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Selective alkylation by photogenerated aryl and vinyl cation

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Chapter 3 | Photogeneration and reactivity of 4-aminophenyl and 4-hydroxyphenyl cations; the influence of the leaving groups

Introduction

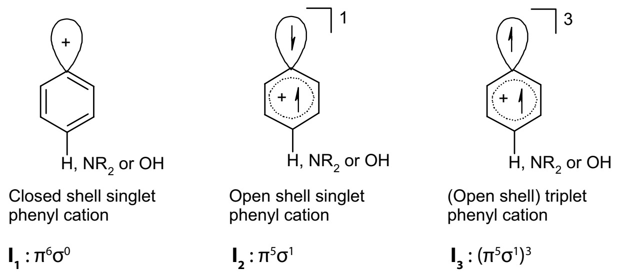
For quite some time now phenyl cations have been proposed as reactive intermediates, mainly in the thermal solvolysis of phenyldiazonium salts[1,2]. Even today the actual mechanism of this thermal dediazoniation reaction is still a matter of debate [3]. Unequivocal means to generate phenyl cations are the radiolytic extrusion of helium from tritiated aromatic compounds[4], and photolytic dediazoniation of photolabile benzenediazonium salts that proceed through an unimolecular mechanism[2,5]. These methods allowed studies of the reactivity of phenyl cations [6], but until recently only singlet species were synthesised[7].

Photochemistry allows preferential generation of triplet excited states over singlet excited states[8]. Appropriate substituents enhance intersystem crossing (ISC) which leads to efficient conversion of the singlet excited state formed after absorption of a photon into a triplet excited state. Alternatively, by adding a suitable sensitiser and by using selective excitation, the photolabile compound will be formed directly in a triplet excited state, by triplet energy transfer. Dissociation of a bond in a triplet excited state yields the reactive intermediate in its triplet manifold and a leaving group. This has been e.g. demonstrated in the photolysis of 4-nitro- and 4-acetyl substituted phenyldiazonium salts[9]. Both substituents enhance ISC which yields triplet phenyl cations as product-forming intermediates, even though the singlet state of these phenyl cations is of lower energy. The reactivity of the phenyl cation thus is a function of the type of substituent (and its position) at the precursor and not necessarily of the stability of the cation itself. A curiosity-driven study was started whether or not it is possible to generate a singlet phenyl cation as product-forming intermediate that possesses a triplet ground state.

Of the parent phenyl cation[10] the singlet closed shell ($\pi^6\sigma^0$) ground state ($^1A_1$) is calculated at the CAS-MP2 level to be 24.6 kcal/mol more stable than the triplet ($\pi^5\sigma^1$) phenyl cation ($^3B_1$)[11]. The open-shell ($\pi^5\sigma^1$) singlet phenyl cation ($^1B_1$) is computed to be 14 kcal/mol higher in energy than the $^3B_1$ cation. At other levels of theory larger or smaller differences are calculated but the trend in stabilities of the isomers stays the same[3e,12,13].

Amino- or hydroxy substituents positioned at the *para* position of a phenyl cation change the order of stability of the isomers[14]. The open-shell triplet phenyl cation $\mathbf{I}_3$ is calculated to be 9 kcal/mol more stable than (amino group), or about equal in energy with (hydroxy group), the closed-shell singlet phenyl cations $\mathbf{I}_1$[15]. Singlet open-shell structures $\mathbf{I}_2$ were not included in these calculations.

Figure 1: The phenyl cations.

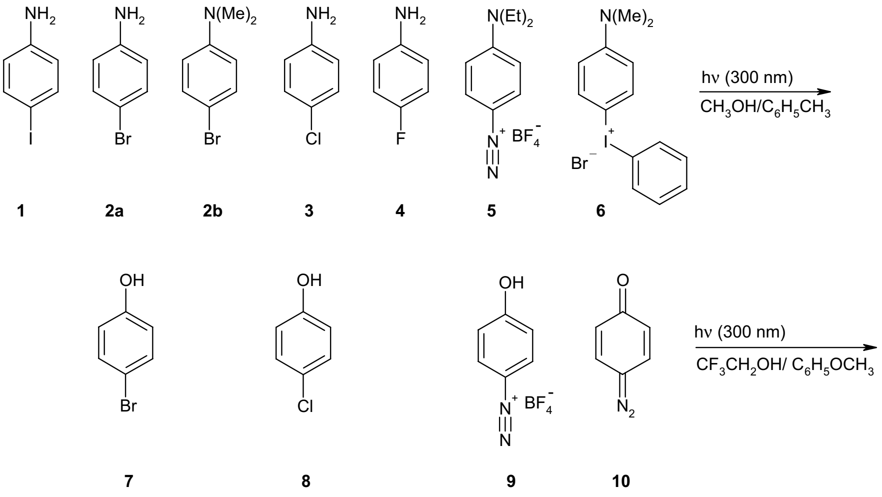


Reports in the literature suggest that the photolysis of 4-chloroaniline is a good entry to the 4-aminophenyl cation in its triplet ground state[6]. In the first part of this work, 4-chloroaniline is therefore subjected to competition experiments with various nucleophiles, which chart the chemoselectivity and the regioselectivity of the alleged phenyl cation intermediate.

With this information in hand, the photochemical behaviour of 4-iodoaniline (**1**), 4-bromoaniline (**2a**), 4-bromo-N,N-dimethylaniline (**2b**), 4-chloroaniline (**3**), 4-fluoroaniline (**4**), N,N-diethylaminobenzenediazonium tetrafluoroborate (**5**) and 4-N,N-dimethylaminophenyl-(phenyl)iodonium bromide (**6**) in methanol in the presence of toluene is compared (Chart 1). The product patterns obtained as a function of the leaving group reflect the reactivity and thus the nature of various 4-aminophenyl cations.

Next, the photochemistry of the 4-hydroxy substituted phenyl cation precursors 4-bromophenol (**7**), 4-chlorophenol (**8**), and 4-hydroxybenzenediazonium tetrafluoroborate (**9**) is studied

Chart 1: Compounds studied.



in trifluoroethanol in the presence of anisole. For purpose of reference and to probe the importance of deprotonation of the 4-hydroxyphenyl cation[17], 4-diazoquinone (**10)** is irradiated under the same reaction conditions.

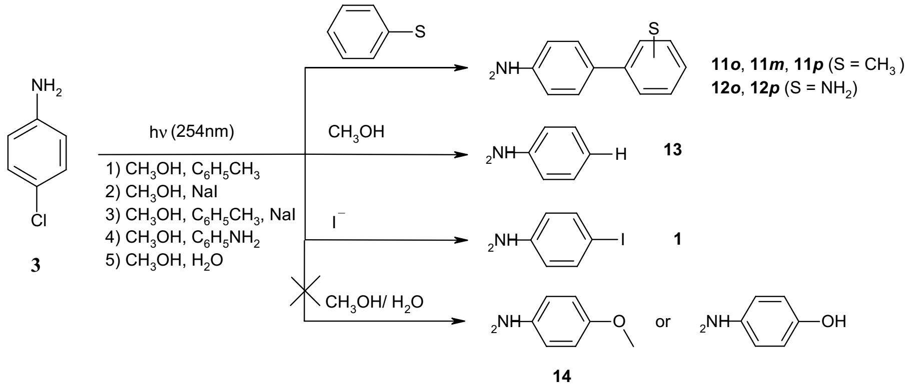
Finally, the structures and stabilities of the singlet and triplet isomers of the 4-aminophenyl and the 4-hydroxyphenyl cations $\mathbf{I}_1$, $\mathbf{I}_2$ and $\mathbf{I}_3$ were studied by quantum chemical methods.

