

Fingerprints of Singlet and Triplet Phenyl Cations

Micha Slegt,^[a] Hermen S. Overkleeft,^[a] and Gerrit Lodder^{*[a]}**Keywords:** Photochemistry / Phenyl cations / Spin multiplicity / Regioselectivity / Chemoselectivity

The photolyses of seven phenyl cation precursors in acetonitrile in the presence of anisole resulted in four distinct product patterns. These patterns are due to the chemoselective and regioselective chemistry of various phenyl cation isomers. This spin-selective chemistry provides a tool with

which to fingerprint the singlet/triplet nature of any phenyl cation.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

The ability to steer reactions along singlet or triplet pathways by electronic excitation has led to the development of valuable chemo-, regio-, and stereoselective reactions.^[1–4] For example, triplet phenyl cations, generated by photolysis, show different chemoselectivity toward nucleophiles^[5] than the photogenerated singlet parent phenyl cation.^[6] Whereas singlet phenyl cations are fairly unselective, triplet phenyl cations display a selectivity for unsaturated compounds (π nucleophiles) over compounds with lone pairs (n nucleophiles).^[7,8] Practical implementations of these results are found in the photolysis of fluoroquinolones, a major class of antibiotics that react with cellular tissue through triplet aryl cations,^[9] and in the photochemistry of the organophosphorous pesticide Fenthion, which degenerates via a singlet phenyl cation intermediate,^[10] both under the influence of (sun)light.

The singlet and triplet natures of phenyl cations, which are among the most reactive intermediates known,^[11] have since long been subjects of intensive study.^[12,13] It was not until the parent phenyl cation was isolated in an argon matrix that its singlet closed-shell ground state (**I**₁, Figure 1) was ascertained.^[14] Isomers of this cation are possible. One electron of the aromatic sextet may be transferred, with spin retention, into the empty sp^2 orbital, yielding a species with a $\pi^5\sigma^1$ electronic configuration: the open-shell singlet phenyl cation (**I**₂). If the transfer occurs with spin inversion the triplet phenyl cation (**I**₃) is formed, which is an open-shell species by nature.

The textbook methods for thermal generation of phenyl cations are β -decay of tritiated precursors^[15] and solvolysis of phenyldiazonium salts.^[6] In all cases studied but one, the tritium decay method yields singlet phenyl cations.^[16]

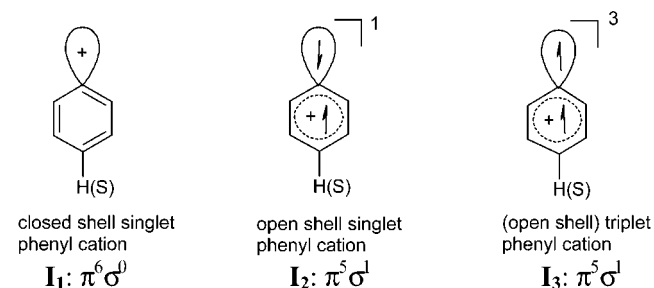
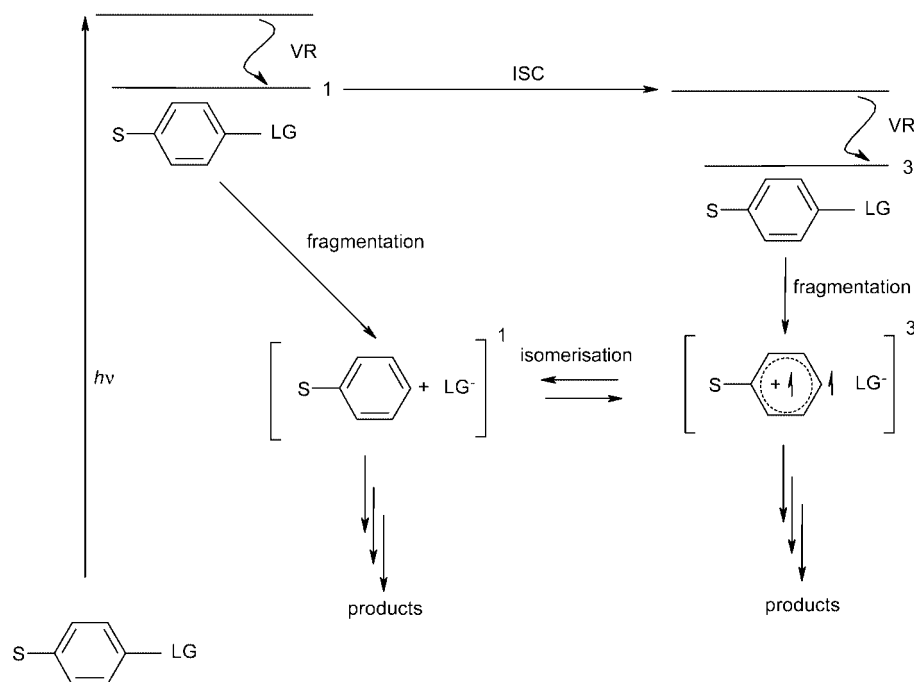


Figure 1. Singlet and triplet phenyl cations.

Whether or not phenyl cations are actually generated through solvolysis of their diazonium salt precursors – in S_N1 reactions – remains unclear.^[17] This is not so if light is used to trigger the loss of the N_2 leaving group.^[5,6,18] In the photolysis of (substituted) phenyldiazonium salts, both singlet and triplet phenyl cations are generated.^[5,6,7a,7b] Another photochemical route to phenyl cations is the photolysis of 4-chloro- (or 4-fluoro-) anilines^[7c,7d,8] or 4-chlorophenols.^[7e] These precursors yield triplet phenyl cations.

Whether photogenerated phenyl cations are singlet or triplet species depends on two factors: namely a) the singlet or triplet nature of the reactive electronically excited state,^[19] and b) the relative stabilities of the singlet and triplet cations.^[20] As depicted in Scheme 1, electronic excitation converts the ground state of the photolabile compound into a vibrationally excited singlet excited state. After vibrational relaxation (VR) to the vibrationally relaxed first singlet excited state, expulsion of the leaving group yields a singlet phenyl cation that can be trapped or can convert into a triplet cation. If the rate of intersystem crossing (ISC) is larger than the rate of bond fission, the singlet excited state is converted into an isoenergetic triplet excited state. After vibrational relaxation to the first triplet excited state, the leaving group is cleaved off, forming a triplet phenyl cation. This ion is either trapped or undergoes conversion to a singlet cation, if that is energetically feasible.

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P. O. Box 9502, 2300 RA Leiden, The Netherlands
E-mail: lodder@chem.leidenuniv.nl



Scheme 1. General scheme for photochemical singlet or triplet phenyl cation formation.

A time-honoured method to characterise cationic reactive intermediates is the determination of the *ortho/meta/para* ratios of aromatic substitution product mixtures. This method turns out to be useful for the type of spin-chemistry discussed above. In this paper we offer a method by which to fingerprint the natures of photogenerated phenyl cations of different background and spin multiplicity based on their different chemo- and regioselectivities toward the nucleophile methoxybenzene (= anisole) in acetonitrile. In the accompanying paper the method is used to probe the singlet/triplet natures of photogenerated naphthyl cations.^[21]

