Selective alkylation by photogenerated aryl and vinyl cation

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Chapter 7 | Photochemical alkylation with a fluorescent label; photochemistry of 9-anthryl- and 9-phenanthryl(phenyl)iodonium tetrafluoroborate

Introduction

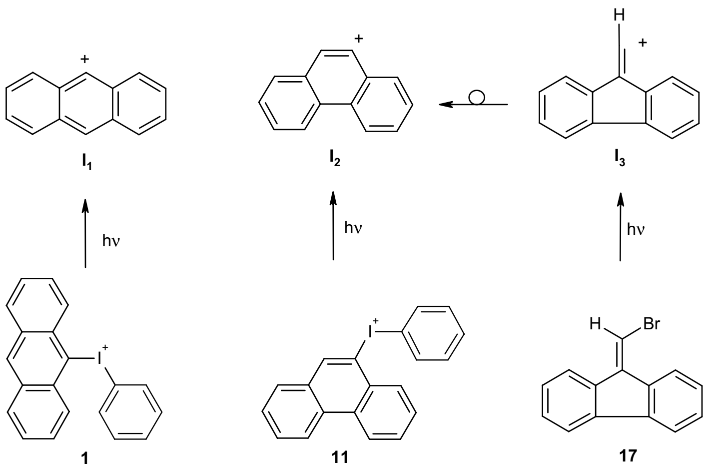
Photolysis of vinyl and phenyliodonium salts has proven to be a powerful entry to vinyl [1] and phenyl cations[2]. Both types of intermediates owe their high reactivity, apart from their electron-deficiency and the hybridisation, to the orthogonal orientation of the vacant orbital of the C^+ atom and the π-orbitals of the neighbouring double bond(s), which precludes stabilisation by overlap of these orbitals[3].

Highly reactive intermediates are usually unselective in their reactions with substrates. This is not the case if the product-forming cation is a triplet and not a singlet closed shell species. Introduction of substituents at the 4-position of phenyl cations alter the singlet-triplet gap and leads to chemo- and regioselectivity in the reaction of these cations with π nucleophiles (unsaturated substrates) vs. their reaction with σ nucleophiles[4]. Benzannelation of the phenyl cation also influences the singlet-triplet gap and thus the reactivity of the aryl cation[5]. The electron-donating effect of the annelating ring and the limited ability of the 1- and the 2-naphthyl cation to adopt the distorted structure normal for closed-shell singlet aryl cations makes the singlet and triplet forms of these cations degenerate in energy, with ensuing chemistry (Chapter 6 of this thesis).

In this chapter the generation of the 9-anthryl cation ($\mathbf{I_1}$) and the 9-phenanthryl cation ($\mathbf{I_2}$) and a study of their reactivity is reported. Cation $\mathbf{I_1}$ was prepared directly by photochemical removal of iodobenzene from iodonium salt **1**. Cation $\mathbf{I_2}$ was prepared directly from iodonium salt **11** and indirectly from **17**, by photogeneration of the primary vinyl cation $\mathbf{I_3}$ which converts to $\mathbf{I_2}$ via a 1,2 phenyl shift (Chart 1).

The ability to make unstable polynuclear aromatic cations such as $\mathbf{I_1}$ and $\mathbf{I_2}$ is not only of fundamental interest. The species can also be employed in arylation reactions with substrates of biological origin to provide them with reporter groups. The cations stem from non-fluorescent precursors, while the tagged molecules after arylation are fluorescent. The extended chromophoric groups (compared to e.g. diphenyliodonium salts) allow excitation with light of $\lambda_{exc} \geq 320$ nm where the biological compounds are transparent and thus not subject to their own photochemistry.

Chart 1: Formation of the 9-anthryl and 9-phenanthryl cations.



Results and Discussion

*Part 1: Photochemical generation of the 9-anthryl cation (**I**$_1$).*

Synthesis

The precursor compounds 9-anthryl(phenyl)iodonium tetrafluoroborate (**1**BF_4) and 9-anthryl(phenyl)iodonium bromide (**1**Br) are synthesised from 9-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxoborolanyl)anthracene and Koser's reagent (hydroxy(tosyloxy))iodobenzene in dichloromethane at –60°C. After one hour of stirring at –60°C, the reaction mixture is warmed to 0°C and extracted three times with a 5% $NaBF_4$ solution or a 5% NaBr solution in demiwater. The organic layer is separated, dried on $MgSO_4$, and the solvent is evaporated. The residue is washed with ethylacetate and pentane and evaporated to dryness. After repeated crystallisation pure **1**BF_4 is obtained in 9% and **1**Br in 15% yield. Both salts are somewhat thermolabile and prior to their use they are washed with diethyl ether and pentane.

*Photolysis of **1**BF_4 and **1**Br in methanol and trifluoroethanol*

The iodonium salts **1**BF_4 and **1**Br are photolyzed in argon-purged methanol at λ_{exc} =254 nm and 350 nm and in argon-purged trifluoroethanol (TFE) at λ_{exc} =254 nm, all at 3°C under an argon atmosphere (Scheme 1, Table 1). As with other iodonium salts, both carbon-iodine bonds of **1** are photolabile and prone to homolysis and heterolysis. Upon A bond cleavage, next to the leaving group 9-iodoanthracene (**2**), the nucleophilic substitution products with the solvent

3-OR and the reduction product benzene (**4**) are produced. Fission of bond B yields the leaving group iodobenzene (**5**) next to the nucleophilic substitution products with the solvent **6**-OR and the reduction product anthracene (**7**). The *ipso*-substitution product 9-phenylanthracene (**8**) may be formed through both cleavages. Nucleophilic substitution with the counter-ion bromide in the photolyses of **1**Br produces **6**-Br but no **3**-Br.

Scheme 1: Product formation upon photolysis of **1**BF_4 and **1**Br in methanol or trifluoroethanol.

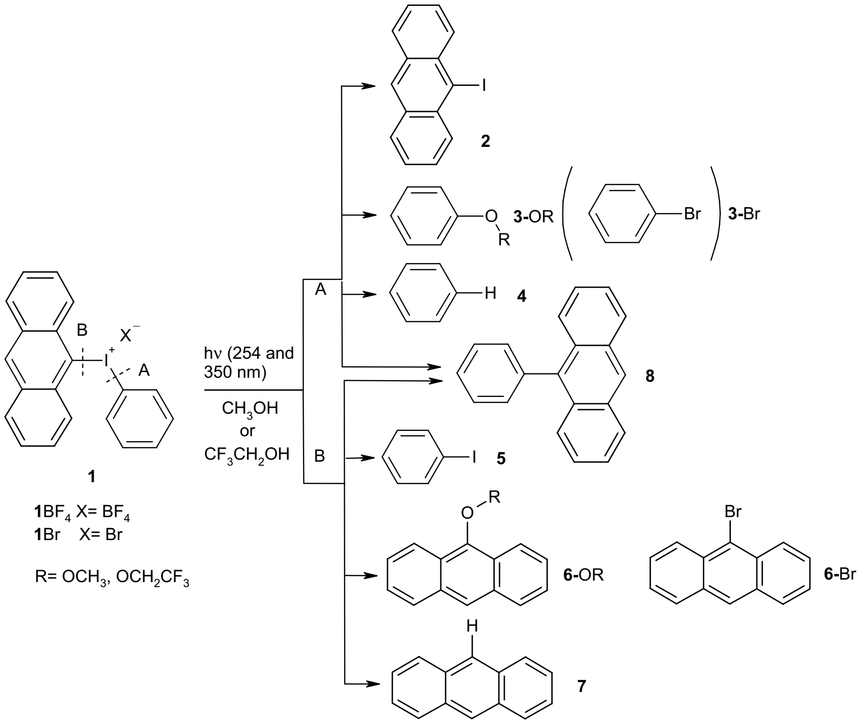


Table 1: Products of the photolyses of **1**BF_4 and **1**Br in methanol at λ_{exc}= 254 nm and 350 nm and of the photolysis of **1**BF_4 in trifluoroethanol at λ_{exc}= 254 nm[a,b].