Results

*Photolysis of 4-chloroaniline (**3**), competition experiments*

The photoreaction of **3** at λ_{exc} = 254 nm was carried out at 0.05 M in methanol in the presence of the nucleophiles toluene (1/1 v/v), iodide (NaI, 0.05 M), a combination of the latter two, and aniline (1/1 v/v). Also the effect of the presence of water (2% and 1 v/v) was evaluated. The primary photoproducts under the various reaction conditions are depicted in Scheme 1.

Scheme 1: The photolysis of **3**, competition experiments.



(1) The photolysis of **3** in methanol in the presence of toluene yields the Friedel-Crafts products 2'-, 3'- and 4'-methyl-4-aminobiphenyl (**11*o***, **11*m*** and **11*p***) in a 78:4:18 ratio, next to the reductive dehalogenation product aniline (**13**). Also 2,4'-aminophenyl-4-chloroaniline is formed in trace amount. (2) With 0.05 M NaI in methanol, the main product is 4-iodoaniline (**1**). Reduction product **13** is produced as well. (3) With toluene as extra nucleophile, **11*o***, ***m***, ***p*** and **1** are the major products accompanied by some aniline (**13**). (4) The photolysis of **3** in methanol in the presence of aniline produces 2'- and 4'-amino-4-aminobiphenyl (**12*o***, **12*p***) in a 88:12 ratio. As side product diazobenzene is formed. (5) The presence of water in methanol does not change the product pattern: In methanol with 2% water and in methanol/water 1/1

v/v, the only photoproduct is aniline (**13**). In all five reactions no 4-aminoanisole (**14**) or 4-aminophenol is produced.

Photogeneration of 4-amino substituted phenyl cations

The irradiations of the 4-haloanilines **1**, **2a, 2b** and **4** (λ_{exc} = 300 nm) at 0.05 M in methanol/toluene (1/1 v/v) all yield the same types of products as the photolysis of **3** (Scheme 1). Differences occur in the conversions and the product profiles (Table 1, entries 1-5). The conversion of starting material is less efficient in the photoreaction of **1**, **2a** and **2b** than with **3** and **4**. The yield of the Friedel-Crafts arylation products **11*o***, **11*m***, **11*p*** is lowest in the photolysis of **1**, **2a** and **2b** and highest in the photoreaction of **3** and **4**. Photoreduction, producing **13**, is not a major product-forming route in the photolysis of **3** and **4** but becomes more important in the photolysis of **2a** and **2b**, and is the major product-forming route in the irradiation of **1**.

A typical feature of these photoreactions is the *o*: *m*: *p* ratio of the Friedel-Crafts products **11**. A low yield of *meta* isomer is obtained with **2a**, **2b**, **3** and **4** whereas in the photolysis of **1** the *meta* and *para* isomer yields are practically the same.

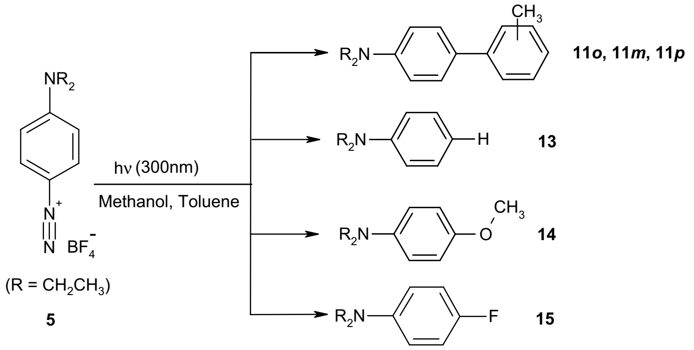
Table 1: Results of the photolyses of **1**-**6** (0.05 M) in methanol/toluene (1/1) at λ_{exc}= 300 nm[a].

Compound	LG	s.m. left	11	11*o*: *m*: *p*	13	14
1	I^-	70	6	79:10:11	20	-
2a	Br^-	87	8	83:6:11	5	-
2b	Br^-	86	7	79:6:15	6	-
3	Cl^-	32	58	78:4:18	6	-
4	F^-	37	53	78:3:19	8	-
5[b]	N_2	nd.	42	65:5:29	6	32[d]
6[b]	PhI	nd.	22[c]	73:8:19	5	6

[a] Percentages of total product formation (GC) after 2 hrs. of irradiation, nd = not determined. [b] Percentages after 1 hour of irradiation. [c] Also arylation of the leaving group occurs yielding **17a** and **17*o***, **17*m***, **17*p*** (*o*, *m*, *p* ratio 73:3:35) in 7%. [d] Also another nucleophilic substitution product, **15**, is formed in 6%.

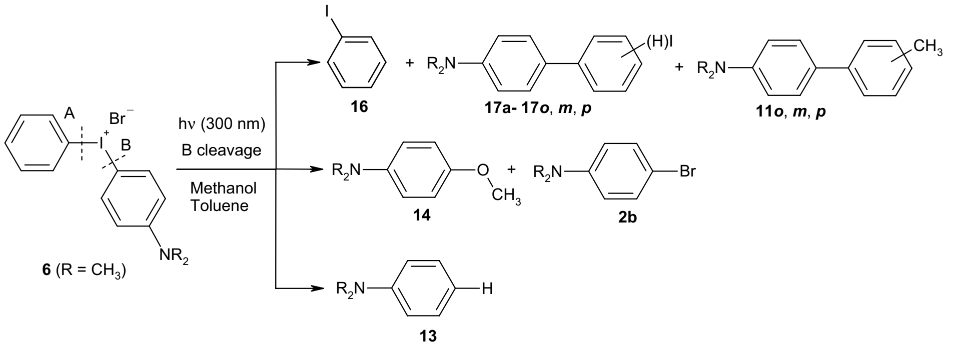
In the photolysis of 4-N,N-diethylaminophenyldiazonium tetrafluoroborate (**5**) in methanol/toluene the main products are 2', 3' and 4'-methyl-4-N,N-diethylaminobiphenyls **11*o***, **11*m***, **11*p*** (R = CH_2CH_3), the Friedel-Crafts products with toluene (Scheme 2). An unusually high percentage of **11*p*** is found (Table 1, entry 6). Here, the nucleophilic substitution product with methanol, 4-N,N-diethylaminoanisole (**14**, R = CH_2CH_3) is also a major product. Minor products are the Schiemann product 4-fluoro-N,N-diethylaminobenzene (**15**) and the reduction product N,N-diethylaniline (**13**, R = CH_2CH_3).

Scheme 2: The photolysis of **5**.



In the photolysis of 4-N,N-dimethylaminophenyl(phenyl)iodonium bromide (**6**) products of cleavage of both C-I bonds are formed but only the products resulting from the cleavage of bond B will be discussed (Scheme 3). Next to the leaving group iodobenzene (**16**), the Friedel-Crafts type products 4-N,N-dimethylaminobiphenyl (**17a**), 2'-, 3'- and 4'-iodo-4-N,N-dimethylamino-biphenyl (**17*o***, **17*m***, **17*p***) and 2'-, 3'- and 4'-methyl-4-N,N-dimethylaminobiphenyl (**11*o***, **11*m***, **11*p***, R = CH_3) are produced, as well as the nucleophilic substitution products 4-methoxy-N,N-dimethylaniline (**14**, R = CH_3) and 4-bromo-N,N-dimethylaniline (**2b**). Also the reduction product N,N-dimethylaniline (**13**, R = CH_3) is formed (Scheme 3, Table 1, entry 7).