Results

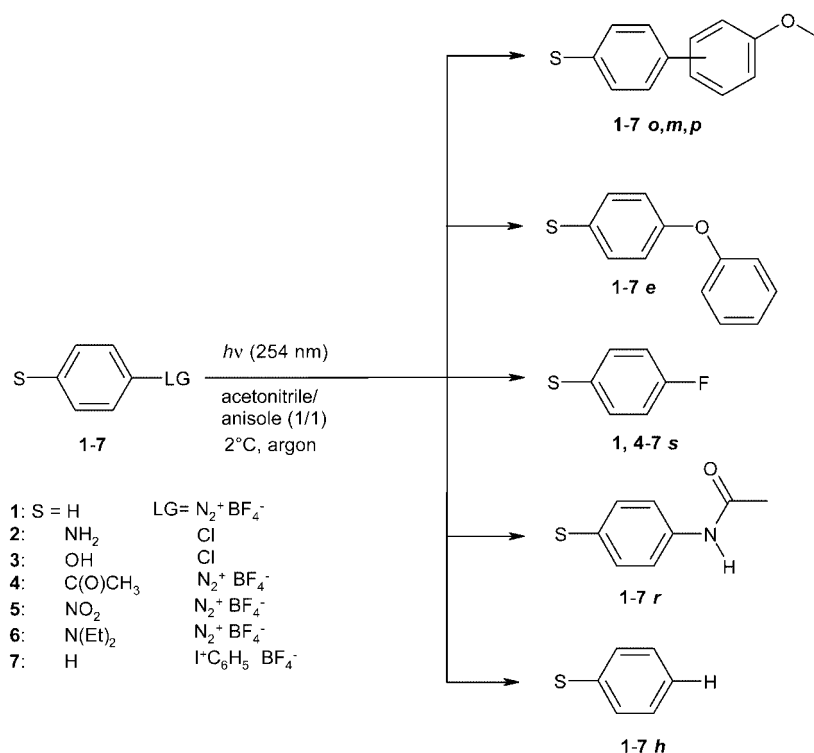
Compounds **1–7**, all proposed or expected precursors of phenyl cations, were photolysed in acetonitrile/anisole (1:1, v/v) (Scheme 2). Excesses of anisole were used to allow alkylation to take place in high yield. Acetonitrile was used as solvent because it is a poor nucleophile and a poor electron donor in comparison with, for instance, methanol. The latter property precludes the formation of products derived from photoinduced electron transfer from the solvent to the substrate.^[22] The reactions were carried out at 2 °C; at that temperature, during the time of irradiation, there is no significant thermolytic product formation (<5%). The results of the photolyses are summarised in Table 1, while Table 2 reports the *ortho/meta/para* ratios of the methoxybiphenyls **1–7o,m,p**.

In all cases the major, or even exclusive, photoproducts are the 2-methoxy-, 3-methoxy- and 4-methoxybiphenyls **1–7o,m,p** (Table 1). The *ortho* isomers of these Friedel–Crafts products are produced more abundantly than the *para* isomers, while low to very low yields of the *meta*-methoxy isomers are obtained (Table 2). However, the *o/m/p* ratios vary with the precursor. In addition to the *C*-alkylation products **1–7o,m,p** in three cases (Entries 1, 6 and 7 of Table 1) *O*-alkylation products – the diphenyl ethers **1e**, **6e** and **7e** – are formed, while in the photolysis of **1** and **6**, *F*-alkylation (Schiemann) products **1s** and **6s** are also produced. The Ritter reaction, alkylation on the nitrogen atom of acetonitrile, yields acetanilide **1r** (= **7r**) (Entries 1 and 7). Finally, small amounts of **1–7h**, where the leaving group is replaced by hydrogen, are found in most reaction mixtures.

Discussion

Phenyldiazonium Tetrafluoroborate (**1**)

The methoxybiphenyls **1o,m,p** produced in the photolysis of **1** in acetonitrile/anisole are proposed to result from attack of the photogenerated phenyl cation on the π -electrons of anisole, as depicted for the *ortho* product in Scheme 3. The formation of diphenyl ether **1e** occurs through attack on the *n*-electrons of the oxygen atom of anisole.^[23] The abstraction of F^- from the counterion BF_4^- (yielding the Schiemann product **1s**) is also a cation-mediated reaction.^[5,24] Attack of the phenyl cation on the nitrogen atom of the acetonitrile solvent is responsible for the formation of acetanilide **1r** (Ritter product).^[25]



Scheme 2. Photolysis of compounds 1–7.

The *ortho/meta/para* ratio of 68:13:19 observed for **1o,m,p** produced in the photolysis of **1** is very similar to the ratio observed in the radiolytical phenylation of anisole, but not similar to the ratios in the thermolyses of various phenyldiazonium salts (Table 3). The similarity in *o/m/p* ratios in the photochemical and radiochemical phenylation of anisole implies that the Friedel–Crafts products in both reactions are produced via the same product-forming reactive intermediate: the (closed-shell) singlet phenyl cation **I₁**.^[26] Clearly, β -decay of tritium, producing helium as leaving group, best resembles the interaction of a photon with a molecule and subsequent extrusion of nitrogen. The different *o/m/p* ratios in the thermal solvolysis of phenyldiazonium salts in relation to the photochemical and radiochemical results support the view on the thermal solvolysis of phenyldiazonium cations in water expressed in a recently published paper, which argues against a discrete $\text{S}_{\text{N}}1$ mechanism.^[17]

In theory, the phenylation products **1o,m,p** might also result from attack on anisole by a photogenerated phenyl radical. This radical would also be the source of benzene (**1h**) produced by hydrogen atom abstraction from the solvent. A possible route for the production of the phenyl radical is photoinduced electron transfer from anisole to the diazonium salt, which should yield $\text{PhN}_2^\cdot$ and next $\text{Ph}^\cdot$.^[31,32] This process would be expected to be most efficient upon irradiation in the charge-transfer bands of the anisole-diazonium salt complex. To investigate the importance of a radical-mediated route towards methoxybiphenyl product formation, a) the reactivity of an independently prepared

phenyl radical was studied, and b) the wavelength dependence of the photolysis reaction of **1** was investigated.

a) Photolysis of iodobenzene, which gives homolytic cleavage of the C–I bond,^[33] in acetonitrile/anisole under the same reaction conditions as used for **1–7** yields **1o,m,p** in a ratio of 75:13:12. The product ratio of **1o,m,p** and **1h** is 2.1:1, quite different from the 5.3:1 ratio observed in the photolysis of **1**.

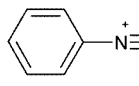
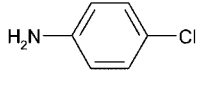
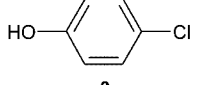
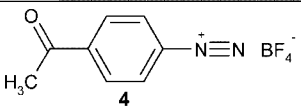
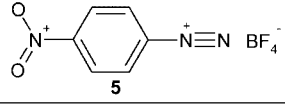
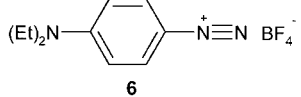
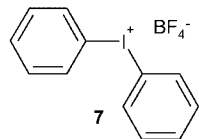
b) Irradiation of **1** at $\lambda_{\text{exc}} = 300\ \text{nm}$ and $\lambda_{\text{exc}} = 350\ \text{nm}$ yields the biphenyls **1o,m,p** in exactly the same *o/m/p* ratio as upon irradiation at $\lambda_{\text{exc}} = 254\ \text{nm}$. The relative amount of benzene increases slightly with the wavelength of excitation: the **1o,m,p/1h** ratio is 5.1:1 at $\lambda_{\text{exc}} = 300$ and 350 nm.

Thus, we conclude that reactions involving the phenyl radical are not a major product-forming route in the photolysis of **1**.

4-Chloroaniline (2)

The photolysis of **2** in acetonitrile/anisole exclusively yields the methoxybiphenyls **2o,m,p** in a ratio of 81:2:17. In relation to the *o/m/p* ratio observed for **1** (Table 2, Entry 1) the relative amount of *meta* product formed is remarkably low. The very limited yield of the *meta*-biphenyl product is reminiscent of the *o/m/p* ratios obtained in the reactions of the triplet species 2,6-dichloro-oxocyclohexadienyl carbene (73:0:27)^[34] and tosyl nitrene (71:2:27)^[35] with anisole. The triplet carbene-type regioselectivity is in agreement with the proposal that the photolysis of **2** produces a phenyl cation **I₃** of triplet nature.^[7c,7d,36]

Table 1. Products of the photolysis of compounds 1–7 in acetonitrile/anisole.^[a]

Photolabile compound \ Photoproducts	1-7 <i>o,m,p</i>	1-7 <i>e</i>	1-7 <i>s</i>	1-7 <i>r</i>	1-7 <i>h</i>
 1	72	2	2	4	12
 2	99	-		-	-
 3	4 ^[b]	-		-	-
	60 ^[c]	-		-	-
 4	88	-	-	-	11
 5	90	-	-	-	4
 6	83	13	2	-	<1
 7	64 ^[d]	<1	-	<1	14

[a] Yields are calculated as percentages of total product formation upon complete conversion after 90 min of photolysis. [b] Only 4% of the precursor was converted after 90 min of photolysis. [c] Reaction carried out in trifluoroethanol/anisole (1:1). [d] The lower yield of methoxybiphenyls is partly caused by the in-cage trapping of the leaving group iodobenzene, yielding iodobiphenyls. Also, only 70% of the salt was converted.