	2	**3**-OR	**3**-Br	**4**	**5**	**6**-OR	**6**-Br	**7**	**8**
1BF_4 (254nm), MeOH	1.2	1.0	-	2.2	26.9	2.7	-	16.7	2.0
1BF_4 (350nm), MeOH	6.3	0.5	-	1.6	20.8	1.3	-	17.5	2.9
1BF_4 (254 nm),TFE	1.9	none	-	2.0	18.7	7.5	-	4.2	4.7
1Br (254nm), MeOH	trace	trace	none	1.0	9.8	0.9	0.7	6.5	0.5
1Br (350nm), MeOH	1.0	trace	none	1.5	9.6	0.7	1.7	8.9	0.5

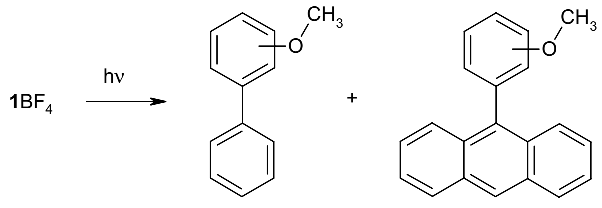
a) The data have been corrected for the small amounts of thermal products formed under the reaction conditions[6]. b) Product compositions after 45 minutes of irradiation (still low conversion).

Two side-products are commonly observed in the reactions: anthrone and anthraquinone. Anthrone is the hydrolysis product of 9-alkoxyanthracene (**6**-OR). Its low yield (ca. 0.2% after 45 minutes of irradiation) has been added to that of **6**-OR. Anthraquinone is formed in varying amounts and results from the photooxidation of **7** and derivatives with residual oxygen[7].

*Photolysis of **1**BF_4 in acetonitrile/anisole and trifluoroethanol/anisole*

To probe the nature of the reactive intermediates involved in the formation of its photoproducts, iodonium salt **1**BF_4 was also photolyzed, at three wavelengths of excitation, in acetonitrile (ACN), and in trifluoroethanol in the presence of anisole[8]. Next to the leaving groups **2** and **5** and the reduction products **4** and **7**, the Friedel-Crafts products 2-, 3-, and 4-methoxybiphenyl (**9*o***, ***m***, ***p***) and 9-(2-, 3-, and 4-methoxyphenyl)anthracene (**10*o***, ***m***, ***p***) are formed (Scheme 2, Table 2). No products of nucleophilic substitution with the solvents acetonitrile and trifluoroethanol (the Ritter products **3**-NHAc and **6**-NHAc, and **3**-OCH_2CF_3 and **6**-OCH_2CF_3) are found.

Scheme 2: Additional products upon photolysis of **1**BF_4 in ACN/Anisole or TFE/Anisole.



9*o*, ***m***, ***p*** **10*o***, ***m***, ***p***

Table 2: Products of the photolysis of **1**BF_4 at λ_{exc}= 254 nm, 300 nm and 350 nm in acetonitrile/ anisole (ACN) and trifluoroethanol/ anisole (TFE)[a,b].

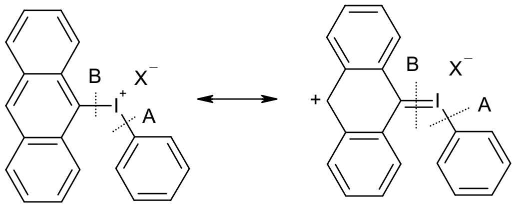
Exp	**2**	**4**	**9**	**9*o***:***m***:***p***	**5**	**7**	**10**	**10*o***:***m***:***p***
ACN(254)	9.5	0.6	4.4	62:11:17	17.7	9.4	8.7	68:4:28
ACN(300)	3.8	2.1	6.2	71:12:17	19.3	4.6	7.1	60:11:29
ACN(350)	1.8	0.9	3.2	74:13:14	13.9	3.2	5.5	60:11:29
TFE(254)	13.6	0.6	3.3	65:8:27	17.3	3.0	7.5	69:3:28
TFE(300)	5.4	1.6	2.3	67:11:22	18.7	2.6	7.0	77:6:17
TFE(350)	0.8	1.2	2.4	72:12:14	11.0	1.0	3.2	62:9:29

[a] Product mixture compositions after 45 minutes of irradiation. [b] Thermolysis of **1**BF_4 under the same reaction conditions does not produce the methoxybiaryls **9** and **10**.

*Photoproducts of **1**BF$_4$ and **1**Br in methanol and in trifluoroethanol*

In all experiments the formation of iodobenzene (**5**), product of the photocleavage of the anthryl C-I$^+$ (B) bond, significantly exceeds the formation of 9-iodoanthracene (**2**), product of fission of the phenyl C-I$^+$ (A) bond. This preponderance is reminiscent of the production of the leaving groups in the photolysis of *para*-dimethylamino-phenyl(phenyl)iodonium bromide (see Chapters 2 and 3) in which the B bond is also cleaved preferentially, probably because of the contribution to the photoinstability by a mesomeric form of the iodonium salt **1** (Scheme 3, **1**-**m**).

Scheme 3: Mesomeric form of **1**: **1**-**m**.