Scheme 3: The photolysis of **6**: B bond cleavage products.



Photogeneration of 4-hydroxy substituted phenyl cations

The photolyses of 4-bromo- and 4-chlorophenol (**7**, **8**) in trifluoroethanol in the presence of anisole produce the Friedel-Crafts products 2'-, 3'-, 4'-methoxy-4-hydroxybiphenyls (**18*o***, ***m***, ***p***) and the reduction product phenol (**19**). Little or no nucleophilic substitution product 4-trifluoroethoxyphenol (**20**) is formed (Scheme 4, Table 2). The photolysis of *para*-hydroxy-benzenediazonium tetrafluoroborate (**9**) yields a larger amount of ether **20** next to the biaryls

18*o*, *m*, *p*, and phenol (**19**). The photoreaction of 4-diazoquinone (**10**) under the same reaction conditions produces the same products (**18*o***, ***m***, ***p***, **19** and **20**) albeit in a different ratio. The photoconversion of **8** is about twice as efficient as that of **7**, under the same reaction conditions. The photolyses of **7** and **9** on one hand and **8** and **10** on the other hand produce **18** in quite different *o*, *m*, *p* ratios.

Scheme 4: The photolyses of **7**-**10**.

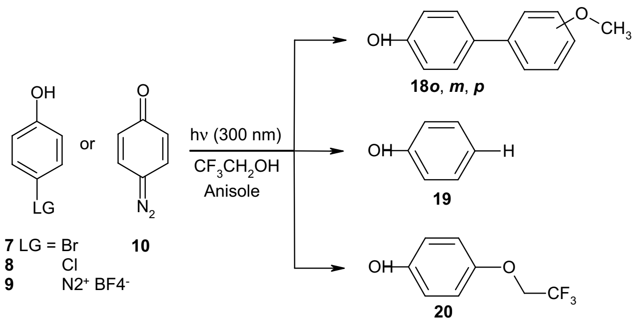


Table 2: Results of the photolyses of **7**-**10** (0.05 M) in trifluoroethanol/ anisole 1/1 v/v, at λ_{exc} = 300 nm[a].

Compound	LG	s.m. left	18	18*o*: *m*: *p*	19	20
7[b]	Br$^-$	32	16	66:14:20	28	0.5
8	Cl$^-$	18	55	80:1:19	3.5	-
9[c]	N_2	nd.	40	66:9:25	9.2	3.1
10	N_2	nd.	74	72:0:28	1.1	2.7

[a] Percentages of total yield (GC) after 2 hrs of irradiation. [b] In this irradiation also some 4-bromoanisole is formed. This side product may stem from photoinduced electron transfer followed by cleavage of the C-Br bond of the radical anion and subsequent recombination of the bromide anion with the radical anion of anisole. [c] Percentages after 1 hour of irradiation.

Quantum chemical studies

To get insight in the mechanisms of reaction of the 4-aminophenyl cation and the 4-hydroxyphenyl cation, it is useful to inspect the electronic states of these ions. The relative energies of the 4-aminophenyl- and 4-hydroxyphenyl cation isomers **I_1**-**I_3** are calculated[18] at the CASSCF(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d) level and the CASSCF(4,5)/6-31G(d)//CASSCF(4,5)/6-31G(d) level, respectively, and compared with literature data on these cations [14,15] and the parent phenyl cation [11,13d] (Table 3). CASSCF(8,8) level of theory calculations on the 4-hydroxyphenyl cation have not yet been successful. For the first time the open-shell singlet phenyl cations **I_2**-NH_2 and **I_2**-OH are considered as actual reactive intermediates.

Table 3: Relative stabilities of the 4-amino and 4-hydroxyphenyl cations $\mathbf{I}_1$-$\mathbf{I}_3$ (kcal/mol).

	Parent[11]	**I**-NH_2	**I**-NH_2[15]	**I**-OH	**I**-OH[15]
Closed-shell singlet ($\mathbf{I}_1$)	0	0[a]	0	0[b]	0
Non-planar singlet ($\mathbf{I}_1'$)	-	-17.5[a]	-	-4.2[b]	-
Open-shell Singlet ($\mathbf{I}_2$)	+38.6	-17.1[a]	-	+3.1[b]	-
Open-shell Triplet ($\mathbf{I}_3$)	+24.6	-33.6[a]	-9.0	-11.5[b]	0.2

[a] CASSCF(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d). [b] CASSCF(4,5)/6-31G(d)//CASSCF(4,5)/6-31G(d).

The parent phenyl cation can be considered as a benzene molecule minus a hydride ion [14]; in that case six π electrons (occupying 3 molecular orbitals) and one vacant σ orbital are present. There are two planes of symmetry, i.e. the plane in which the nuclei lie and a plane orthogonal thereupon: the cation has C_{2v} symmetry[11-14]. The closed-shell singlet state ($\mathbf{I}_1$) is represented as structure $\mathbf{I}_1$ ($\pi^6\sigma^0$) (Figure 1). It is also possible that the vacant orbital is occupied by one of the π electrons; the open-shell structure ($\pi^5\sigma^1$) is either a singlet ($\mathbf{I}_2$) or a triplet state ($\mathbf{I}_3$). (structures $\mathbf{I}_2$ and $\mathbf{I}_3$ in Figure 1). Published ab initio molecular orbital calculations indicate that the ground state of the parent phenyl cation is a singlet closed shell species ($\pi^6\sigma^0$)($\mathbf{I}_1$)[11]. At the CAS-MP2 level of calculation this state is 24.6 kcal/mol more stable than the triplet ($\pi^5\sigma^1$) state ($\mathbf{I}_3$). The open-shell ($\pi^5\sigma^1$) singlet phenyl cation ($\mathbf{I}_2$) is computed to be 14 kcal/mol higher in energy than the $\mathbf{I}_3$ cation at the optimum geometry of the phenyl radical. At the B3LYP/6-31G* level of calculation smaller energy gaps between $\mathbf{I}_1$, $\mathbf{I}_3$ and $\mathbf{I}_2$ were predicted: 0.0, 18.9 and 23.9 kcal/mol, respectively[13d]. It was noticed that optimisation of the $\mathbf{I}_2$ state leads to a structure that is a second order saddle point[11].

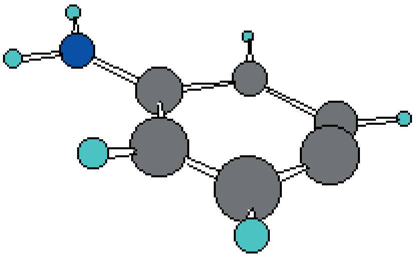
Already at calculations at the STO-3G level it was found that the geometries of the phenyl cation in the singlet $\mathbf{I}_1$ and triplet $\mathbf{I}_3$ state are quite different. In the singlet state the angle at the cationic center, α =147.3°, is widened with respect to the normal angle in benzene but not yet 180°. Thus the s character of the vacant orbital is reduced and the s character of the two other σ orbitals at the same atom is increased leading to a shortening of the C1-C2 and C1-C6 bond lengths. The triplet geometry is close to that of benzene (α =127.6°)[14].

