo*-**27d**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.24$, 136.85, 132.56, 130.06 (aromat. C and olefin. C); 127.61, 113.69 (2 aromat. CH); 55.24 (CH_3O); 47.78, 44.50, 44.37 (CH); 38.83, 37.00, 35.33, 34.36, 30.50, 29.17, 27.89, 26.58, 26.04 (CH_2). – *endo*-**27d**: ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.56$, 137.18, 134.05, 129.68 (aromat. C and olefin. C); 128.60, 113.36 (2 aromat. CH); 55.24 (CH_3O); 46.09, 41.58, 39.53 (CH); 36.47, 32.33, 31.34, 30.00, 29.25, 28.68, 27.79, 27.33, 26.46 (CH_2). – MS (70 eV): *m/z* (%) = 296 (12) [M^+], 162 (97) [$C_{12}H_{18}^+$], 138 (100) [$C_9H_{10}O^+$], 94 (19), 91 (14). – $C_{21}H_{28}O$ [M^+]: calcd. 296.2140; found 296.2142 (MS).

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