1

1-m

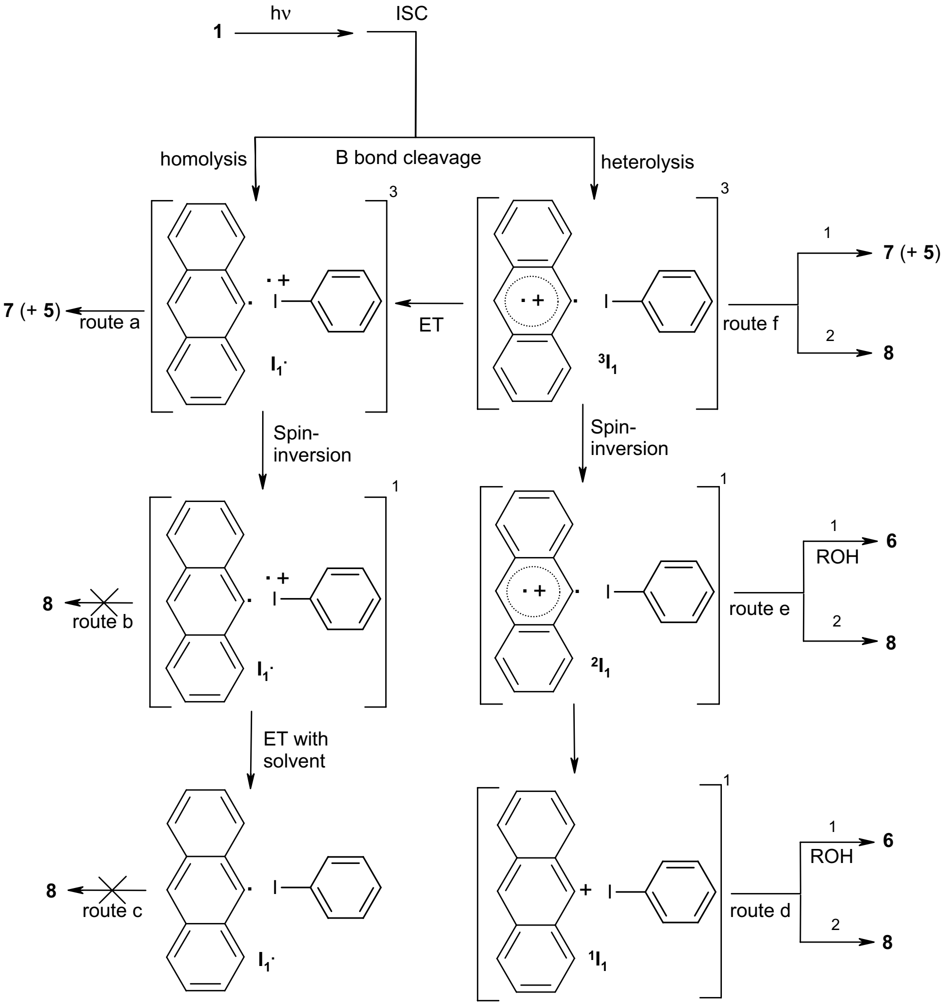
X = BF$_4$, Br

The production of anisole (**3**) upon A bond photocleavage of **1** in methanol, like the formation of that product in the photolysis of benzenediazonium tetrafluoroborate[8], and in the β-decay of [1,4]-ditritiobenzene in methanol[9], shows that a singlet phenyl cation (Ph^+) is generated. The product of nucleophilic addition of trifluoroethanol to Ph^+ (**3**-OCH_2CF_3) is not found, in line with the lower nucleophilicity of that solvent. Also, no nucleophilic substitution products with either of the counter-ions, tetrafluoroborate or bromide (**3**-F or **3**-Br) are observed. The reduction product benzene (**4**) may have been formed via hydrogen atom abstraction from the solvent by the phenyl radical (Ph•), generated upon homolysis of bond A. Alternatively, as argued in the preceding chapters, the formation of **4** may have occurred via hydrogen atom abstraction by the triplet phenyl cation, generated upon heterolysis of bond A, followed by electron transfer.

The production of 9-methoxyanthracene (**6**-OMe) in methanol is an indication of the photogeneration of the 9-anthryl cation in its closed-shell singlet manifold ($^1\mathbf{I}_1$) (Scheme 4, route d_1), in analogy with the formation of anisole by trapping of the closed shell phenyl cation by methanol. Alternatively, **6**-OMe may be produced from the singlet open-shell aryl cation ($^2\mathbf{I}_1$) (route e_1). Such a singlet carbenoid cation produces ethers, when trapped by methanol, as demonstrated for 4-N,N-diethylaminobenzenediazonium tetrafluoroborate in Chapters 3 and 4. Next, the electron-donating capacity of the annelating rings in an 9-anthryl cation, like that of the NR_2 group in the singlet 4-amino phenyl cation, is expected to enable the production of the open-shell singlet cation $^2\mathbf{I}_1$ out of a initially formed non-planar singlet closed shell cation $^1\mathbf{I}_1$' (Scheme 5) because of the large delocalisation of the positive charge in these systems.

The relatively high yield of **6**-OCH_2CF_3 in the photolysis of **1** in the less nucleophilic solvent trifluoroethanol is supportive of a carbene type insertion reaction rather than a nucleophilic addition reaction. The formation of **6** is therefore ascribed to the trapping of the open-shell singlet anthryl cation $^2\mathbf{I}_1$ (Scheme 4, route e_1).

Scheme 4: Possible reactive intermediates in the photolysis of **1** (B bond cleavage).



The production of **6**-Br in the photolysis of **1**Br in methanol also signals the intermediacy of an open-shell rather than a closed shell anthryl cation $^{1}\mathbf{I}_{1}'$. The bromide anion, a soft Lewis acid, for HSAB reasons is a good trap for the soft Lewis base open-shell cations $^{3}\mathbf{I}_{1}$ and $^{2}\mathbf{I}_{1}$ and less so for the hard Lewis base closed shell species $^{1}\mathbf{I}_{1}'$ [10].

Photoreduction yielding **7** is a major process in the photoreaction of **1**BF_4 and **1**Br. Its formation may occur via hydrogen atom abstraction from the solvent by the 9-anthryl radical ($\mathbf{I}_{1}\bullet$), produced via homolysis of the anthryl C-I bond in triplet excited **1** (Scheme 4, route a). $\mathbf{I}_{1}\bullet$ may also be produced via electron-transfer within the heterolytically formed triplet [$^{3}\mathbf{I}_{1}$ / **PhI**] pair (Scheme 4, route ET). This triplet cation may also produce **7** directly by abstraction of a hydrogen atom from the solvent, followed by electron transfer (route f_1).

The excess of reduction product **7** over alkylation product **8** in methanol hints at $\mathbf{I}_{1}\bullet$ rather than $^{3}\mathbf{I}_{1}$ as product-forming intermediate because triplet aryl cations usually display a preference for alkylation over hydrogen atom abstraction [8]. In the better cation-stabilising solvent trifluoroethanol the yields of hydrogen atom abstraction product **7** and alkylation product **8** are about the same, indicating that in this solvent relatively more $^{3}\mathbf{I}_{1}$ than $\mathbf{I}_{1}\bullet$ is generated compared to in methanol.

Other than in the photolyses of diphenyliodonium and naphthyl(phenyl)iodonium salts reported in Chapters 2 and 6 in this thesis, Friedel-Crafts type product formation upon B (and A) bond cleavage, is limited to one product, the *ipso* compound **8**. Clearly, *ipso* recombination of the fragments is far more efficient than regio-isomeric reaction steps. Since the photolysis of **1** gives mainly cleavage of bond B, the *ipso* selectivity is attributed to the reactivity of a reactive anthryl intermediate with iodobenzene rather than the reactivity of a phenyl intermediate with 9-iodoanthracene.

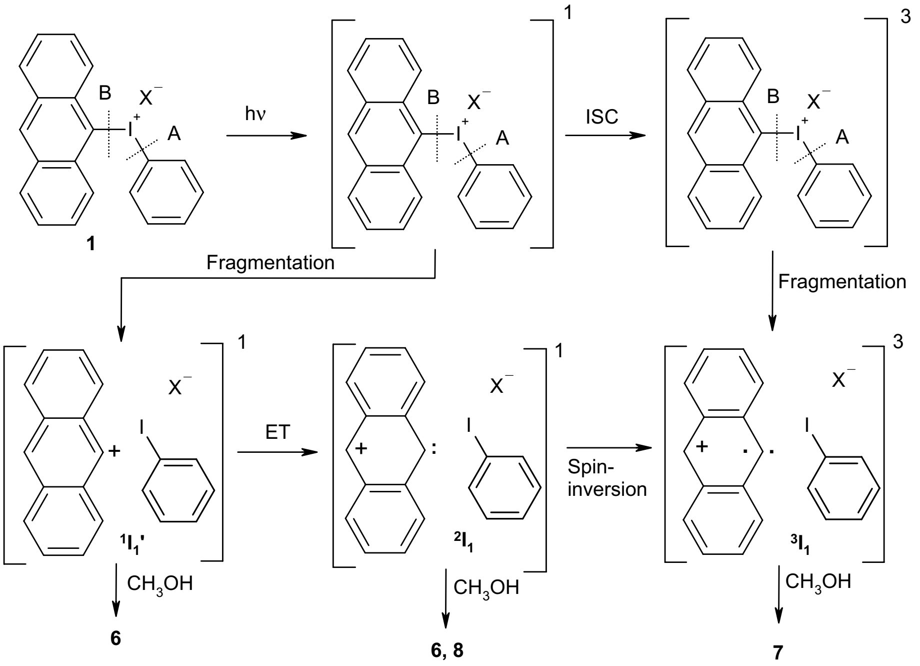
Recombination of the singlet [$\mathbf{I}_{1}\bullet$ / $\mathbf{PhI}^{\bullet+}$] pair (route b), formed by spin-inversion from the corresponding triplet pair, is ruled out as the source of **8** because the thermolysis of diphenyliodonium hexafluorophosphate, which produces the [**Ph•** / $\mathbf{PhI}^{\bullet+}$] pair, forms *o*-, *m*- and *p*-iodobiphenyl next to biphenyl. A similar pattern is expected for the [$\mathbf{I}_{1}\bullet$ / $\mathbf{PhI}^{\bullet+}$] pair. Attack of $\mathbf{I}_{1}\bullet$ on iodobenzene (route c), formed by ET with the solvent, is expected to produce a similar product pattern as the attack of a phenyl radical on iodobenzene (with *o*, *m*, *p* iodobiphenyls in a ratio of 55:28:17[11]). This product pattern is not found. Consequently, formation of **8** does not involve the intermediacy of $\mathbf{I}_{1}\bullet$.