The calculational results for the 4-aminophenyl cation (Table 3) differ from those for the parent phenyl cation. First, the order of stability for the lowest singlet and triplet state is inverted. The triplet 4-aminophenyl cation is calculated to be about 16 kcal/mol more stable than the lowest singlet 4-aminophenyl cation. Second, there are different changes in the geometry for the singlet state. Whereas in the triplet state the C_{2v} symmetry is preserved, the lowest singlet state has C_s symmetry; there is only one plane of symmetry, i.e. the plane in which the atoms lie. The width of the angle (α = 134.2°) is reduced with respect to the parent phenyl cation (α = 147.3°) and the 4-aminophenyl cation is no longer a planar molecule.

The CASSCF wave function for the singlet closed shell ($\mathbf{I}_1$) state was poorly described by one single configuration as was published before[16b]. Assuming the 4-aminophenyl cation to be planar and symmetrical, like the parent phenyl cation, a construct of the closed shell and an open-shell structure can be made. In C_{2v} symmetry the electron configurations $\mathbf{I}_1$ and $\mathbf{I}_2$ have a different symmetry and will not interact. If planarity of the cation is not imposed, an interaction between the open-shell and the closed shell configurations occurs, leading to a lower singlet state $\mathbf{I}_1$' with α = 134.2° (Figure 2). The energy gap between the lowest singlet state and the planar state is small, only 0.4 kcal/mol. There are two mirror states $\mathbf{I}_1$', because the dihedral angle C1C2-C3C4 can be positive or negative. The planar state ($\mathbf{I}_2$) is probably a saddle point and acts as a barrier between the mirror states. These results indicate that the 4-aminophenyl cation in its lowest singlet state vibrates between two non-planar mirror geometries separated by a barrier very close in energy.

The ground state of the 4-hydroxyphenyl cation is CASSCF(4,5)/6-31G(d)// CASSCF(4,5)/6-31G(d) calculated to be a triplet ($\mathbf{I}_3$). The lowest singlet cation, just like the 4-aminophenyl cation, has C_S symmetry ($\mathbf{I}_1$') and is about 6 kcal/mol less stable than the triplet cation. The main difference with the aminophenyl cation is the energy gap between $\mathbf{I}_1$' and $\mathbf{I}_2$ which is larger with the 4-hydroxyphenyl cation. These results contradict published calculations on the 4-hydroxyphenyl cation that indicate that the singlet and triplet state are isoenergetic[15]. Calculations for the 4-hydroxyphenyl cations at the CASSCF(8,8)/6-31G(d) level of theory could not be completed before the publication of this thesis.

Figure 2: Structure of $\mathbf{I}_1$'-NH_2.



Discussion

Competition studies

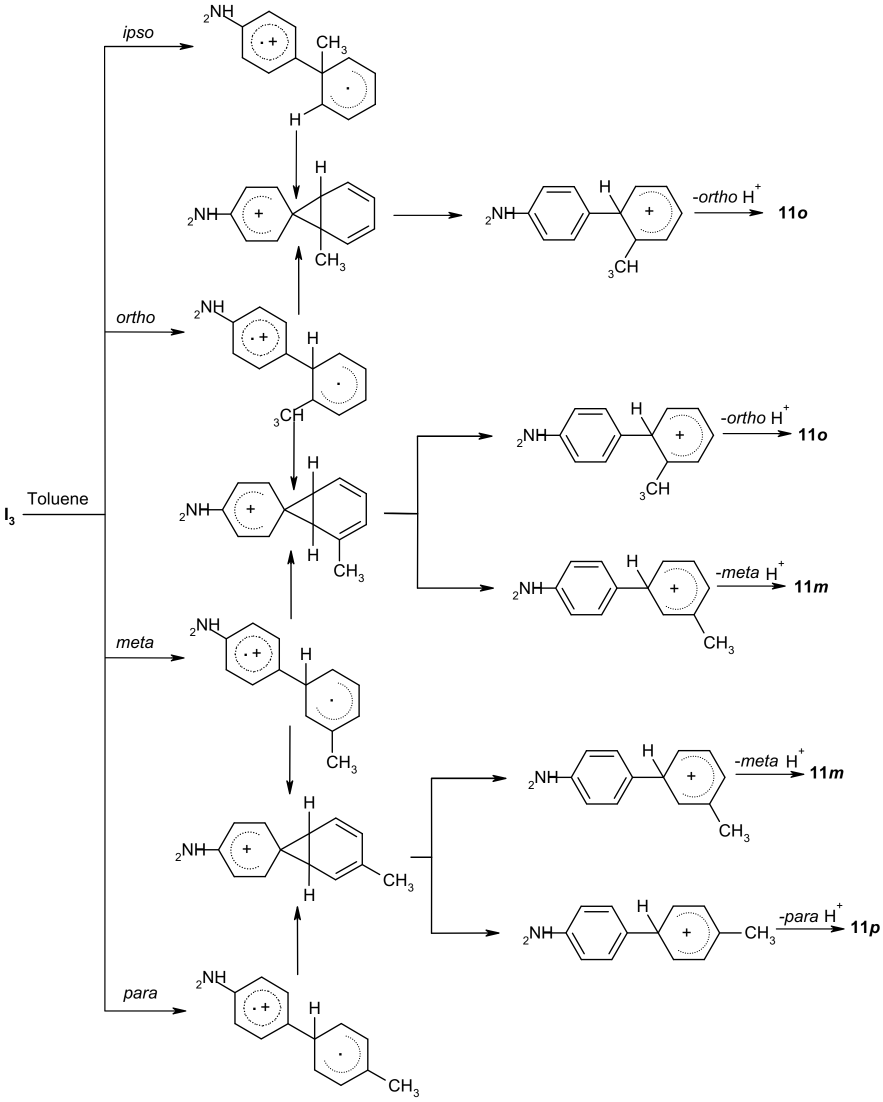
The product-forming intermediate in the photolysis of **3** is efficiently trapped by iodide, toluene, and aniline but not by methanol or water. In its reaction with toluene and aniline it shows a remarkable regioselectivity, *o*: *m*: *p* 73:4:23 and 88:0:12, respectively. As to the nature of the reactive species, four possibilities can be envisioned 1) It is a phenyl radical. 2) It is a non-planar singlet closed shell phenyl cation (**I**$_1$'-NR$_2$. 3) It is a carbene like cation **I**$_2$-NR$_2$. 4) It is a triplet phenyl cation **I**$_3$-NR$_2$.

(1) The photolysis of iodobenzene, which is known to produce Ph• [19], under the same reaction condition as used for **3** yields **11** in an *o*: *m*: *p* ratio of 68:20:11. A similar ratio was found in the photolysis of dibenzoylperoxide, producing phenyl radicals, in toluene (*o*: *m*: *p* = 68:18:14[20]). These ratios, and especially the high yield of *meta* product, do not agree with the **11*o*: *m*: *p*** ratio produced in the photolysis of **3** in the presence of toluene. Further, the ratio between **11** and **13** in the phenyl radical reaction (1.1:1) is different from that in the photolysis of **3** (9.1:1). Finally, photohomolytic cleavage of the C-Cl bond of **3** is unlikely because C-Cl bond homolysis from the triplet excited state is endothermic [21]. Thus, a phenyl radical is not a (major) product-forming intermediate in the photolysis of **3**. (2) The non-planar singlet 4-aminophenyl cation (**I**$_1$') is expected to display the same reactivity as the parent closed shell phenyl cation (**I**$_1$). The radiolysis of ditritiobenzene, which produces the parent closed-shell singlet phenyl cation, in toluene yields **11** in an *o*: *m*: *p* ratio of 44:30:26[22]. The much lower *meta* methylbiaryl yield in the photolysis of **3** argues against the intermediacy of a singlet closed shell phenyl cation. (3) **I**$_2$-NR$_2$ is expected to react like a singlet carbene or nitrene. Carbene and nitrene intermediates typically yield a low amount of *meta* product in their reaction with toluene (47:0:52 and 61:1:38 respectively)[23] as is the case in the photolysis of **3**. If **I**$_2$-NR$_2$ is an intermediate in the photolysis of **3**, a ratio of **11*o***, ***m*** and ***p*** as with the carbene and nitrene intermediates may be expected. Such a ratio is not found. (4) Cation **I**$_3$-NR$_2$ can be considered to be a triplet carbenoid species. The addition of **I**$_3$ to toluene proceeds with the regioselectivity of the addition of a phenyl radical to toluene, producing a distonic triplet diradical cationic species (Scheme 5). After spin-inversion, this intermediate closes intra-molecularly to yield one or two cationic spiro-complexes. The spiro-intermediates preferentially open to their more stable cyclohexadienyl cation prior to the loss of a proton, leading to the methylbiaryl products **11**.