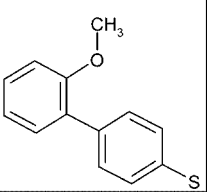
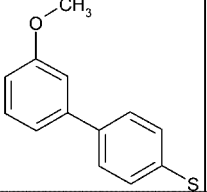
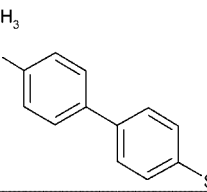
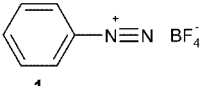
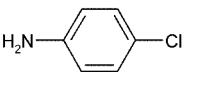
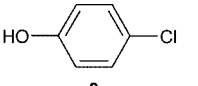
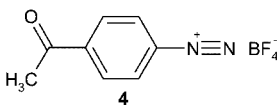
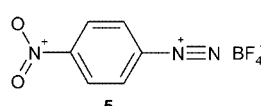
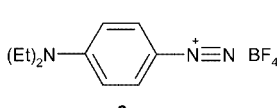
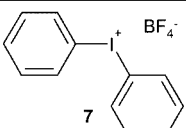
Triplet phenyl cations possess an open-shell diradical structure, rather reminiscent of a triplet carbene. Triplet carbenes add to C=C double bonds in two radical-mediated steps to form cyclopropyl rings. We propose that the first step of the biphenyl formation is the addition of a radical to anisole (Scheme 4). This step produces a triplet (Wigner's rules^[37]) distonic diradical cation. After spin-inversion, the second step comprises closure towards a phenonium ion, which can take place in two directions. Formation of σ complexes and proton loss lead to the biphenyls. Their isomer pattern is thus determined in three steps. The first step takes place with the same regioselectivity as the attack of a phenyl radical on anisole (vide supra). In the second step, the direction of closure to the phenonium ions will presumably be preferentially towards the more stable species. According to PM3 calculations the 1,2 complex is less stable (by 5 kcal mol⁻¹) than the 2,3 and 3,4 complexes, which are degenerate in energy. The third step, opening of the phenonium ions, should preferentially lead to the more stable, *ortho* or *para* methoxy-substituted cyclohexadienyl cation.

Thus, attack of the triplet cation at the *meta* position of anisole rarely yields the *meta* biphenyl product. The chemoselectivity observed with **2** is discussed later together with those observed with **3**, **4** and **5** (vide infra).

4-Chlorophenol (**3**)

The photolytic behaviour of **3** is solvent-dependent: the reaction occurs much more readily in trifluoroethanol than in acetonitrile.^[38,39] Therefore, **3** was not only irradiated in acetonitrile/anisole, but also in trifluoroethanol/anisole. In both solvent systems the only products are **3o,m,p** in a ratio of 80:1:19. These results agree with the chemo- and regioselectivity of product formation observed in the photolysis of **2** and are therefore due to the triplet phenyl cation mechanism of Scheme 4. The product-forming intermediate is either the triplet phenyl cation or the deprotonated form thereof: the triplet 4-oxocyclohexa-3,5-dienylidene. Independent generation of that species by photolysis of 4-diazo-

Table 2. *ortho/meta/para* ratios of the methoxybiphenyl photoproducts.^[a]

Photolabile compound \ Photoproducts			
 1	1o: 68%	1m: 13%	1p: 19%
 2	2o: 81%	2m: 2%	2p: 17%
 3	3o: 81% ^[b]	3m: 0% ^[b]	3p: 19% ^[b]
	3o: 81% ^[c]	3m: 0% ^[c]	3p: 19% ^[c]
 4	4o: 75%	4m: 13%	4p: 12%
 5	5o: 75%	5m: 12%	5p: 13%
 6	6o: 64%	6m: 3%	6p: 33%
 7	7o: 69%	7m: 12%	7p: 19%

[a] Percentages are averages of the yields in three separate experiments; the maximum experimental error is $\pm 2\%$. [b] Photolysis in acetonitrile/anisole (1:1). [c] Photolysis in trifluoroethanol/anisole (1:1).

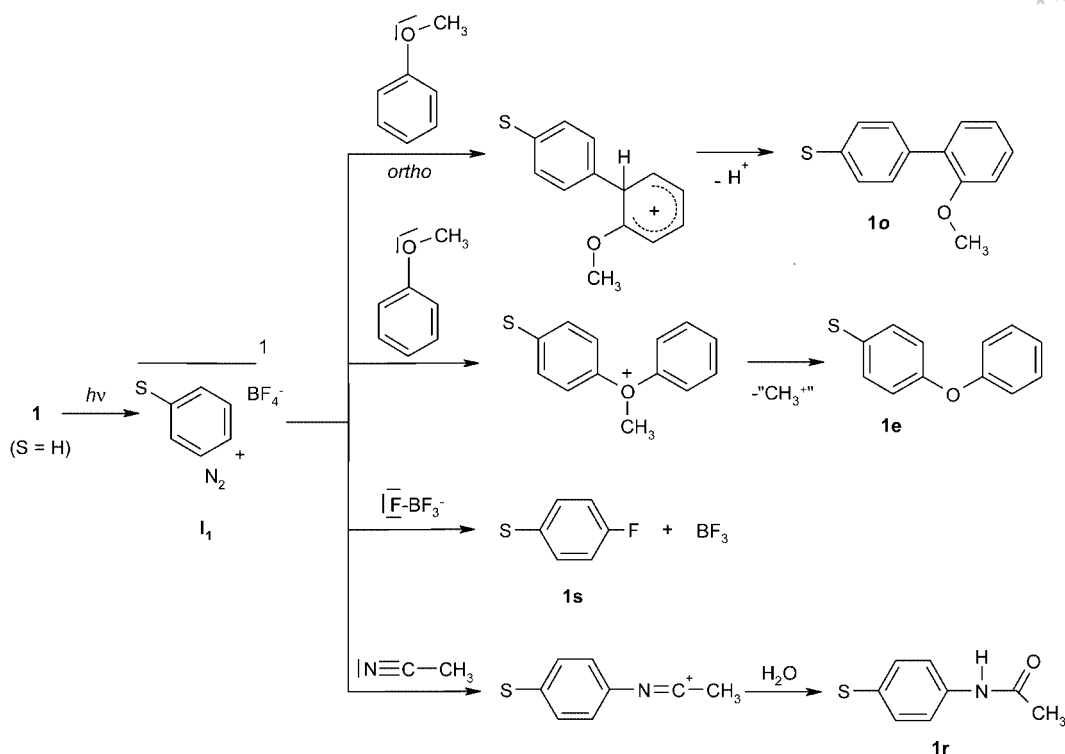
quinone under the same reaction conditions as used for **3** yields **3o,m,p** in a 72:0:28 ratio.^[40a] Therefore, 4-oxocyclohexadienylidene is unlikely to be the product-forming intermediate. Presumably, unlike in water,^[7c,38,39] the rate of the reaction of the triplet cation with the nucleophile anisole exceeds its rate of deprotonation.

4-Acetylphenyldiazonium (**4**) and 4-Nitrophenyldiazonium (**5**) Tetrafluoroborates

The photolyses of **4** and **5** in acetonitrile/anisole yield the methoxybiphenyls **4o,m,p** and **5o,m,p** in ratios of 75:12:13 and 75:13:12, respectively (Table 2, Entries 4 and 5). As in the case of **2** and **3**, no ether or Ritter products are formed (Table 1). Also no Schiemann product is formed. The *o/m/p* ratio observed in the case of **5** is slightly different from

the ratio reported for its thermal solvolysis in a mixture of acetonitrile, benzene and anisole, which yields **5o,m,p** in a ratio of 77.7:9.9:12.4.^[41] This difference may be due to the occurrence of a pure S_N1 mechanism in the photolysis and of an S_N1/S_N2 borderline mechanism in the thermolysis. No thermal solvolysis data for **4** are known.