A singlet closed shell anthryl cation ($^{1}\mathbf{I}_{1}$ or $^{1}\mathbf{I}_{1}'$) is expected to display regioselectivity in its reaction with iodobenzene (route d_2) which is similar to the Friedel-Crafts product formation in the detritiation of [1,4]-ditritiobenzene in the presence of chlorobenzene (with *o*, *m*, *p* chlorobiphenyls in a ratio of 50:29:21) [12]. The triplet anthryl cation ($^{3}\mathbf{I}_{1}$) is expected to display the same regioselectivity toward iodobenzene (route f_2) as found in the photolysis of 4-dimethylaminophenyl(phenyl)iodonium tetrafluoroborate (with *o*-, *m*- and *p*-iodobiphenyl in a ratio of 82:3:15)[13], which is argued to produce a triplet phenyl cation-iodobenzene pair. Thus, formation of solely the *ipso*-substitution product **8** does not occur via $^1\mathbf{I}_1$ (thus also not via $^1\mathbf{I}_1'$) or $^3\mathbf{I}_1$ as product-forming intermediate.

The selective formation of *ipso* product **8** is ascribed to the intermediacy of the open-shell singlet anthryl cation ($^2\mathbf{I}_1$) (route e_2). This species may react through two pathways with iodobenzene: formal insertion into the C-I bond, or addition to one of the double bonds of the aromatic ring. Since here only *ipso* product **8** is formed, unlike the typical products of carbenes[14] or nitrenes[15] with aromatic substrates, the electron-deficient carbenoid species $^2\mathbf{I}_1$ is thought to insert into the C-I bond, followed by loss of I^+.

The formation and trapping of the singlet open-shell anthryl cation $^2\mathbf{I}_1$ poses an interesting question regarding its generation. According to literature [5] and B3LYP/6-31G* calculations [16] the 9-anthryl cation $\mathbf{I}_1$ has a triplet (open-shell) ground state (S-T gap is -13.4 kcal/mol and -15.4 kcal/mol, respectively). Generation of the triplet cation $^3\mathbf{I}_1$ along the lines in Scheme 4 precludes the formation of the open-shell singlet species $^2\mathbf{I}_1$ because that would be a strongly endothermic process. So an alternative route of formation must exist for $^2\mathbf{I}_1$ (Scheme 5). This route is proposed to be similar to that of the formation of singlet aminophenyl cations, in which a singlet non planar closed shell $\mathbf{I}_1'$-NR_2 is initially formed that converts into an open-shell species $^2\mathbf{I}_1$-NR_2 (Chapters 3 and 4). The formation of intermediates from iodonium salt **1**, according to Scheme 5, is unlike the schemes employed in the literature[2] to account for the results of the photolysis of iodonium salts (Chapter 2, Scheme 1). The relative photoinstability of iodonium salt **1** (Scheme 3), compared to e.g. the parent diphenyliodonium salt, is thought to cause more efficient fission of C-I bonds in the singlet excited state rather than cleavage in the triplet excited state, even though a heavy atom is present in the molecule. The initially produced non-planar singlet anthryl cation $\mathbf{I}_1'$ produced initially converts to the singlet open-shell cation $^2\mathbf{I}_1$. This species is the product-forming intermediate in most of the trapping reactions.

Scheme 5: Formation of intermediates upon electronic excitation of **1** (B bond cleavage).



Wavelength dependence of product formation

The ratio of A bond cleavage to B bond cleavage products is wavelength-dependent: A/B = 1/23 at λ_{exc} = 254 nm and 1/3 at λ_{exc} = 350 nm. At λ_{exc} = 254 nm in acetonitril (Experimental Section, Table S1) the anthryl ligand is a more efficient antenna for UV light than the phenyl ligand of the parent compound ($\varepsilon_{254} = 9.1*10^3$). A preference for B bond cleavage may be expected. Further, the energy content of the light is enough to cause fission of the anthryl C-I bond that possesses partial double bond character (Scheme 3). At λ_{exc} = 350 nm the energy of the photons is probably not enough to cause fission of bond B even though most of the light will be harvested by the anthryl ligand. According to the theoretical evaluation in Chapter 2, the fission of the bond opposite to the excited ligand is a feature of iodonium salt photolysis.

*Photoproducts of **1**BF$_4$ in acetonitrile/ anisole and trifluoroethanol/ anisole*

The *o*, *m*, *p* ratios observed in the phenylation products **9*o*, *m*, *p*** at λ_{exc} = 254 nm in acetonitrile and in trifluoroethanol (Table 2) are similar to the ratio observed in the β-decay of ditritiobenzene in anisole (65:13:22) [12]. This indicates the intermediacy of the closed-shell singlet phenyl cation as arylating agent. Changing the excitation wavelength from 254 nm via 300 nm to 350 nm leads to a shift from *para* to *ortho* product formation. The *o*, *m*, *p* ratio of **9*o*, *m*, *p*** at λ_{exc} = 350 nm resembles that of the photolysis of iodobenzene in anisole (75:13:12), and is probably the result of a phenyl radical as arylating agent. Thus, the ratios of **9*o*, *m*, *p*** in acetonitrile and trifluoroethanol reflect a shift from the phenyl cation (at λ_{exc} = 254 nm) to the phenyl radical (at λ_{exc} = 350 nm) as product-forming intermediate. Attempts to generate the 9-anthryl radical from **6**-Br were not successful; no product formation was found.

The *o*, *m*, *p* ratios of the arylation products **10*o*, *m*, *p*** are also wavelength-dependent (Table 2, column 9). At λ_{exc}= 254 nm in acetonitrile/anisole the ratio resembles ratios found upon generation of an open-shell singlet aryl cation intermediate (64:3:33)[8]. Excitation at 300 or 350 nm gives **10*o*, *m*, *p*** ratios which show that a mix of closed-shell singlet and open-shell singlet anthryl cations reacts with anisole. The same is true for the irradiation of **1**BF_4 in trifluoroethanol/anisole at λ_{exc}= 254 nm and 350 nm. However, for reasons yet unknown, at λ_{exc}= 300 nm an *o*, *m*, *p* ratio is observed which indicates a triplet anthryl cation as intermediate.

Part 2: Photochemical generation of the 9-phenanthryl cation ($\mathbf{I}_2$).

Syntheses

9-Phenanthryl(phenyl)iodonium tetrafluoroborate (**11**) is synthesised from equimolar amounts of 9-phenanthrene boronic acid, iodobenzene diacetate and two equivalents of hydrogen tetrafluoroborate (dissolved in ether) in dichloromethane at –20°C. Extraction of the reaction mixture with a 5% $NaBF_4$ solution in demiwater, separation of the organic layer, drying on $MgSO_4$, followed by evaporation of the solvent yields **11** in 30%. 9-Bromomethylene-9*H*-fluorene (**17**) is prepared from methylene-9*H*-fluorene (**19**), which in turn was prepared by dehydration of 9-fluorenemethanol, by bromination and dehydrobromination according to a literature procedure[17].

*Photolysis of **11** in methanol*

Photolysis of iodonium salt **11** in argon-purged methanol at λ_{exc} = 254 nm at 4 °C under an argon atmosphere gives the primary photoproducts depicted in Scheme 6 and Table 3. Cleavage of bond A produces the nucleophilic substitution product anisole (**3**-OMe) and the reduction product benzene (**4**), next to the leaving group 9-iodophenanthrene (**12**)[18]. Fission of bond B yields the leaving group iodobenzene (**5**) as well as the nucleophilic substitution product 9-methoxyphenanthene (**14**-OMe) and the reduction product phenanthrene (**15**). All four possible Friedel-Crafts products, 9-(2-, 3-, and 4- iodophenyl)phenanthrene (**13*o***, ***m***, and ***p***) and the *ipso*-substitution product 9-phenylphenanthrene (**13*i***) are formed, but the former only in trace amounts.

Scheme 6: Product formation upon photolysis of **11** in methanol.