With aniline instead of toluene as substrate the preference for *ortho* biaryl formation is magnified while the percentage of *para* product is lower and the percentage of *meta* product is zero. This is completely in line with the mechanism proposed in Scheme 5. Attack of **I**$_3$-NR$_2$ on aniline forms distonic diradical cation complexes just as in the reaction with toluene. The spin-inversion and closure to phenonium ions will also be similar. However, the preference for opening toward the more stable amino-substituted cyclohexadienyl complex will reflect the larger stability of the *ortho* and *para* amino isomers, compared to the *meta* isomer. Therefore formation of **12*o***, ***p*** is heavily favored over formation of **12*m***.

The triplet cation **I**$_3$-NR$_2$ as product-forming intermediate in the photolysis of **3** explains not only the regioselectivity toward arenes but also the distinct chemoselectivity toward n-nucleophiles and π-nucleophiles. Cation **I**$_3$-NR$_2$ is a soft Lewis Acid and is not affected by a hard

Scheme 5: Mechanism of product formation upon attack of the triplet 4-aminophenyl cation **I$_3$**-NR$_2$ on toluene.



Lewis base such as methanol or water. It is efficiently trapped, however, by toluene and aniline and even more so by the iodide anion, which are soft Lewis bases.

Presumably, the carbenoid cation **I$_3$**-NR$_2$ also abstracts a hydrogen atom from the solvent (although less efficiently than it attacks π-nucleophiles) which produces the radical cation of aniline. This species forms aniline (**13**) by acquiring an electron. Formation of **13** via photo-homolytic cleavage of the C-Cl bond of **3** followed by hydrogen atom abstraction by the phenyl radical from the solvent is unlikely because C-Cl bond homolysis from the triplet excited state is endothermic[21] and because the product ratios found in the photolysis of **3** do not agree with a radical as intermediate (*vide supra*).

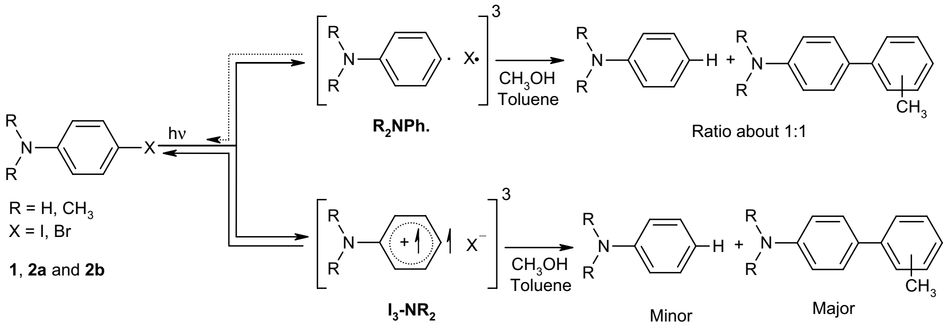
Triplet cation $\mathbf{I}_3$-NR$_2$ may have been formed via two routes. (1) Heterolytic cleavage of the C-Cl bond of singlet excited **3** produces singlet cation $\mathbf{I}_1'$-NR$_2$ ($\mathbf{I}_2$-NR$_2$) which spin-inverts to $\mathbf{I}_3$-NR$_2$. According to the MO calculations in Table 3, this spin-inversion is quite exothermic, which allows it to compete with reactions of $\mathbf{I}_1'$-NR$_2$ ($\mathbf{I}_2$-NR$_2$) with nucleophiles. (2) Singlet excited **3** intersystem crosses to triplet excited **3**, which cleaves to triplet $\mathbf{I}_3$-NR$_2$. All available experimental observations point to route (2). The involvement of triplet excited **3** is substantiated by triplet-triplet absorption studies using **3** and **4**[21]. Also, the S→T conversion quantum yield efficiencies of 4-halogen substituted anilines are high, the triplet excited states thus are efficiently formed[24]. Support for heterolysis from the triplet state is found in a recent microwave dielectric absorption measurement study of **3** which shows that the triplet excited state of **3** possesses ion pair character[25]. The fact that **3** photosolvolyzes readily in polar solvents[16], but refrains from doing so in apolar solvents is also supportive: a polar solvent makes the C-Cl bond heterolysis in the triplet state an exothermic process. Polar solvents stabilise both the charge transfer state and the development of charge in the elongating C-Cl bond.

The 4-Amino substituted phenyl cations

The photolysis of 4-iodoaniline (**1**) produces the biaryls **11*o***, ***m***, ***p*** in a ratio of 79:10:11 and **11** and reduction product **13** in a ratio of 1:3.3 (Table 1, entry 1). These results differ from the data of the photolysis of iodobenzene, which produces a phenyl radical[19], under the same reaction conditions (ratio **11*o***: ***m***: ***p*** is 68:20:11, ratio **11**: **13** is 1.1:1). Thus, the pattern of photoreactivity of **1** is unlike that of the aminophenyl radical, even though that species has been proposed as intermediate in the photolysis of **1**[21]. The results also differ from the data of the photolysis of **3**, which produces $\mathbf{I}_3$-NR$_2$ (ratio **11*o***, ***m***, ***p*** is 78:4:18, ratio **11**: **13** = 9.6:1): the product pattern is also not that of $\mathbf{I}_3$-NR$_2$. We propose that the pattern is due to the presence of two reactive intermediates, the 4-aminophenyl radical R$_2$NPh• and the triplet cation $\mathbf{I}_3$-NR$_2$, side by side (Scheme 6).

The low overall yield, disproportionate to the low bond dissociation energy (BDE) of the C-I bond in the triplet excited state compared to that of the C-Cl or C-F bond[21], hints at a “hidden” reaction. One or both of the intermediates formed is efficiently trapped by the leaving group, remaking the starting material. The triplet radical pair R$_2$NPh•/ I• generated upon photolysis of **1**, will not recombine before singlet radical pair formation takes place. Radical R$_2$NPh• is therefore expected to significantly react through hydrogen atom abstraction. On the other hand, cation $\mathbf{I}_3$-NR$_2$ is efficiently trapped by the iodide leaving group, as shown in the photolysis of **3** in NaI/ methanol (Scheme 1). This trapping reforms starting material and causes the

Scheme 6: The mechanisms of the photolyses of **1**, **2a** and **2b**; hidden reaction.



low productive yield. A fraction of **I**$_3$-NR$_2$ reacts out of cage, along with R$_2$NPh•, with toluene which leads to the observed **11*o***, ***m***, ***p*** ratio.