The observed *o/m/p* ratios of the biphenyl photoproducts of **4** and **5** are similar to the *o/m/p* ratio of the products of the 4-nitrophenyl radical with anisole, which is known from three separate sources to be 69:15:16, 68:16:16 and 72:12:16.^[42–44] This suggests that the attack on anisole is governed by the radical qualities of an intermediate. However, this species is not the 4-acetylphenyl or the 4-nitrophenyl radical, formed by photoinduced electron transfer between the diazonium salts **4** and **5** and anisole. This was shown by performing the photoreactions at $\lambda_{exc} = 300$

Scheme 3. Mechanism of formation of photoproducts from **1**.Table 3. Reported *o/m/p* ratios in the reactions between the phenyl cations from various precursors and anisole.

Reported ratio	Precursor	Ref.
68:13:19	phenyldiazonium BF_4^- ($h\nu$) ^[a]	this work
65:13:22	1,4-ditritiobenzene (β -decay)	[26]
56.0:12.5:31.5	phenyldiazonium BF_4^- (Δ) ^[b]	[23]
59:10:31	phenyldiazonium BF_4^- (Δ) ^[c]	[23]
55.2:13.4:31.6	phenyldiazonium BF_4^- (Δ) ^[d]	[27]
64.0:8.5:27.5	phenyldiazonium BF_4^- (Δ) ^[e]	[28]
57.6:10.9:31.5	phenylazotriphenylmethane/TFA (Δ) ^[f]	[29]
61.8:9.7:28.7	phenyldiazonium triflate (Δ) ^[g]	[30]

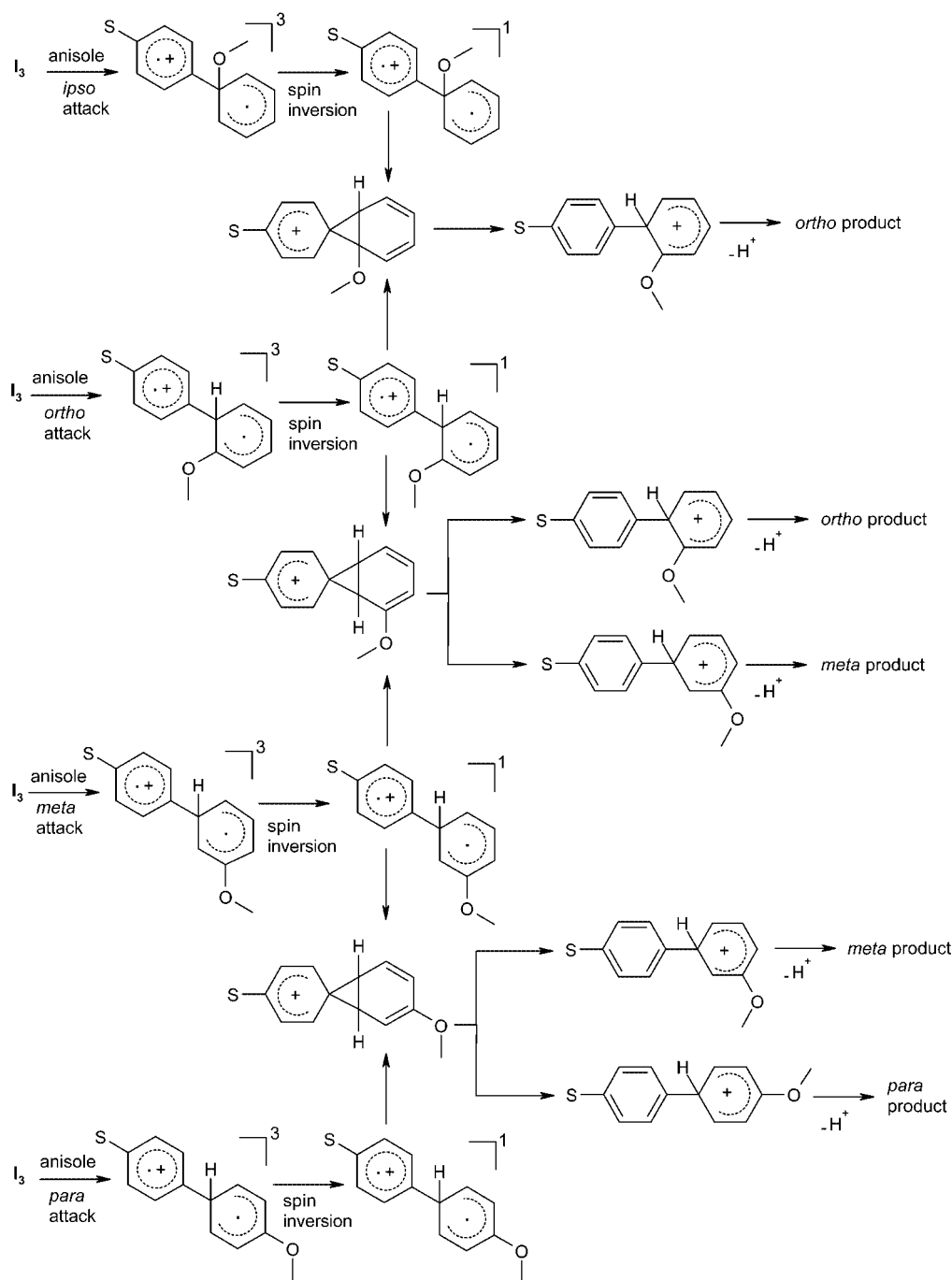
[a] Molar ratio diazonium salt to anisole 1:460. [b] Molar ratio diazonium salt to anisole 1:80. [c] In pure anisole. [d] Molar ratio diazonium salt to anisole 1:14. [e] Molar ratio diazonium salt to anisole 1:50. [f] Molar ratio starting material to anisole 1:25. [g] Molar ratio diazonium salt to anisole 1:38.

and 350 nm, wavelengths closer to the charge-transfer absorption bands than $\lambda_{\text{exc}} = 254 \text{ nm}$.^[31] No variations in *o/m/p* ratios and only slight increases in the amount of the radical-derived arenes **4h** and **5h** were found (**4h/4o,m,p** = 1:7.8 at $\lambda_{\text{exc}} = 254 \text{ nm}$, 1:7.6 at $\lambda_{\text{exc}} = 300 \text{ nm}$ and 1:7.6 at $\lambda_{\text{exc}} = 350 \text{ nm}$) (**5h/5o,m,p** = 1:24 at $\lambda_{\text{exc}} = 254 \text{ nm}$, 1:22 at $\lambda_{\text{exc}} = 300 \text{ nm}$ and 1:19 at $\lambda_{\text{exc}} = 350 \text{ nm}$).

The difference between the *o/m/p* ratios observed in the photolysis of **4** and **5** and that seen in the photolysis of **1**, as well as the differences in product profiles (Table 1, Entries 4 and 5 vs. 1), reflect the difference in the natures of the reactive intermediates responsible for product formation, in agreement with the proposal that irradiation of **4**

and **5** produces triplet phenyl cations^[7a,7b] and that of **1** a singlet phenyl cation.^[6] Both the nitro and the acetyl substituents are known to enhance intersystem crossing when attached to an aromatic moiety. Upon excitation of a salt to a singlet excited state, ISC to a triplet excited state takes place (Scheme 1). The subsequent fragmentation will yield a triplet phenyl cation. This phenyl cation is trapped before it can spin-invert to a singlet state.