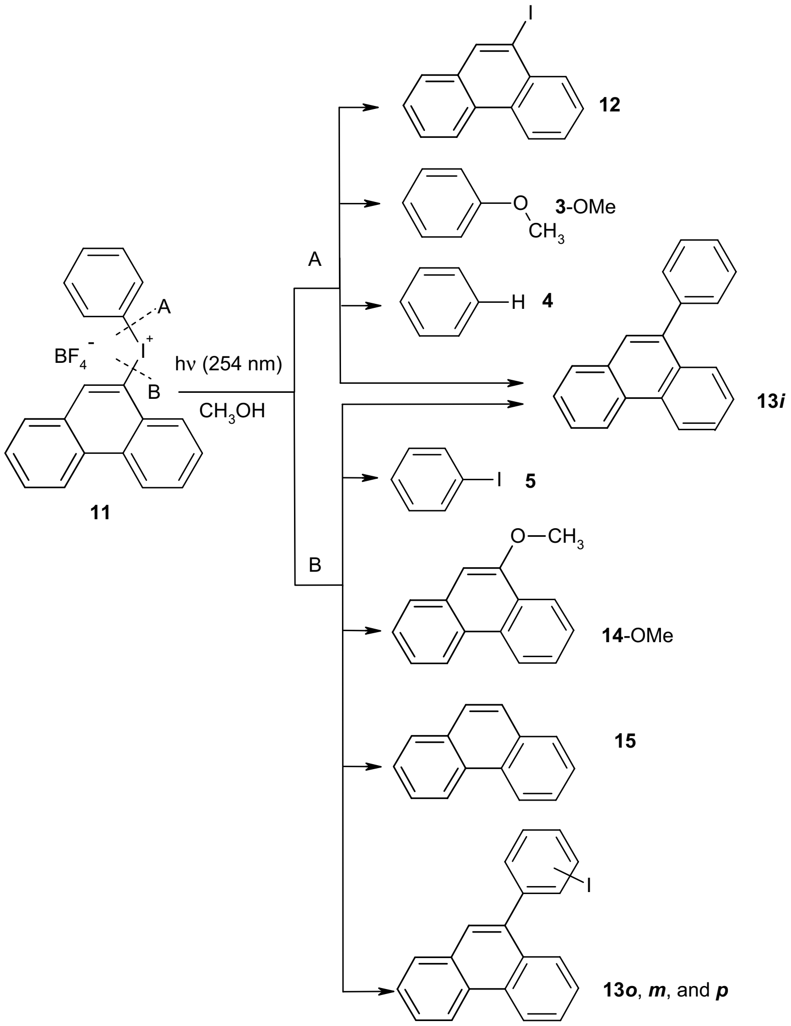


Table 3: Products of the photolysis of **11** in methanol at λ_{exc} = 254 nm at 4 °C[a,b,c].

Products:	**12**	**3**-OCH_3	**4**	**5**	**14**-OCH_3	**15**	**13**	**13o**: **m**: **p**	**13*i***
%	5	2	n.d.[c]	30	12	47	trace	76:6:19	1

[a] Under the reaction circumstances of the photolysis, thermolysis does not take place. [b] The composition of the product mixture after 90 minutes of irradiation. [c] The GC peak of benzene is obscured by those of the solvents, therefore the amount of **4** could not be determined (= n.d).

*Photolysis of **11** in trifluoroethanol/anisole*

To fingerprint the reactive intermediates formed in the irradiation of **11**, the salt is photolyzed in trifluoroethanol/anisole[8]. Next to the leaving groups **12** and **5** and the reduction products **4** and **15**, as new products 2-, 3-, and 4-methoxybiphenyl (**9*o***, ***m***, ***p***) and 9-(2-, 3-, and 4-methoxyphenyl)phenanthrene (**16*o***, ***m***, ***p***) are formed (Table 4). Of the products of nucleophilic substitution with the solvent trifluoroethanol (**3**-OCH_2CF_3 and **14**-OCH_2CF_3), only the latter is produced.

Because no literature data on the reactivity of phenanthryl radicals and cations toward anisole are available, the irradiation of 9-bromophenanthrene (**11**-Br) and 9-phenanthrenediazonium tetrafluoroborate (**11**-N_2) is performed under the same reaction conditions (Table 4). The photolysis of 9-bromophenanthrene (**11**-Br) yields mainly the reduction product phenanthrene (**15**) accompanied by the Friedel-Crafts products **16*o***, ***m***, ***p***. The photolysis of **11**-N_2 produces the reduction product phenanthrene (**15**), the nucleophilic substitution products 9-fluorophenanthrene (**14**-F) and 9-trifluoroethoxy phenanthrene (**14**-OCH_2CF_3), and the Friedel-Crafts products **16*o***, ***m***, ***p***.

Table 4: Products of the photolysis of compounds **11** in trifluoroethanol/anisole at λ_{exc}= 254 nm at 4 °C[a,b,c,d].

	s.m.	**12**	**3**-OCH_2CF_3	**4**	**9**	**9*o*:*m*:*p***	**5**	**14**-OCH_2CF_3	**15**	**16**	**16*o*:*m*:*p***
11	n.d.	15	none	n.d.[c]	11	66:11:23	19	2	0.4	10	65:11:25
11-Br	29	-	-	-	-	-	-	-	59	13	62:23:15
11-N_2	n.d.	-	-	-	-	-	-	10[b]	28	3	68:15:17

[a] The composition of the product mixture after 50 minutes of irradiation. [b] Also 5% of **14**-F is formed.
[c] The GC peak of benzene is obscured by those of the solvents, therefore the amount of **4** could not be determined (= n.d). [d] Under the reaction circumstances of the photolysis, thermolysis does not take place.

*Photoproducts of **11** in methanol*

The photolysis of **11** produces the leaving groups iodobenzene (**5**) and 9-iodophenanthrene (**12**) in a ratio of 6:1. This preference for B bond cleavage is less outspoken than in the case of **1**, where the ratio is 22:1. Like other π-donating substituents[19], the phenanthryl moiety is capable of delocalising the positive charge of the iodonium cation, but less so than the anthryl moiety.

Fission of bond B of **11** produces 9-methoxyphenanthrene (**14**-OMe) which is a strong indication for the occurrence of the 9-phenanthryl cation (**I**$_2$) formed through heterolytic cleavage of that bond. Just as anisole is the trapping product of the singlet closed shell phenyl cation, produced in the photolysis of benzenediazonium tetrafluoroborate or in the β-decay of ditritiobenzene, **14**-OMe is the trapping product of the singlet closed shell cation ^{1}**I**$_2$ by methanol. As discussed for the anthryl cation $\mathbf{I}_1$, trapping of the open-shell singlet cation $^2\mathbf{I}_2$ with methanol via a singlet carbene-type insertion into the O-H bond is also a possible pathway.

The major product of the irradiation of **11** is phenanthrene (**15**). This reduction product is either formed through homolysis of the C-I bond in triplet excited **11** followed by hydrogen atom abstraction from the solvent by the phenanthryl radical $\mathbf{I}_2$• or through hydrogen atom abstraction by the triplet cation $^3\mathbf{I}_2$ formed by heterolysis of the C-I bond in triplet excited **11**, followed by electron transfer.

The *ortho*, *meta* and *para* Friedel-Crafts products **13*o***, ***m***, ***p*** can be formed through all intermediates possible upon photohomolysis and photoheterolysis of bond B (cf. Scheme 4), the *ipso*-substitution product **13*i*** can even be formed through both A and B bond cleavage. The products **13*o***, ***m***, ***p*** are found in a ratio (75:6:19) very similar to the ratio in which the fragments of diphenyliodonium hexafluorophosphate recombine upon photolysis in the triplet sensitiser acetone at λ_{exc}= 300 nm (76:6:18)[2]. The latter ratio is due to the trapping of the triplet phenyl cation by the iodobenzene leaving group. Therefore **13*o***, ***m*** and ***p***, and also **13*i***, are attributed to the trapping of the triplet phenanthryl cation $^3\mathbf{I}_2$ by iodobenzene.