The photolyses of bromoanilines **2a** and **2b** produce the biaryls **11*o***, ***m***, ***p*** in ratios of 83:6:11 (R=H) and 79:6:15 (R=CH$_3$) and **11** and **13** in ratios of 1.6:1 and 1.2:1. These data reflect the position of **2** in between **3** and **1**. As with **1**, homolysis and heterolysis probably occur side by side (Scheme 6). Here, also an "hidden" reaction takes place because the low overall yield is not in line with the BDE of the C-Br bond in the triplet excited state, compared to that of the C-Cl or the C-F bond[21]. The heterolytic cleavage of the C-Br bond is reversible but less so (and the heterolyses of the C-Cl or the C-F bond even less so) than the heterolytic C-I bond cleavage in the case of **1**, because bromide is a harder nucleophile than iodide. This leaves a larger fraction of **I**$_3$-NR$_2$ to react with toluene.

The photolysis of fluoroaniline **4** produces the same product-forming intermediate as **3** does: the triplet 4-aminophenyl open-shell cation **I**$_3$. This conclusion is based on the low yield of the *meta* product (the photoreactions of **3** and **4** produce **11*o***, ***m***, ***p*** in a ratio of 78:4:18 (with **3**) and 78:3:19 (with **4**)). Another indication for the intermediacy of **I**$_3$-NR$_2$ is the essentially equal preference for the formation of biaryls **11** over **13** (9.7: 1 with **3** and 6.6:1 with **4**). Further, no 4-aminoanisole (**14**), signalling the occurrence of the closed-shell singlet phenyl cation **I**$_1$-NR$_2$, is produced.

The photolysis of diazonium salt **5** produces the Friedel-Crafts products **11** (in an *o*, *m*, *p* ratio of 65:5:29) as well as the substitution products 4-methoxy-N,N-diethylaniline (**14**, R= CH$_2$CH$_3$) and 4-fluoro-N,N-diethylaniline (**15**) (Scheme 2). Both the *o*: *m*: *p* ratio, in particular the high percentage of *para* isomer, and the product profile however, are unlike any other ratio or profile observed thus far in this series of experiments (Table 1). The *o*: *m*: *p* ratio does not resemble the ratios observed with singlet phenyl cations, but does remind of the ratio obtained for triplet cation **I**$_3$-NR$_2$. On the other hand, the formation of O- and F-alkylation products **14** (R= CH$_2$CH$_3$)and **15** are typical for the closed-shell singlet cation **I**$_1$-NR$_2$. Is is proposed that the combination of singlet-type chemoselectivity and triplet-type regioselectivity is due to the closed-shell singlet phenyl cation $\mathbf{I}_1$'-NR$_2$ in combination with the open-shell singlet phenyl cation $\mathbf{I}_2$-NR$_2$ as the reactive intermediates responsible for product formation. After electronic excitation of **5**, extrusion of nitrogen takes place from the singlet excited state. This generates cation $\mathbf{I}_1$'-NR$_2$ which is trapped, in part, by the solvent methanol, forming **14** and, in part, by the counter-ion BF$_4^-$, producing **15**. According to quantum chemical studies in vacuum (Table 3), $\mathbf{I}_2$-NR$_2$ is slightly higher in energy than $\mathbf{I}_1$'-NR$_2$. Formation of cation $\mathbf{I}_2$-NR$_2$ from $\mathbf{I}_1$'-NR$_2$ in solvent by intramolecular electron transfer may well be feasible. The species may exist next to each other.

$\mathbf{I}_2$-NR$_2$ adds to toluene in a singlet carbene fashion and produces the spiro-complexes directly (Scheme 5). Opening to the more stable cyclohexadienyl cations and proton loss produce **11**. $\mathbf{I}_2$-NR$_2$ may be responsible for a larger share of the product formation. In that case, methyl ether **14** is produced by trapping of $\mathbf{I}_2$-NR$_2$ by methanol through singlet carbene type O-H bond insertion, instead of by trapping of $\mathbf{I}_1$'-NR$_2$.

The photolysis of iodonium salt **6** through route B yields the Friedel-Crafts products **11*o***, ***m***, ***p*** and **17*o***, ***m***, ***p*** in ratios of 73:8:19 and 72:3:25, respectively. The relatively low percentages of *meta* product is reminiscent of results of the photolysis of **3** and **4** and thus are typical for $\mathbf{I}_3$-NR$_2$ chemistry. The (acetone) sensitised irradiation of diphenyliodonium hexafluorophosphate, which presumably generates the parent $\mathbf{I}_3$ yields Friedel-Crafts alkylation products in a similar ratio: 71:5:24 [26]. The ratio of **11*o*, *m*, *p***, **17a** and **17*o*, *m*, *p*** to reduction product **13** (5.8:1) is alike the chemoselectivity of $\mathbf{I}_3$-NR$_2$ in the irradiation of **3** (9.6:1) and **4** (6.6:1). The formation of **17a**, the *ipso* substitution product, is also conveniently explained with cation $\mathbf{I}_3$-NR$_2$ as intermediate. Upon *ipso* addition to idobenzene a distonic diradical cation is formed, which after electron transfer and loss of an iodinium cation produces biphenyl **17a**.(For a more detailed discussion, see Chapter 2).

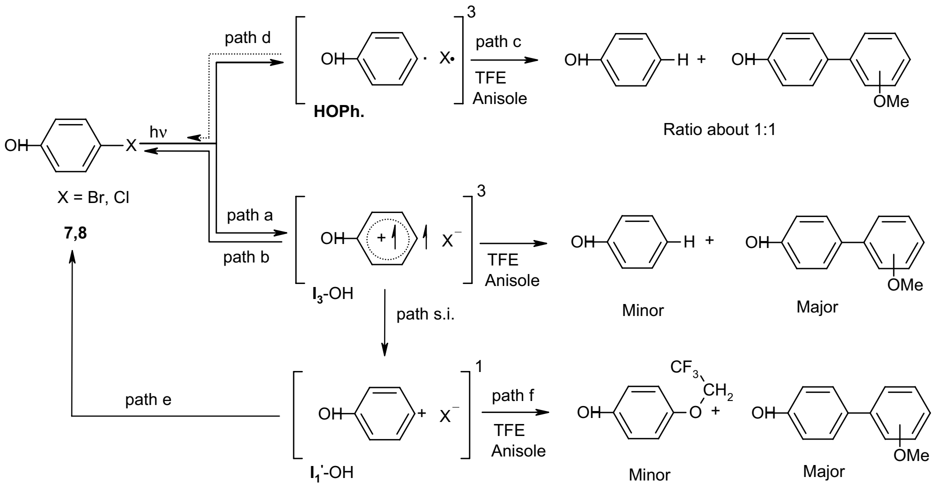
The nucleophilic substitution product 4-bromoaniline (**2b**) may also have been formed by trapping of $\mathbf{I}_3$-NR$_2$, now by the counter-ion Br$^-$. As discussed earlier, HSAB considerations rationalise this: triplet cation $\mathbf{I}_3$ is a soft Lewis acid while bromide is a relatively soft Lewis base.