Remarkably, the *o/m/p* ratios observed with **4** and **5** are different from the *o/m/p* ratios observed with **2** and **3**, even though both series involve triplet phenyl cations. Scheme 5 explains why the triplet phenyl cations derived from **4** and **5** produce biphenyls with a different regioselectivity than the triplet phenyl cations derived from **2** and **3**. Other than in the mechanism proposed for the photolysis of **2** and **3** in Scheme 4, the closure of the diradical cation toward the phenonium ion here does not take place (Scheme 5). The *para* EWG substituents are not able to harbour the positive charge and thereby reduce the carbenoid character of the reactive species involved. The methoxy biphenyls **4o,m,p** and **5o,m,p** are formed after intramolecular electron transfer and loss of a proton. This means that the *o/m/p* ratio of the photoproducts is solely governed by the radical addition step to anisole. This is also the case in the reaction of the 4-NO₂ phenyl radical with anisole.^[42–44] This explains why the *o/m/p* biphenyl product ratio observed for **5** with anisole (75:12:13) agrees with the ratio observed for the radical reaction (69:15:16, 68:16:16 and 72:12:16). It also explains why that ratio, as well as that observed for **4** (75:13:12), is the same as the ratio observed for the reaction of the parent



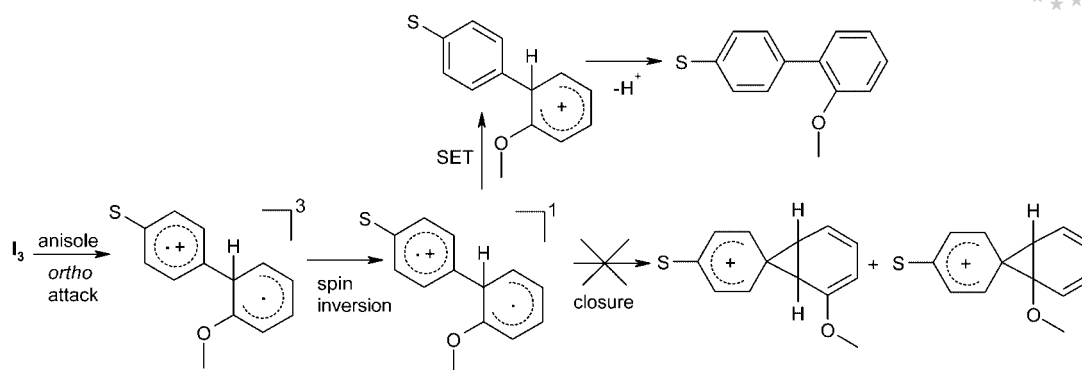
Scheme 4. Mechanism of product formation upon attack of an EDG-substituted triplet phenyl cation (I_3) on anisole ($S = NH_2, OH$).

phenyl radical (produced by photolysis of iodobenzene, vide supra) with anisole (75:13:12).

The EDG- and EWG-substituted triplet phenyl cations produced from **2**, **3**, **4** and **5** display remarkable chemoselectivity. The n -electrons of anisole, acetonitrile and BF_4^- have no appeal for the electron-deficient intermediate. Only reaction with π -electrons occurs. An explanation for this behaviour is that the dispersed charge and electron density of triplet phenyl cations makes them soft electrophiles (Lewis acids), which preferentially react with soft nucleophiles (Lewis bases), according to the HSAB principle.

4-(Diethylamino)phenyldiazonium Tetrafluoroborate (**6**)

The photolysis of **6** yields the methoxybiphenyls **6o**, **m**, **p** in a ratio of 64:3:33 (Table 2, Entry 6). Also, *O*- (**6e**) and *F*- (**6s**) -alkylation products are formed (Table 1). Neither the *o/m/p* ratio nor the product profile match that of the parent diazonium salt **1**, and neither do they match the ratios and the profiles observed in the photolysis of **2**, **3**, **4** and **5**. In particular, the twofold higher yield of Friedel–Crafts product *para* **6p** and the considerable yield of the *O*-alkylation product **6e** stand out. Thus, the product-forming intermedi-

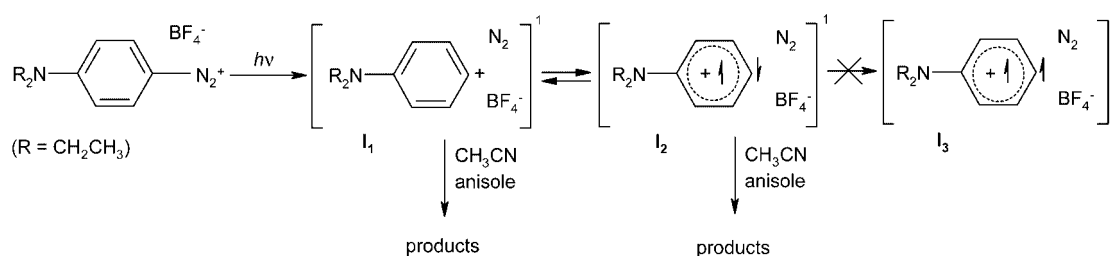


Scheme 5. *ortho* attack of an EWG-substituted triplet phenyl cation (I_3) on anisole [$S=C(=O)CH_3$, NO_2].

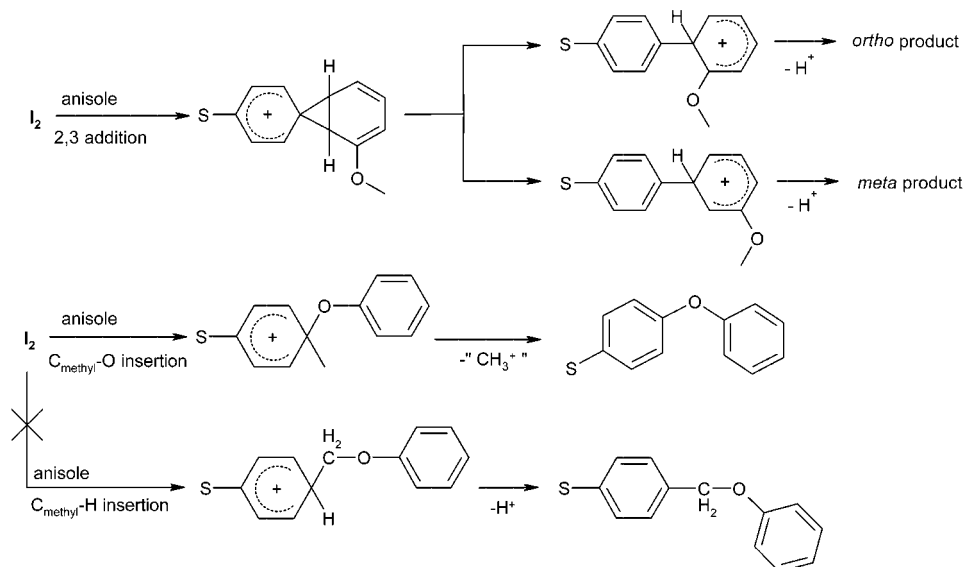
ate is neither a closed-shell singlet phenyl cation nor a triplet phenyl cation.

Presumably, diazonium salt **6** fragments in the singlet excited state and gives the closed-shell singlet phenyl cation I_1 , which equilibrates with the singlet open-shell phenyl cation I_2 (Scheme 6). The singlet open-shell isomer of the parent phenyl cation (I_2-H) has been studied computationally,^[13b,13c] but was not considered a viable reactive intermediate, because it lies much higher in energy than both the

closed-shell singlet (I_1-H) and the triplet phenyl cation (I_3-H).^[13d] This is not the case for the 4-aminophenyl cation. According to CASSCF(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d) calculations, (nonplanar) I_1-NH_2 is only 0.4 kcal mol⁻¹ more stable than I_2-NH_2 . Triplet I_3-NH_2 is about 16 kcal mol⁻¹ more stable than I_1-NH_2 and I_2-NH_2 .^[40b] The polarity of the solvent system would be expected to govern the equilibrium between I_1 and I_2 . In the relatively apolar solvent system used, the open-shell species,



Scheme 6. Mechanism of the photolysis of 4-(diethylamino)phenyldiazonium salt **6**.



Scheme 7. Reactions between the open-shell singlet phenyl cation I_2 and anisole [$S = N(Et)_2$]. The depicted 2,3 mode of attack serves as an example; the 1,2 and 3,4 modes of attack also take place.

with its more dispersed positive charge, may increase in importance over the closed-shell species. The singlet open-shell isomer **I**₂ reacts with anisole with singlet carbene-like behaviour before it can spin-convert into its more stable triplet manifold **I**₃ (Scheme 6). That reaction yields phenonium ions in one step (Scheme 7). After opening to the more stable σ complex and loss of a proton, the methoxybiphenyls **6o,m,p** are produced. Thus, unlike the biphenyl formation from **2** and **3**, and also unlike that from **4** and **5**, the regioselectivity of biphenyl formation from **6** is determined in two steps: a) the selectivity of the initial singlet carbene-like addition to anisole, and b) the formation of the more stable σ complex.