*Photoproducts of **11** in trifluoroethanol/anisole*

The *o*, *m*, *p* ratio of biaryls **9*o***, ***m***, ***p*** and **16*o***, ***m***, ***p*** (Table 4) are similar to the ratios observed upon photolysis of benzenediazonium tetrafluoroborate (68:13:19) and diphenyliodonium tetrafluoroborate (69:12:19) under the same reaction conditions[8], and also similar to the ratio reported for the β-decay of ditritiobenzene in anisole (65:13:22)[12]. As the latter three reactions all produce the singlet closed shell phenyl cation, products **9** and **16** are ascribed to the trapping of the closed shell phenanthryl cation $^1\mathbf{I}_2$ by anisole. The formation of the nucleophilic substitution product with the solvent **14**-OCH_2CF_3 supports this proposal. Formation of this ether is evidence for the intermediacy of the singlet closed shell phenanthryl cation $^1\mathbf{I}_2$. Its production from $^2\mathbf{I}_2$ is less likely because the amount of ether product is relatively small. As observed with the open-shell singlet anthryl cation $^2\mathbf{I}_1$, trapping of open-shell singlet species with trifluoroethanol is an relatively efficient reaction.

Further, arylation of anisole by the phenanthryl intermediate, producing **16**, is 25 times more abundant than formation of reduction product **15**. This finding clearly signals that the product-forming intermediate is not the phenanthryl radical ($\mathbf{I}_2$•), because with that intermediate the hydrogen atom abstraction reaction is expected to dominate. This was demonstrated to be the case by photolyzing 9-bromophenanthrene (**11**-Br) under the same reaction conditions. This gives 4.5 times more reduction product **15** than arylation products **16** (Table 4).

The control experiment in which 9-phenanthrenediazonium tetrafluoroborate (**11**-N_2) is photolyzed in trifluoroethanol/anisole, in the expectation that the closed shell cation $^1\mathbf{I}_2$ would be generated, indeed yields the nucleophilic substitution products **14**-F and **14**-OCH_2CF_3 derived from that ion. Surprisingly, a large amount of reduction product **15** is formed. Presumably, the diazonium salt is, in part, subject to photoinduced reduction by anisole. This produces phenanthryl-N_2• and next nitrogen and the phenanthryl radical $\mathbf{I_2}$• which abstracts a hydrogen atom from the solvent to yield phenanthrene (**15**). The *o*: *m*: *p* ratio in the arylation products **16** indicates that they are formed through both $^1\mathbf{I_2}$ and $\mathbf{I_2}$•.

The singlet closed shell phenanthryl cation $^1\mathbf{I_2}$, which reacts with anisole and solvent, is probably produced along the routes described for $^1\mathbf{I_1}$ in Scheme 4: hυ→ isc→$^3\mathbf{I_2}$→ $^2\mathbf{I_2}$ → $^1\mathbf{I_2}$. This triplet to singlet conversion may be energetically feasible in solution, even though $^1\mathbf{I_2}$ is B3LYP/6-31G*-calculated to be 4.8 kcal/mol less stable than $^3\mathbf{I_2}$ in vacuum (Experimental Section, Table S2)[16]. This singlet-triplet gap is much smaller, and thus less prohibitive, than in the case of the anthryl cation $\mathbf{I_1}$ (15.4 kcal/mol). In view of the method of calculation and the effect of solvent on singlet-triplet gaps observed with the naphthyl cations (See Chapter 5, Table 3) it is safe to assume that $^1\mathbf{I_2}$ and $^3\mathbf{I_2}$ are more or less isoenergetic.

*Photolysis of 9-bromomethylene-9H-fluorene (**17**) in methanol*

The photolysis of vinylic halide **17** in argon-purged methanol under argon atmosphere yields in part the same products as the photolysis of **11** (Scheme 7, Table 5).

Next to the vinylic nucleophilic substitution product 9-methoxymethylene-9*H*-fluorene (**18a**), (its hydrolysis product 9-formylfluorene (**18b**), and the vinylic reduction product methylene-9*H*-fluorene (**19**), the aromatic substitution product 9-methoxyphenanthrene (**14**-OCH_3) and the aromatic reduction product phenanthrene (**15**) are formed. Also a hitherto unidentified product with molecular mass 288, 290 (formally the addition product of methanol to **17**) is produced.

*Photoproducts of **17** in methanol*

The formation of 9-methoxy-9H-methylenefluorene (**18a**) (and its acid hydrolysis product **18b**) signals that the photolysis of **17** occurs (in part) through heterolysis of the C-Br bond. The primary vinyl cation $\mathbf{I_3}$ formed is trapped by methanol which produces vinyl ether **18a** (Scheme 8). Also heterolysis of the C-Br bond followed by electron-transfer with the leaving group[20,1d], of the C-Br bond also takes place. This generates the vinyl radical $\mathbf{I_3}$• which by hydrogen atom abstraction produces methylene-9*H*-fluorene (**19**). The formation of the trapping product of the phenanthryl cation $\mathbf{I_2}$ with methanol (i.e. **14**-OCH_3) marks the ability of vinyl cation $\mathbf{I_3}$ to undergo a 1,2 phenyl shift across the C=C bond[21] (Scheme 8). Such a shift has also been found in the thermolysis of methylene-9*H*-fluorene-9-diazonium salt[22]. The driving force for the rearrangement must be the instability of the primary vinyl cation $\mathbf{I_3}$ compared to the

Scheme 7: Product formation upon photolysis of **17** in methanol.

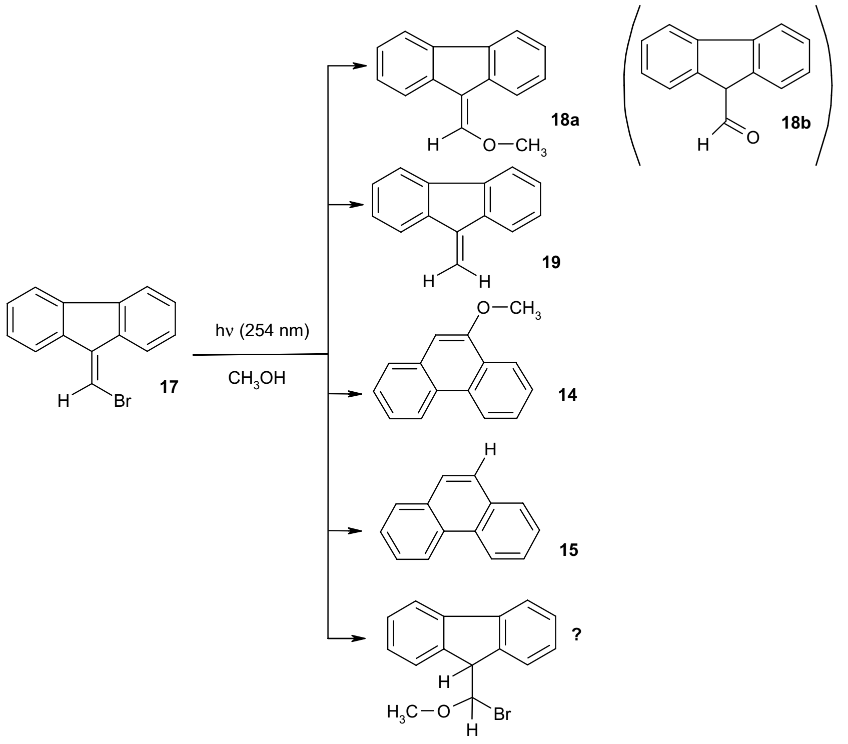


Table 5: Products of the photolysis of **17** in methanol at λ_{exc} = 254 nm at 4°C[a,b].