The formation of ether **14** in the photolysis of **6** is not in agreement with triplet phenyl cation chemistry. The ether is either the trapping product of $\mathbf{I}_1$'-NR$_2$ with methanol or the carbene type O-H bond insertion product of $\mathbf{I}_2$-NR$_2$ with methanol, as proposed in the case of **5**. Thus, singlet excited **6** partially might cleave to $\mathbf{I}_1$'-NR$_2$ (which next forms $\mathbf{I}_2$-NR$_2$) and partially gives intersystem crossing to triplet excited **6** which cleaves to $\mathbf{I}_3$-NR$_2$. This sequence of events is not the same as in the literature mechanism for diphenyliodonium photochemistry[27] (See also discussion in Chapter 2 and Scheme 7 in Chapter 4).

The 4-hydroxy substituted phenyl cations

The photoreaction of 4-bromophenol (**7**) produces the biaryls **18*o*, *m*, *p*** in a ratio of 66:14:20 (Table 2, entry 1). This ratio is quite similar to the one observed in the radiolysis of 1,4-ditritiobenzene in anisole (65:13:22)[22] and is therefore ascribed to the reactivity of the closed-shell singlet cation **I**$_1$'-OH (Scheme 7, path f). This conclusion does not contradict the expectation that the triplet excited state of **7** gives the C-Br bond fission and produces triplet cation **I**$_3$-OH (path a). The singlet 4-hydroxyphenyl cation minimum (**I**$_1$'-OH) is a non-planar closed shell species which is calculated to be less stable than the triplet state (**I**$_3$-OH) (Table 3). With the aid of a polar solvent, which reduces the energy gap between these species, it may be possible for the triplet cation **I**$_3$-OH, generated from the triplet excited state, to spin-invert to its singlet manifold **I**$_1$'-OH (Path s.i.). The quote of **I**$_3$-OH is efficiently trapped by the bromide anion (path b), while the fraction **I**$_1$'-OH is trapped less efficiently by bromide than by anisole. Some trapping of **I**$_1$'-OH also takes place by the poor nucleophile trifluoroethanol, yielding a small amount of ether **20** (path f) The excess of reduction product **19** formed relative to alkylation product **18** does not contradict a **I**$_3$-OH based machanism. As **I**$_3$-NR$_2$ in the photolysis of **1**, **2a** and **2b**, cation **I**$_3$-OH is effeciently trapped by the bromide leaving group, regenerating **7** (path b). The radical intermediate HOPh• is not trapped by the bromide atom (path d) and proceeds via a hydrogen atom abstraction to reduction product **19** (path c).

Scheme 7: The mechanisms of the photolyses of **7** and **8**.



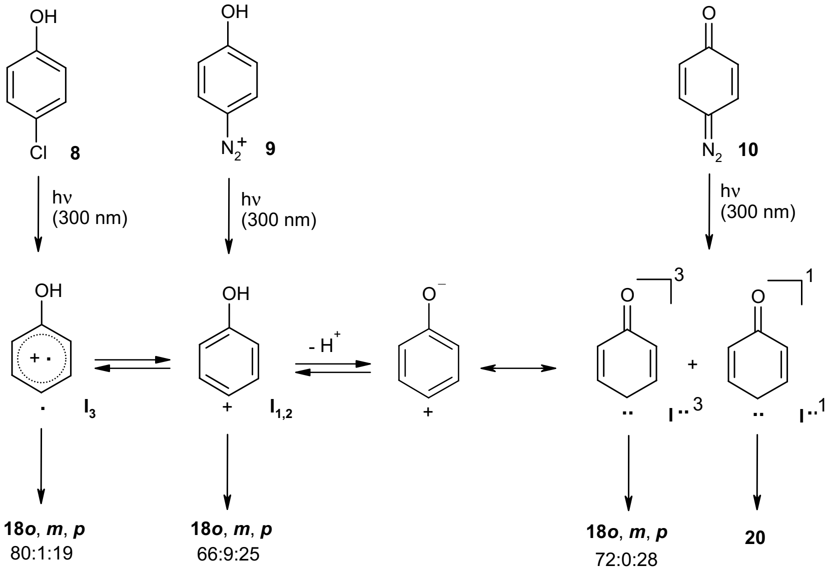
The photolysis of 4-chlorophenol (**8**) produces the biaryls **18*o*, *m*, *p*** in a ratio of 80:1:19 and **18** and the reduction product **19** in a ratio of 16:1. Such data pertain to triplet cation regioselectivity and chemoselectivity. Triplet cation **I**$_3$-OH is probably generated through cleavage of the C-Cl bond of the triplet excited state of **8**, just like in the photolysis of **3**[28] (path a). Contrary to the irradiation of **7**, the triplet cation **I**$_3$-OH is not trapped by the leaving group; path b does not apply to **8**. Also contrary to the irradiation of **7**, no ether **20** (path f) is found in the irradiation of **8**. Cation **I**$_1$'-OH produced from **I**$_3$-OH, is now trapped by the chloride anion (path e).

Photohomolysis and product-formation through hydrogen atom abstraction (path c) is not efficient with **8**.

The photolysis of diazonium salt **9** produces **18*o*, *m*, *p*** in a ratio of 66:9:25. That ratio has no obvious match with ratios typical for a closed-shell singlet phenyl cation (*o*: *m*: *p* = 65:13:22)[22], typical for a phenyl radical (*o*: *m*: *p* = 76:12:12)[19] or typical for the triplet cation **I**$_3$-OH generated in the photolysis of **8** (80:1:19). It is proposed that, as in the case of **5**, more than one cationic reactive intermediate is responsible for product formation, most likely the closed-shell singlet cation **I**$_1$'-OH and the open-shell singlet **I**$_2$-OH. **I**$_2$-OH adds to anisole in a singlet carbene fashion and forms spiro-complexes directly (see Scheme 5). These complexes open to the more stable cyclohexadienyl cations, which lose a proton and form **18**. The relatively high percentage of **18*p*** is due to that singlet carbenoid behaviour. The ether **20** is either the product of trapping of **I**$_1$'-OH by trifluoroethanol or the product of trapping of **I**$_2$-OH via carbene insertion in the O-H bond of TFE.

The photolysis of 4-diazo-2,5-cyclohexadien-1-one (**10**) yields the Friedel-Crafts products **18*o*, *m*, *p*** in a ratio of 72:0:28. The lack of *meta*-biaryl formation and the *o*/*p* ratio of about 2.5/1 are practically the same as the isomer ratios obtained in the reactions of 2,6-dichloro-oxocyclohexadienyl carbene[29] and tosylnitrene[30] with anisole. The photochemistry of **10** produces the 4-oxocyclohexadienyl carbene I••, probably of triplet nature[31,32] (Scheme 8). A stepwise addition to anisole gives spiro intermediates that rearrange to **18*o*, *m*, *p***. Ether **20** is presumably formed by carbene insertion into the O-H bond of TFE and subsequent rearrangement. Insertion is a typical singlet carbene type reaction[33].

Scheme 8: Product-forming intermediates in the photolyses of **8**, **9** and **10**.



4-Chlorophenol (**8**), the 4-hydroxybenzenediazonium salt **9** and 4-diazo-2,5-cyclohexadien-1-one (**10**) give **18*o*, *m*, *p*** in different ratios (Scheme 8). This shows that they have no common intermediate and answers the question whether or not the hydroxy cations **I**$_1$ - **I**$_3$ deprotonate to **I••**[17] prior to their reaction with nucleophiles, here with anisole. They do not.