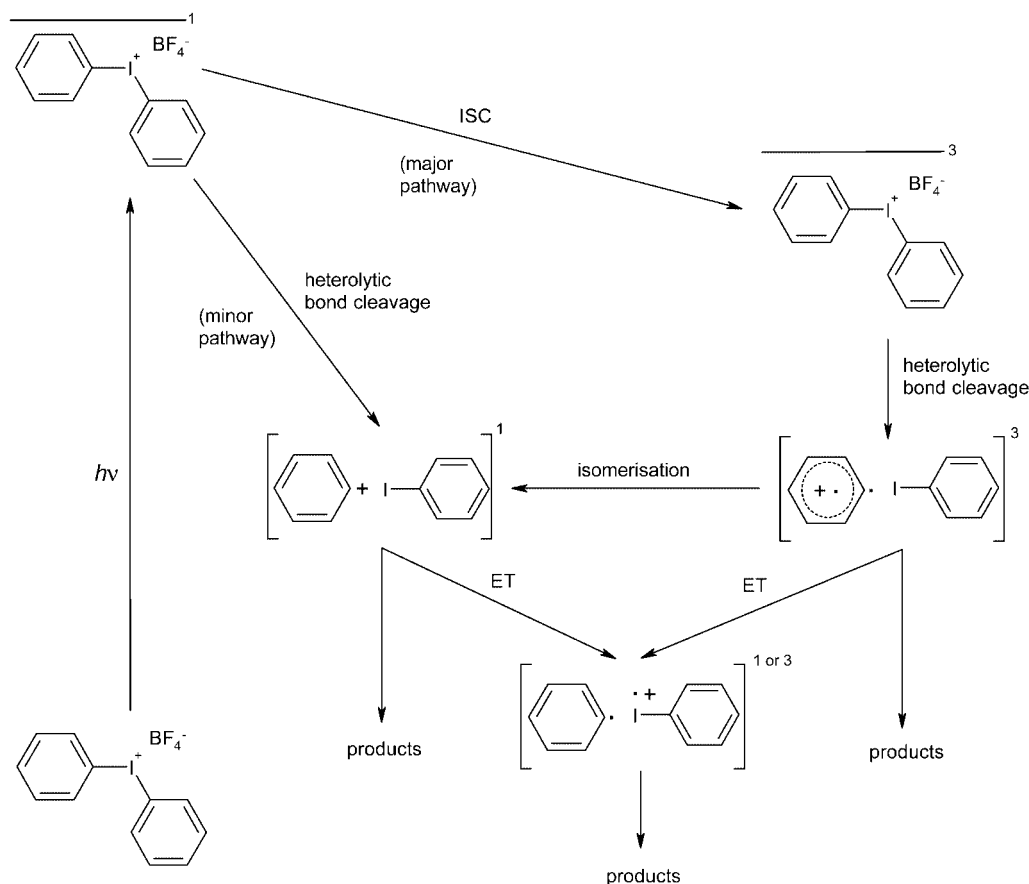
The excess of diphenyl ether **6e** produced in the photoreaction of **6** can be interpreted by assuming a singlet carbene-type insertion by the open-shell phenyl cation **I**₂ in the C_{methyl}–O bond of anisole (Scheme 7). No C_{methyl}–H insertion product is found.

The conversion of the closed-shell singlet into the open-shell triplet phenyl cation (**I**₁ $\rightarrow$ **I**₃) is generally thought to consist of one single step. The trapping of the open-shell singlet 4-(diethylamino)phenyl cation **I**₂ disturbs this picture. The cationic molecule undergoes considerable structural changes in its conversion from the closed-shell singlet to an open-shell triplet. Therefore, the displacement of the nuclei and the spin inversion process may be separate reaction steps.

Diphenyliodonium Tetrafluoroborate (**7**)

Diphenyliodonium salts are often used in photolithography and in the photographic industry.^[45] When subjected to UV light, they are reported to react through phenyl cations, stemming from the cleavage of a C–I bond in the singlet excited state, or through phenyl radicals, thought to originate from a C–I bond fission in the triplet excited state.^[46] The photolysis of **7** in acetonitrile/anisole yields the methoxybiphenyls **7o,m,p** (= **1o,m,p**) in a 68:12:19 ratio. Within experimental error this ratio is the same as the ratio seen in the photolysis of phenyldiazonium tetrafluoroborate (**1**). In addition, the *O*- and *N*-alkylation products diphenyl ether (**7e** = **1e**) and acetanilide (**7r** = **1r**) are also formed, again as in the irradiation of **1**.

Study of the photoreaction of **7** in the presence of anisole as a function of the wavelength of excitation shows that at $\lambda_{\text{exc}} = 300 \text{ nm}$,^[47] products **7o,m,p** are formed in the *o/m/p* ratio of 70:12:18, equal within experimental error to the ratio observed in the experiment at $\lambda_{\text{exc}} = 254 \text{ nm}$ (69:12:19). Further, the relative amounts of phenyl radical-derived benzene [**7h** = (**1h**)] are the same at both wavelengths (**7h/7o,m,p** = 1:4.1) and much less than the amount of benzene produced upon independent generation of the phenyl radical by photolysis of iodobenzene under the exact same reaction conditions (**7h/7o,m,p** = 1:2.1; vide supra).



Scheme 8. Proposed mechanism of the photolysis of diphenyliodonium tetrafluoroborate (**7**).

This indicates that a phenyl radical is not a major product-forming intermediate in the photolysis of **7**.

Both the methoxybiphenyl isomer ratio and the product profile in the photolysis of **7** indicate that product formation largely takes place through a closed-shell singlet phenyl cation. This is quite surprising because the iodine atom would be expected to enhance the rate of ISC and produce a triplet excited state and next a triplet cation after C–I bond fission.

Several transient absorption studies of the photolysis of **7** on the nano- and picosecond timescales reveal the radical cation of iodobenzene as an intermediate.^[48,49] Its presence has been used as support for the longstanding homolytic mechanism for triplet state dissociation, yielding the iodobenzene radical cation and a (not detected) phenyl radical.^[46,50] The iodobenzene radical cation, however, may be a secondary intermediate rather than a primary one. A triplet phenyl cation/iodobenzene pair produced on a femtosecond timescale may, by electron transfer, yield the iodobenzene radical cation observed on the nano- and picosecond timescales. The triplet phenyl cation also spin-inverts to the lower-energy singlet closed-shell phenyl cation, the product-forming intermediate in the photolysis of **7** (Scheme 8). It is proposed that C–I⁺ bond cleavage primarily takes place in the triplet excited state.

The mechanism proposed in Scheme 8 is supported by results for diphenyliodonium, diphenylbromonium and diphenylchloronium hexafluorophosphate photochemistry reported in the literature.^[46b] The *o/m/p* ratios of the halobiphenyls produced by the in-cage phenylation of halobenzenes are fingerprints for the nature of the reactive intermediates. The photolysis of the diphenylchloronium salt in acetonitrile yields chlorobiphenyls in an *o/m/p* ratio of 48:31:21. Practically the same ratio is found for the diphenylbromonium salt: 51:30:19. These ratios indicate a closed-shell singlet phenyl cation as reactive intermediate.^[26] However, for the diphenyliodonium salt the *o/m/p* ratio is 73:13:15. Diphenyliodonium salt photolysis carried out in the high-energy triplet-sensitising solvent acetone produces an even more different *o/m/p* ratio of 70:5:24.^[46a,46b] The low yield of *meta* product observed in the case of the iodonium salt is reminiscent of the photolyses of **2** and **3**, which involve triplet phenyl cations. Even without the aid of a sensitizer, diphenyliodonium salts produce triplet excited states with considerable efficiency. Cleavage of a C–I bond in a triplet state produces a triplet phenyl cation that is either trapped by in-cage iodobenzene or spin-inverts to its singlet ground state.

Conclusions

The photolysis of seven photolabile compounds, known to produce phenyl cations, in acetonitrile in the presence of anisole yields methoxybiphenyls in four distinct *o/m/p* ratios. The differences in regioselectivity are due to the different natures of the product-forming intermediates, resulting in different mechanisms of reaction: a singlet closed

shell, a singlet open shell, an EDG-substituted triplet cation, and an EWG-substituted triplet phenyl cation. The different natures of the various phenyl cation isomers also cause the differences in chemoselectivity. This spin-selective chemistry provides a tool to fingerprint the singlet/triplet nature of any phenyl cation.