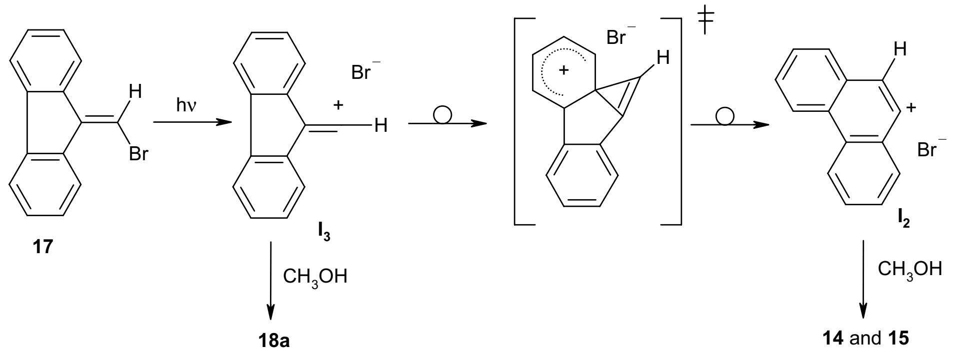
Products	**17**	**18a+b**	**19**	**14**-OMe	**15**	**?**
%	9	2	14	36	trace	39

[a] Under the reaction circumstances of the photolysis, thermolysis does not take place. [b] The composition of the product mixture after 120 minutes of irradiation.

aryl cation $\mathbf{I}_2$ (9.4 kcal/mol according to B3LYP/6-31G* calculations). With a phenyl group instead of a hydrogen atom at the α-position, which leads to a benzylic type stabilised vinyl cation, the shift is not observed [23]. The driving force for $\mathbf{I}_3$ to $\mathbf{I}_2$ allows rearrangement of $\mathbf{I}_3$ to effectively compete with addition of methanol to $\mathbf{I}_3$ (ratio **14**-OMe: **18** = 18:1).

A most remarkable photoproduct of **17** is the rearranged reduction product phenanthrene (**15**). It is well-established that vinyl cations undergo 1,2 phenyl shifts across the C=C bond[21]. Vinyl radicals, however, do not[24]. Possibly, upon irradiation, **17** produces the triplet vinyl cation $^3\mathbf{I}_3$ which upon rearrangement yields the triplet phenanthryl cation $^3\mathbf{I}_2$ which may be trapped by the bromide anion yielding **11**-Br (a product not observed) or abstract a hydrogen atom from the solvent and subsequently undergo electron-transfer to yield **15**. Alternatively, **15** is the

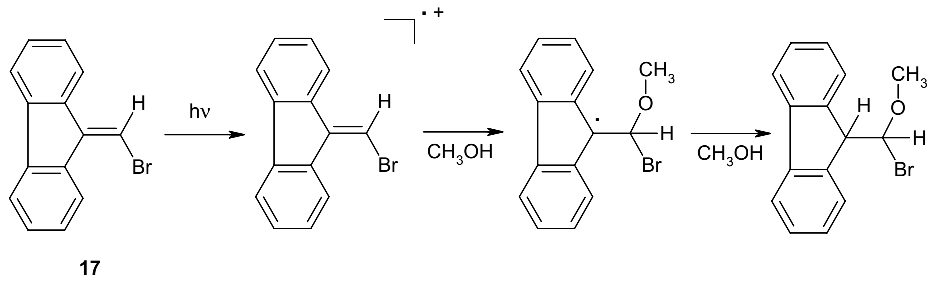
Scheme 8: Formation of the phenanthryl cation **I**$_2$ from the vinylic cation **I**$_3$.



result of electron-transfer between the aryl cation **I**$_2$ and the bromide leaving group[25], producing the **I**$_2$•/Br• radical pair. The aryl radical can abstract a hydrogen atom to yield **15**.

The product with mass 288, 290 is tentatively assigned to be the product of addition of methanol to **17**. This type of reactivity is encountered before in this thesis (Chapter 5, Scheme 5) and is thought to be photo-induced formation of the radical cation of **17** (via electron-transfer with the solvent) which next reacts with methanol (Scheme 9).

Scheme 9: Mechanism of formation of the m = 288, 290 product.



Conclusions

For the first time the 9-anthryl cation **I**$_1$ and the 9-phenanthryl cation **I**$_2$ have been generated and their reactivity has been studied. Trapping studies indicate that the product-forming intermediate, formed by photolysis of iodonium salt **1**, is the open-shell singlet state ^{2}**I**$_1$ of cation **I**$_1$. The photolysis of **1** is wavelength-dependent: at λ_{exc} = 254 nm the anthryl C-I bond of the iodonium salt is preferentially cleaved while at λ_{exc} = 300 and 350 nm that preference is less outspoken.

Trapping studies of $\mathbf{I}_2$ show that it reacts in its closed-shell singlet state $^1\mathbf{I}_2$ in both routes through which the cation was produced: directly, by photolysis of the corresponding phenanthryl iodonium salt, or indirectly, by photolysis of the vinylic bromide 9-bromomethylene-*9H*-fluorene. The latter compound yields a primary vinyl cation $\mathbf{I}_3$ which undergoes rearrangement to $\mathbf{I}_2$. In the direct route, the singlet cation is preceded by the triplet cation $^3\mathbf{I}_2$, which forms by heterolysis of the C-I bond in the triplet excited state of the salt. The triplet cation is partly trapped by the leaving group iodobenzene, and partly isomerises to the (probably) more stable singlet closed shell species. In the indirect route it is not clear at which stage triplet/singlet conversion takes place.

The above results open a new perspective for the tagging of substrates with a fluorescent moiety. The precursors **1**, **11** and **17** do not fluorescence, because of the presence of a heavy atom in the molecule, but the tag after the alkylation event does. This offers the possibility to track the tagged substrate without interference of the pre-fluorescent photolabile group.

Experimental Section

Materials

The compounds 9-anthryl(phenyl)iodonium tetrafluoroborate (**1**BF_4) and 9-anthryl(phenyl)-iodonium bromide (**1**Br) are synthesised from 9-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxoborolanyl) anthracene and Koser's reagent (hydroxy(tosyloxy)iodobenzene) in dichloromethane at –60°C. After 1 hour of stirring at –60°C, the reaction mixture is warmed to 0°C and extracted three times with a 5% $NaBF_4$ solution or one with a 5% NaBr solution in demiwater. The organic layer is separated, dried on $MgSO_4$, and the solvent is evaporated. The residue is washed with ethylacetate and pentane and evaporated to dryness. Product **1**-BF_4 is obtained, after 5 crystallisations from THF/pentane, in 9% yield. NMR (^{1}H, DMSO d6, δ): 7.20-7.35 (t, 3H); 7.35-7.50 (d, 2H); 7.60-7.75 (t, 2H); 7.75-7.90 (t, 2H); 7.90-8.00 (d, 2H); 8.10-8.30 (d, 2H); 8.55-8.70 (d, 2H); 8.95-9.05 (s, 1H). IR (neat, cm^{-1}): 386, 454, 518, 679-696-734, 1018 (BF_4^-), 1676, 3000.

Table S1: UV-VIS data for compound **1**BF_4 at $1.0*10^{-5}$ M.

Solvent	$\lambda_{max,1}$ (nm)	$\varepsilon_{max,1}$ ($M^{-1}cm^{-1}$)	$\lambda_{max,2}$ (nm)	$\varepsilon_{max,2}$ ($M^{-1}cm^{-1}$)
Acetonitrile	386.0	$8.1*10^3$	254.0	$1.3*10^5$
Acetic Acid	385.5	$8.3*10^3$	254.0	$1.3*10^5$
Trifluoroethanol	385.0	$7.9*10^3$	251.0	$1.5*10^5$
Methanol	385.0	$8.8*10^3$	254.0	$1.5*10^5$

Product **1**Br is obtained in 15% yield. NMR (^{1}H, DMSO d6, δ): 7.15-7.35 (m, 5H); 7.55-7.70 (t, 2H); 7.70-7.85 (t, 2H); 7.85-7.95 (d, 2H); 8.10-8.20 (d, 2H); 8.50-8.60 (d, 2H); 8.90-8.95 (s, 1H).