Conclusion

The distinctive regioselectivities and chemoselectivities observed in the photolysis of the 4-aminophenyl cation precursors **1**-**6** demonstrate that these cations can be generated in different manifolds through different excited states. Whether a singlet or triplet cation is produced depends on the leaving group. With **1**-**4** (leaving groups: iodide, bromide, chloride and fluoride) cleavage of the carbon-halogen bond occurs in the triplet excited state yielding triplet cation **I**$_3$-NR$_2$, which reacts much like a triplet carbene. With **5** (leaving group: nitrogen) cleavage occurs in the singlet excited state, which yields the non-planar closed-shell singlet cation **I**$_1$'-NR$_2$ and the open-shell singlet cation **I**$_2$-NR$_2$. Photolysis of **6** (leaving group: iodobenzene) gives both **I**$_3$-NR$_2$ and **I**$_2$-NR$_2$ (through **I**$_1$'-NR$_2$). Similar observations have been made for the 4-hydroxyphenyl cation precursors **7**-**9**. With (bromide or) chloride as leaving group the triplet cation species **I**$_3$-OH is produced, with nitrogen as leaving group the singlet cation(s) **I**$_2$-OH (through **I**$_1$'-OH). These intermediates do not deprotonate prior to their reaction with nucleophiles, as shown by the generation of that deprotonated species by photolysis of diazoquinone **10**. The assignments of the nature of the various phenyl cations are supported by the results of the CASSCF calculations.

Experimental Section

Materials

Starting materials **1**, **2a**, **2b**, **3**, **4**, **5**, **7** and **8** are commercially available. Aryl halides **1**, **2a**, **2b**, **3**, **4**, **7** and **8** were used as received. Diazonium salt **5** was dissolved in acetonitrile and crystallised with pentane prior to use. Compounds **9**[34] and **10**[35] were synthesised according to literature procedures. Iodonium salt **6** was prepared from 4-N,N-dimethylaminobenzene boronic acid and hydroxy(tosyloxy)iodobenzene (1/1 mol/mol) in 40 mL tetrahydrofuran at melting ice temperature. After stirring for 90 minutest he organic layer was evaporated. The residue was redissolved in dichloromethane and extracted 3 times with a saturated NaBr solution. The organic layer is dried with MgSO$_4$ and evaporated. The bromide salt obtained was purified by three crystallisations from dichloromethane and pentane. The yield of pure **6** was 28%. ^{1}H NMR (300MHz, MeOH d$_3$, δ): 2.9-3.1 (s, 6H), 6.7-6.8 (d, 2H), 7.4-7.5 (t, 2H), 7.6-7.7

(t, 1H), 7.8-7.9 (d, 2H), 8.0-8.1 (d, 2H). IR (neat): 457 cm^{-1}, medium (C-I^{+})[36]; 652, 682, 745 cm^{-1}, strong, peaks characteristic of diphenyliodonium salts; 1063 cm^{-1}, medium (C-N); 1599 cm^{-1}, strong (C=C aromatic); 2850 cm^{-1}, weak (C-H methyl); 3050 cm^{-1}, weak (C-H aromatic). UV: in MeOH, λ_{max} = 304.0 nm, ε_{max} = 2.03 * 10^{4} and in ACN, λ_{max} = 311.1 nm, ε_{max} = 1.70 * 10^{3}. Toluene and anisole were distilled under Argon to obtain GC purity. Diethyl ether, tetrahydrofuran and dichloromethane were distilled prior to use. Methanol, trifluoroethanol, toluene and anisole were Argon purged before their use in the photolysis experiments.

Photochemistry

The photochemical reactions were carried out under argon in quartz tubes equipped with a rubber seal. The starting materials were dissolved at 0.05M in 10 mL of the designated solvents mixtures. *n*-Decane was used as internal standard. For experiments followed in time, the solutions are placed in a merry-go-round apparatus. A Hanau low pressure Hg TNN-15/32 lamp placed in a water cooled quartz tube is used to supply light with a main emission at λ = 254 nm. The product studies were carried out in a Rayonet Reactor (RPR200) fitted with 7 254 nm or 300 nm lamps equipped with a magnetic stirrer. The photolyses were followed as a function of time by taking aliquots (0.050 mL sample). The samples of the photolyses of **1**, **2a**, **2b**, **3**, **4**, **7** and **8** were analyzed by direct injection of aliquots on GC and GC-MS. The aliquots of the irradiations of **5**, **6**, **9** and **10** were added to 0.5 mL water + 0.050 mL diethyl ether. The organic layers were analyzed by GC and GC-MS and the assignment of the structures was confirmed by coinjection of commercially available or independently prepared products. After completion of the irradiations, the reaction mixtures were poured in 10 mL water and extracted two times with 5 mL diethyl ether. The combined ether fractions were GC and GC-MS analyzed.

Photoproducts

The products **1**, **2b**, **13**, **14** (R=H), **16**, **19** and **20** were identified by means of GC, GC-MS and coinjection with the commercially obtained reference samples. Of all *o*, *m*, *p* biaryl mixtures **11*o*, *m*, *p*** (R=H, CH_3, CH_2CH_3) the *ortho* and *para* isomers were independently synthesised, from commercially available starting materials, employing a literature Suzuki cross-coupling procedure[37]. Products **12*m*** and ***p*** were synthesised in two steps from 4-acetanilidobenzeneboronic acid and 3-bromo- and 4-bromoacetanilide. After Suzuki cross-coupling [38], the biaryls were deacetylated in ethanol/ hydrochloric acid[39]. Basic work-up gave the products, ready for coinjection. Biaryl **17a** was synthesised following a literature procedure[40]. Iodobiaryls **17*o***, ***m***, ***p*** were prepared (among other products) by heating a mixture of 0.02 mol diazotised 4-N,N-dimethylaminoaniline and 0.02 mol iodobenzene to 50°C for 12 hours. The assignment of the *o*, *m*, *p* isomers is based on the assumption that these products elude from the GC column in the usual order 1 = *ortho*, 2 = *meta*, 3 = *para*. Biaryls **18*o*** and **18*p*** were prepared through a literature Suzuki cross-coupling procedure [41]. Alkylaminoanisoles **14** (R=CH_3, CH_2CH_3) were prepared by refluxing 5% solutions of diazotised 4-N,N-dimethylaminoaniline or **5**, in methanol for 8 hrs, after evaporation of the solvent the product were ready for coinjection. Schiemann product **15** was prepared from **5**, according to literature [42]. Finally, commercially obtained 4-aminophenol was coinjected and observed to be no product in the photolysis of **3** in the presence of water.

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 Avance DPX 300 MHz, using CD_3OH as solvent. As analytical GC a Hewlett-Packard 6890 model was used, equipped with a 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 a 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.

Quantum Chemical Calculations

The relative stabilities of the 4-amino- and 4-hydroxyphenyl catios were evaluated with CAS-SCF instead of with (U)B3LYP methods because the latter may not be suitable for open-shell singlet species[43]. First, the relative stabilities of the 4-aminophenyl cations were CASSCF(2,2)/6-31G(d) calculated with C_{2v} symmetry. The singlet open-shell cation is lower in energy than the closed shell species. Both cations are found to be saddle points on the potential energy surface. With larger CASSCF and with the planarity of the cations let loose (CASSCF(8,8)/6-31G(d) level of theory) the non-planar closed shell species is a minimum and the open-shell species has become a saddle point. The minimum consists of two species with a positive and negative dihedral angle and with Cs symmetry.

For the 4-hydroxyphenyl cation the same approach was chosen. By the time of publication of this thesis only calculations at (4,5)CASSCF/6-31G(d) level of theory had been successful.

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