The fingerprint of the phenyl cation produced in the photolysis of diphenyliodonium tetrafluoroborate indicates that the product-forming intermediate is a singlet species, despite the presence of the heavy atom iodine. An alternative for the widely accepted mechanism of phenyliodonium salt photolysis (often applied in photolithography) is proposed.

Experimental Section

Materials: Starting materials **2**, **3** and iodobenzene are commercially available and were used as received. Diazonium salt **6** is commercially available and was dissolved in acetonitrile and brought to crystallisation by addition of *n*-pentane prior to use. Compounds **1**,^[51] **4**,^[52] **5**^[51] and **7**^[53] were synthesised by the literature procedures. Anisole was distilled under argon to obtain GC purity. Acetonitrile, trifluoroethanol and anisole were argon-purged prior to their use in the photolysis experiments.

Photochemistry: The photochemical reactions were carried out under argon in quartz tubes with rubber seals. The starting materials were dissolved at 0.05 M in acetonitrile/anisole (1:1, v/v, 10 mL) or trifluoroethanol/anisole (1:1, v/v, 10 mL). *n*-Decane was used as internal standard. The tubes were placed in a Rayonet Reactor (RPR200) fitted with seven 254 nm, 300 nm or 350 nm lamps and equipped with a magnetic stirrer. The photolyses of the salts **1**, **4**, **5**, **6** and **7** were followed as a function of time by taking aliquots (0.050 mL samples) and adding them to water (0.5 mL) + diethyl ether (0.050 mL). The organic layers were analysed 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 into water (10 mL) and extracted twice with diethyl ether (5 mL). The combined ether fractions were analysed by GC and GC-MS. The photolyses of **2**, **3** and iodobenzene were followed, and the products analysed, by direct injection of aliquots on GC and GC-MS.

Photoproducts: The products **1h** (= **7h**), **4h**, **5h**, **6h**, **1s** (= **7s**), **1r** (= **7r**), **1e** (= **7e**), **1o**, and **1p** were identified by means of GC, GC-MS and coinjection with the aid of commercially obtained reference samples. Of all *o/m/p* biphenyl mixtures **2–6o,m,p** the *para* and *ortho* isomers were independently synthesised, from commercially available starting materials, by parallel Suzuki cross-coupling.^[54] *p*-Iodoaniline, *p*-iodophenol, *p*-iodoacetophenone, *p*-iodonitrobenzene and 1-(diethylamino)-4-iodobenzene (1 mmol each) were dissolved together under argon in THF (50 mL). As catalyst, Pd(PPh₃)₄ was added (5 × 10^{−2} mmol, 1 mol-% with respect to total amount of iodo compounds). Cesium carbonate was used as base in equimolar amount with respect to the total amount of iodo compounds (5 mmol). After addition of 4-methoxyphenylboronic acid (6 mmol), the temperature of the solution was raised to reflux and kept at reflux overnight. The reaction mixture was filtered through Celite and dried with calcium chloride. After evaporation of the THF, the slurry was dissolved in dry diethyl ether (20 mL), filtered and analysed by GC and GC-MS to confirm the identity of the product. The five products were formed in yields varying from 20 to 90%.

The parallel Suzuki cross-coupling reaction was repeated with (2-methoxyphenyl)boronic acid, which gave the five desired *ortho* isomers in 20% to 90% yields. Schiemann product **6s** was prepared from **6** by the literature method.^[55] Diphenyl ether **6e** was prepared (among other products) by heating a mixture of diazotised 4-(diethylamino)aniline (0.02 mol) and phenol (0.02 mol) in acetonitrile (2 mL) to 50 °C for 1 h. Of the iodobiphenyls produced in trace amounts in the irradiation of **7**, the *ortho* and *para* products were synthesised separately by diazotisation of 2- and 4-aminobiphenyl in 50% water/concentrated aqueous HCl at melting ice temperature, treatment with KI followed by extraction with diethyl ether, washing of the organic layer with a Na₂S₂O₃ solution (5%) and brine, and evaporation of the solvent.

Equipment: UV spectra were recorded at room temperature with a double-beam Varian DMS 200 spectrophotometer, if applicable with pure solvent in the reference cell. ¹H NMR spectra were recorded on a JEOL 200 instrument, in CDCl₃ as solvent. For analytical GC a Hewlett–Packard 6890 model was used, equipped with a automatic injector, fitted with a CP-Sil5-CB column (25 m, ϕ = 0.25 mm, 1.2 μ m) and with hydrogen as carrier gas. The Flame-Ionisation Detector (FID) was calibrated with 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, ϕ = 0.25 mm, 0.25 μ m) with helium as carrier gas. The GC was coupled to a Finnigan Mat SSQ 710 mass spectrometer, with employment of electron impact as the ionisation method. The GC-MS data were analysed with Xcaliber.