Both salts are somewhat thermolabile, and they are washed with diethyl ether and pentane prior to their use. 9-Bromoanthracene (**6**-Br) is commercially available.

9-Phenanthryl(phenyl)iodonium tetrafluoroborate (**11**BF_4) is synthesised from equimolar amounts of 9-phenanthrene boronic acid, iodobenzene diacetate and two equivalents of hydrogen tetrafluoroborate (dissolved in ether) in dichloromethane at –20°C. Extraction of the reaction mixture with a 5% $NaBF_4$ solution in demiwater, separation of the organic layer and drying on $MgSO_4$, followed by evaporation of the solvent yields **11**BF_4 in 30% yield. NMR (^1H, $CDCl_3$, δ): 6.7-6.8 (d, 2H); 7.1-7.3 (q, 1H); 7.3-7.5 (t, 2H); 7.6-7.8 (m, 4H); 7.8-7.95 (d, 2H); 8.5-8.6 (d, 2H); 8.7 (s, 1H). NMR (^{13}C, Solid): 114.1 (C-I^+ phenanthryl), 119.6 (C-I^+ phenyl), 121.9, 126.6, 128.8, 131.6, 132.9, 133.8, 135.1, 136.3, 139.3. IR (neat, cm $^{-1}$): 406, 430, 449, 504, 519, 648-678-719-748, 1018 (BF_4^-), 3064. 9-Phenanthryldiazonium tetrafluoroborate **11**-N_2 is prepared from the corresponding amine by diazotation in 15% aqueous hydrotetrafluoroboric acid with 1.1 equivalent sodium nitrite at melting ice temperature. 9-Bromophenanthrene (**11**-Br) is commercially available.

9-Bromomethylene-9*H*-fluorene (**17**) is prepared from methylene-9*H*-fluorene (**19**), which in turn was prepared by dehydratation of 9-fluorenylmethanol, by bromination in CCl_4 followed by dehydrobromination with a saturated $NaHCO_3$ solution in demiwater[17]. After extraction with CCl_4, the combined organic layers are dried on $MgSO_4$ and the solvent is evaporated. The yield of **17** is 80% (based on **19**) NMR (^1H, $CDCl_3$, δ): 7.26 (s, 1H), 7.40 (m, 4H), 7.60 (d, 2H), 7.66 (d, 2H).

Photochemistry

The photochemical reactions in methanol or trifluoroethanol were carried out in quartz tubes equipped with a rubber seal, that are placed in a merry-go-round apparatus. A Hanau TNN-15/32 low pressure mercury lamp placed in a water cooled quartz tube is used to supply light with a main emission at $\lambda = 254$ nm. For the irradiations 0.02 M solutions of the photolabile compounds **1**BF_4, **1**Br, **6**-Br, **11**BF_4, **11**-Br, **11**-N_2 or **17** in 10 mL methanol are prepared. 25 µL n-decane is added as internal standard. Samples (200 µl) are taken at t = 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 90 and 120 minutes of irradiation. Up till 50 minutes for compounds **1**, 90 minutes for compounds **11**, and 120 minutes for compound **6** and **17** the conversions are still low and all products are primary photoproducts. The samples are added to 500 µL water and 300 µL ethylacetate. The organic layers are analyzed by GC and GC-MS. The 90 minutes irradiation mixtures are poured into 50 mL water and extracted with 10 mL ethylacetate. The organic layer is separated and dried on $MgSO_4$. The solvent is evaporated and the residues were redissolved in 0.5 mL dichloromethane for GC and GC-MS analysis.

The products studies at λ_{exc}= 254, 300 and 350 nm are carried out in a Rayonet Reactor (RPR200) fitted with seven 254, 300 or 350 nm lamps. Samples and analysis as above.

The photochemical reactions in acetonitrile/anisole and trifluoroethanol/anisole were carried out in quartz tubes equipped with a rubber seal. The starting materials were dissolved at 0.02 M in 10 mL 1/1 (v/v) acetonitrile/anisole or 1/1 (v/v) trifluoroethanol/anisole. 25 µL *n*-Decane was used as internal standard. The tubes were placed in a Rayonet Reactor (RPR200) fitted with seven 2539 Å lamps. The photolyses of the photolabile compounds were followed as a function of time by taking aliquots (0.2 mL sample) and adding them to 0.5 mL water + 0.3 mL ethylacetate. The organic layers were analyzed by GC and GC-MS.

Photoproducts

The assignment of the structures of the photoproducts by GC and GC-MS was confirmed by coinjection of commercially available or independently prepared products. Compounds **3**-OCH_3, **3**-NHAc (not observed in the product mixtures), **3**-Br, **4**, **5**, **6**-Br, **7**, **8**, **9*o***, ***m***, ***p***, **11**-Br, and **15** are commercially available. Products **2**[26], **3**-OCH_2CF_3[4d], **6**-OCH_3[27], **6**-OCH_2CF_3[28], **6**-NHAc (not observed in the product mixtures)[29], **10*o***, ***m***, ***p***[30], **12**[26], **13*i***[31], **14**-OMe[32], **14**-F[33], **18a**[34] and **18b**[34], and **19**[35] are prepared according to literature procedures. The structures of **13*o***, ***m***, ***p***, **16*o***, ***m***, ***p*** and **14**-OCH_2CF_3 are assigned tentatively.

Quantum Chemical Calculations

Little or no information is available about the ground state multiplicity and the singlet-triplet gaps of anthryl, phenanthryl and larger aromatic cations. A short preliminary quantum chemical study is performed mapping the ground state of various aryl cations, their singlet-triplet gaps and aspects of their structures (Table S2). The results of the B3LYP/6-31G* are compared with the most recent theoretical data calculations on the properties of aryl cations[5,36,37].

Table S2: Results of the quantum chemical studies.

Method	Property	Phenyl	1-Naphthyl	9-Anthryl	9-Phenanthryl	1-Pyrenyl
AM1	S-T gap	+7.1	-14.4	-1.0	-13.9	-27.8
AM1	$^1C^+$ ∠	141°	143°	143°	144°	142°
AM1	$^3C^+$ ∠	131°	129°	131°	130°	130°
(U)HF 6-31G*	S-T gap	-11.0	-28.2	-42.2	-34.0	-47.2
(U)HF 6-31G*	$^1C^+$ ∠	146°	148°	113°	149°	148°
(U)HF 6-31G*	$^3C^+$ ∠	125°	125°	127°	127°	125°
B3LYP 6-31G*	S-T gap	+22.6	-2.6	-15.4	-4.8	-14.8
B3LYP 6-31G*	$^1C^+$ ∠	147°	149°	143°	142°	137°
B3LYP 6-31G*	$^3C^+$ ∠	124°	127°	128°	127°	126°
Literature[5]	S-T gap	+19.6	-0.6	-13.4	-	-15.3[37]
Literature[5]	$^1C^+$ ∠	147.3°	148.6°	-	-	-
Literature[5]	$^3C^+$ ∠	127.7°	-	-	-	-

Equipment

UV spectra were recorded at room temperature on a double beam Varian DMS 200 Spectrophotometer, if applicable with pure solvent in the reference cell. ^{1}H-NMR spectra were recorded on a DMX 300, using DMSO D_6 as solvent. As analytical GC a Hewlett-Packard 6890 model was used, equipped with an automatic injector, fitted with a CP-Sil5-CB column (25 m, ø = 0.25 mm, 1.2 μm) using hydrogen as carrier gas. The Flame-Ionisation Detector (FID) was calibrated using commercially available reference chemicals. HP Chemstation was used for the analysis of the analytical data. Mass spectra were measured on a GC-MS set-up consisting of a Hewlett-Packard 5890 series 2 model GC, equipped with an automatic injector, fitted with a AT-5MS column (30 m, ø = 0.25 mm, 0.25 μm) using helium as carrier gas. The GC was coupled to a Finnigan Mat SSQ 710 mass spectrometer, employing electron-impact as the ionisation method. The GC-MS data was analyzed with Xcaliber.

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