- [1] A. G. Griesbeck, M. Abe, S. Bondock, *Acc. Chem. Res.* **2004**, *37*, 919–928.
- [2] a) M. Jones Jr, R. A. Moss, in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones Jr), John Wiley & Sons, Hoboken, **2004**, pp. 273–328; b) H. Tomioka, in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones Jr), John Wiley & Sons, Hoboken, **2004**, pp. 375–461; c) B. B. Wright, M. S. Platz, *J. Am. Chem. Soc.* **1984**, *106*, 4175–4180; d) P. B. Grasse, B.-E. Brauer, J. J. Zupancic, K. J. Kaufmann, G. B. Schuster, *J. Am. Chem. Soc.* **1983**, *105*, 6833–6845.
- [3] a) M. S. Platz, in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones Jr), John Wiley & Sons, Hoboken, **2004**, pp. 501–560; b) A. Albini, G. Bettinetti, G. Minoli, *J. Am. Chem. Soc.* **1997**, *119*, 7308–7315.
- [4] D. E. Falvey, in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, M. Jones Jr), John Wiley & Sons, Hoboken, **2004**, pp. 593–650.
- [5] S. M. Gasper, C. Devadoss, G. B. Schuster, *J. Am. Chem. Soc.* **1995**, *117*, 5206–5211.
- [6] a) W. Ando, in *The Chemistry of Diazonium and Diazo Groups* (Ed.: S. Patai), Wiley, Chichester, **1978**, part 1, pp. 341–487; b) H. Zollinger, in *The Chemistry of the Triple-bonded Functional Groups* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1983**, part 1, pp. 603–669.
- [7] a) F. Milanese, M. Fagnoni, A. Albini, *Chem. Commun.* **2003**, 216–217; b) S. Milanese, M. Fagnoni, A. Albini, *J. Org. Chem.* **2005**, *70*, 603–610; c) M. Fagnoni, M. Mella, A. Albini, *Org. Lett.* **1999**, *1*, 1299–1301; d) B. Guizzardi, M. Mella, M. Fagnoni, M. Freccero, A. Albini, *J. Org. Chem.* **2001**, *66*, 6353–6363; e) S. Protti, M. Fagnoni, M. Mella, A. Albini, *J. Org. Chem.* **2004**, *69*, 3465–3473; f) M. Fagnoni, *Lett. Org. Chem.* **2006**, *3*, 253–259.
- [8] a) P. Boule, K. Othmen, C. Richard, B. Szczepanik, G. Grabner, *Int. J. Photoenergy* **1999**, *1*, 49; b) K. Othmen, P. Boule, B. Szczepanik, K. Rotkiewicz, G. Grabner, *J. Phys. Chem. A* **2000**, *104*, 9525–9534.
- [9] a) E. Fasani, M. Mella, D. Caccia, S. Tassi, M. Fagnoni, A. Albini, *Chem. Commun.* **1997**, 1329–1330; b) E. Fasani, A. Proffumo, A. Albini, *Photochem. Photobiol.* **1998**, *68*, 666–674; c) E. Fasani, F. F. Barberis Negra, M. Mella, S. Monti, A. Albini, *J. Org. Chem.* **1999**, *64*, 5388–5395.
- [10] S. Torrisi, S. Sortino, *J. Agric. Food Chem.* **2004**, *52*, 5943–5949.
- [11] *Dicoordinated Carbocations* (Eds.: Z. Rappoport, P. Stang), Wiley, Chichester, UK, **1997**, chapter 2, pp. 10–97.
- [12] a) R. Gleiter, R. Hoffmann, W. D. Stohrer, *Chem. Ber.* **1972**, *105*, 8–24; b) H. H. Jaffe, K. G. Koser, *J. Org. Chem.* **1975**, *40*, 3082–3084; c) J. D. Dill, P. von R. Schleyer, J. S. Binkley, R. Seeger, J. A. Pople, E. Haselbach, *J. Am. Chem. Soc.* **1976**, *98*, 5428–5431.
- [13] a) M. Kraus, S. Roszak, *J. Mol. Struct. (THEOCHEM)* **1994**, *310*, 155–160; b) J. Hrusak, D. Schroder, S. Iwata, *J. Chem. Phys.* **1997**, *106*, 7541–7549; c) A. Nicolaiades, D. M. Smith, F. Jensen, L. Radom, *J. Am. Chem. Soc.* **1997**, *119*, 8083–8088; d) M. Aschi, J. N. Harvey, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1059–1062; e) J. N. Harvey, M. Aschi, H. Schwarz, W. Koch, *Theor. Chem. Acc.* **1998**, *99*, 95–99.
- [14] a) M. Winkler, W. Sander, *Angew. Chem. Int. Ed.* **2000**, *39*, 2014–2016; b) M. Winkler, W. Sander, *J. Org. Chem.* **2006**, *71*, 6357–6367.
- [15] M. Speranza, *Chem. Rev.* **1993**, *93*, 2933–2980.
- [16] A. Filippi, G. Lilla, G. Occhiucci, C. Sparapani, O. Ursini, M. Speranza, *J. Org. Chem.* **1995**, *60*, 1250–1264.
- [17] B. R. Ussing, D. A. Singleton, *J. Am. Chem. Soc.* **2005**, *127*, 2888–2899.
- [18] a) P. S. J. Canning, H. Maskill, K. McCrudden, B. Sexton, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 789–800; b) D. Smith, Z. B. Maksic, H. Maskill, *J. Chem. Soc. Perkin Trans. 2* **2002**, 906–913.
- [19] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, Wiley, Chichester, UK, **1995**.
- [20] a) J. D. Dill, P. von R. Schleyer, J. A. Pople, *J. Am. Chem. Soc.* **1977**, *99*, 1–8; b) K. K. Laali, G. Rasul, G. K. S. Prakash, G. A. Olah, *J. Org. Chem.* **2002**, *67*, 2913–2918.
- [21] M. Slegt, F. Minne, H. Zuilhof, H. S. Overkleeft, G. Lodder, *Eur. J. Org. Chem.* **2007**, 5353–5363; preceding paper.
- [22] G. J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*, VCH Publishers, New York, **1993**.
- [23] H. Eustathopoulos, J. Court, J. M. Bonnier, *J. Chem. Soc. Perkin Trans. 2* **1983**, 803–807.
- [24] H. Suschitzky, *Adv. Fluorine Chem.* **1965**, *4*, 1–30.
- [25] J. J. Ritter, P. P. Minieri, *J. Am. Chem. Soc.* **1948**, *70*, 4045–4048.
- [26] G. Angelini, Y. Keheyen, M. Speranza, *Helv. Chim. Acta* **1988**, *71*, 107–119.
- [27] R. A. Abramovitch, F. F. Gadallah, *J. Chem. Soc. B, Phys. Org.* **1968**, 497–500.
- [28] M. Kobayashi, H. Minato, E. Yamada, N. Kobori, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 215–219.
- [29] N. Kamigata, M. Kobayashi, H. Minato, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1231–1235.
- [30] N. Kamigata, R. Hisida, H. Minato, M. Kobayashi, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1016–1018.
- [31] D. Kosynkin, T. M. Bockman, J. K. Kochi, *J. Am. Chem. Soc.* **1997**, *119*, 4846–4855.
- [32] T. M. Bockman, D. Kosynkin, J. K. Kochi, *J. Org. Chem.* **1997**, *62*, 5811–5820.
- [33] a) D. R. Augood, J. I. G. Cadogan, D. H. Hey, G. H. Williams, *J. Chem. Soc.* **1953**, 3412–3417; b) R. L. Dannley, E. C. Gregg, R. E. Phelps, C. B. Coleman, *J. Am. Chem. Soc.* **1954**, *76*, 445–448.
- [34] M. J. S. Dewar, K. Narayanaswami, *J. Am. Chem. Soc.* **1964**, *86*, 2422–2427.
- [35] R. A. Abramovitch, J. Roy, V. Uma, *Can. J. Chem.* **1965**, *43*, 3407–3418.

- [36] M. Hara, T. Sunagawa, Y. Oseki, T. Majima, *J. Photochem. Photobiol. A: Chem.* **2004**, *163*, 153–158.
- [37] E. Wigner, *Z. Phys.* **1927**, *40*, 492–500; E. Wigner, *Z. Phys.* **1927**, *40*, 883–892; E. Wigner, *Z. Phys.* **1927**, *43*, 624–652.
- [38] a) G. Grabner, C. Richard, G. Köhler, *J. Am. Chem. Soc.* **1994**, *116*, 11470–11480; b) A. P. Durand, R. Brown, D. Worall, F. Wilkinson, *J. Chem. Soc. Perkin Trans. 2* **1998**, 365–370.
- [39] I. Manet, S. Monti, M. Fagnoni, S. Protti, A. Albin, *Chem. Eur. J.* **2005**, *11*, 140–151.
- [40] a) M. Slegt, *Selective Alkylation by Photogenerated Aryl and Vinyl Cations*, Thesis, Leiden University, **2006**, p. 63; b) See ref. 40a, p. 55.
- [41] N. Kamigata, M. Kobayashi, H. Minato, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2047–2050.
- [42] R. A. Abramovitch, O. A. Koleoso, *J. Chem. Soc. B* **1969**, 779–785.
- [43] N. Arai, K. Narasaka, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1707–1714.
- [44] R. Itô, T. Migita, N. Morikawa, O. Simamura, *Tetrahedron* **1965**, *21*, 955–961.
- [45] J. V. Crivello, in *Radiation Curing In Polymer Science and Technology*, J. P. Fouassier, J. F. Rabek, Chapman & Hall, London, **1993**, Vol. 2, pp. 435–471.
- [46] a) J. L. Dektar, N. P. Hacker, *J. Org. Chem.* **1990**, *55*, 639–647; b) J. L. Dektar, N. P. Hacker, *J. Org. Chem.* **1991**, *56*, 1838–1844; c) N. P. Hacker, D. V. Leff, J. L. Dektar, *J. Org. Chem.* **1991**, *56*, 2280–2282.
- [47] The photoreaction of **7** at 350 nm, in our set-up, did not yield reproducible product formation, probably because it is very inefficient at this excitation wavelength due to the lack of absorption.
- [48] R. J. Devoe, M. R. V. Sahyun, N. Serpone, D. K. Sharma, *Can. J. Chem.* **1987**, *65*, 2342–2349.
- [49] a) E. Klemm, E. Riesenberger, A. Graness, *Z. Chem.* **1983**, *23*, 222; b) S. P. Pappas, J. H. Jilek, *Photogr. Sci. Eng.* **1979**, *23*, 140; c) S. P. Pappas, B. C. Pappas, L. R. Gatechair, W. Schnabel, *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 69–76; d) S. P. Pappas, L. R. Gatechair, J. H. Jilek, *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77–84; e) S. P. Pappas, B. C. Pappas, L. R. Gatechair, J. H. Jilek, W. Schnabel, *Polym. Photochem.* **1984**, *5*, 1–22.
- [50] J. W. Knapczyk, J. J. Lubinkowski, W. E. McEwen, *Tetrahedron Lett.* **1972**, *35*, 3739–3742.
- [51] P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton, A. W. Timms, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1135–1150.
- [52] P. S. J. Canning, K. McCrudden, H. Maskill, B. Sexton, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2735–2740.
- [53] M. Ochiai, M. Toyonari, T. Nagoaka, D.-W. Chen, M. Kida, *Tetrahedron Lett.* **1997**, *38*, 6709–6712.
- [54] N. Miyaoura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483.
- [55] G. Schiemann, W. Winkelmüller, *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 727–730.

Received: April 17, 2007

Published Online: September 14, 2007