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Cationic arylation through photo(sensitised) decomposition of diazonium salts. Chemoselectivity of triplet phenyl cations

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The photodediazoniation of some 4-X-phenyldiazonium tetrafluoborates in MeCN leads to the singlet phenyl cations (X = H, *tert*-butyl, NMe_2, CN), which add to the solvent yielding the corresponding acetanilides. Triplet sensitisation, however, leads to the triplet phenyl cation, which is reduced in neat solvent and is trapped by π nucleophiles (allyltrimethylsilane and benzene), resulting in an ionic analogue of the Meerwein or Gomberg arylations. With the 4-nitro derivative intersystem crossing prevails over dediazoniation from the singlet and with the 4-cyano competes with it, so that in those cases the triplet phenyl cation is formed also upon direct irradiation.

Diazonium salts[1] are used in organic synthesis either as weak electrophiles in the reaction with activated nucleophiles[2,3] or as precursors of aryl *radicals* (generated through reductive dediazoniation) in the Meerwein arylation of olefins, the Gomberg–Bachmann arylation of aromatics, and the Sandmeyer and Pschorr syntheses.[4] Thermal and/or photochemical formation of aryl *cations*, has a lesser role and is involved in the reaction with counter ion BF_4^- (Schiemann fluorination), and in the reaction with hydroxylic solvents to yield phenols or aryl ethers. Indeed, the exploration of the reactivity of aryl cations[5] and a more extensive application in organic synthesis is highly desirable.[6] Importantly, calculations evidence a different structure for aryl cations in the singlet *vs.* the triplet state, the former corresponding to a localized carbocation (**I**), the latter with charge delocalized over the ring and a carbene character at the divalent carbon (**II**) (Fig. 1).[7]

The singlet is the lowest state, except with strong electron-donating substituents on the ring, but not necessarily the reactive state when photochemically generated as demonstrated by Schuster and coworkers.[8] We recently reported an alternative generation of triplet 4-aminophenyl cation, *via* the photoheterolysis of *p*-chloro(fluoro)anilines and found that it reacted with π nucleophiles (olefins and (hetero)aromatics) and not with σ nucleophiles (except when charged).[9] The chemoselectivity of the triplet cation was appealing, overcoming the unselective reaction with the solvent characteristic of the singlet. This finding and the report by Steenken *et al.*[10] of the cationic arylation of mesitilene fostered a re-examination of the photodecomposition of diazonium salts for the generation of substituted phenyl cations in either spin state, in particularly of the triplet.

We thus report the photodecomposition of some *para*-substituted diazonium tetrafluoroborates **1a–e** in MeCN in the presence of allyltrimethylsilane and benzene as representative π nucleophiles, under conditions where reduction of diazonium cation is avoided.

Irradiation of the fluoborates **1b–e** in MeCN gave the corresponding acetanilides **4** in good to excellent yields along with variable but small amounts of hydro-dediazoniation products **2** and fluorinated derivatives **3** (Scheme 1 and Table 1). Thus, the singlet excited diazonium salt fragments and yield the singlet aryl cation (**5**^{1}) which is trapped by the solvent. The 4-nitrophenyldiazonium salt **1a** behaved differently, yielding nitrobenzene as the main product and no *p*-nitroacetanilide **4a** (see comment below). In the presence of allyltrimethylsilane (ATMS, 1 M) or benzene (3.75 M) **1a** gave a good yield of the arylation products, *p*-allylnitrobenzene (**6a**) and *p*-nitrobiphenyl (**7a**) respectively, in the place of **2a** and **3a** (Table 1 and Scheme 2; with twice as much benzene the yield of **7a** reached 87%).

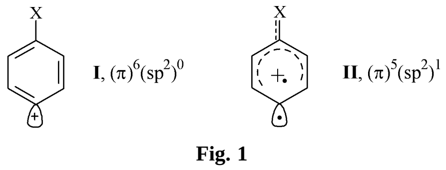
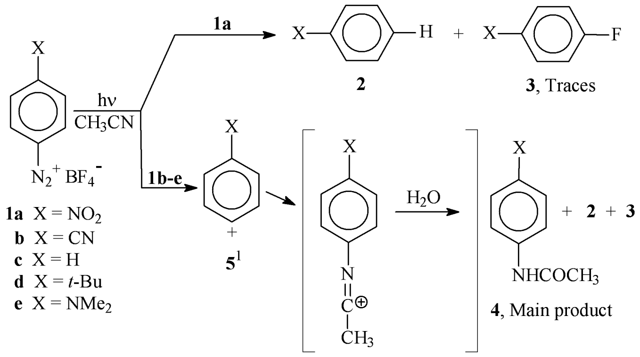


Fig. 1

With the 4-cyano derivative **1b** the arylation was fairly efficient (up to 44%) but acetanilide **4b** was also formed. In the other cases, the yield of acetanilide was little affected by the presence of π nucleophiles though a certain amount of products **6** or **7** was formed.



Scheme 1

Table 1 Yield of arylation products through the irradiation of salts **1** in MeCN in the presence of π nucleophiles[11]

		Product yield[a] (%)			
Salt	Nucleophile	Arylated[b]	**2**[c]	**3**[c]	**4**[c]
1a	None	—	24		
1a	ATMS[d]	**6a**, 51	5		
1a	C_6H_6[e]	**7a**, 74, 87[f]	6		
1b	none	—	5, *49*	7, *0*	69, *0*
1b	ATMS[d]	**6b**, 47, *48*	5, *6*	1, *0*	7, *0*
1b	C_6H_6[e]	**7b**, 44, *84*	4, *10*	9, *0*	35, *0*
1c	None	—	[g]	[g]	76, *5*
1c	ATMS[d]	**6c**, 5[c], *47*	[g]	[g]	81, *5*
1c	C_6H_6[e]	**7c**, 9[c], *32*	[g]	[g]	60, *9*
1d	None	—	4, *68*		86, *0*
1d	ATMS[d]	**6d,** 2[c], *48*	4, *34*		89, *6*
1d	C_6H_6[e]	**7d**, 12[c], *17*	12, *61*		70, *0*
1e	None	—	2, *29*		68, *0*
1e	ATMS[d]	**6e**, 2[c], *55*	3, *13*		87, *0*
1e	C_6H_6[e]	**7e**, 25[c], *41*	2, *2*		63, *0*

[a] In italic are the yields upon xanthone sensitisation. [b] Isolated yield. [c] 0 = GC yields < 0.5%, no figure reported when both zero. [d] Reaction in the presence of 1 M ATMS. [e] Reaction in the presence of 3.75 M benzene. [f] Reaction in the presence of 7.5 M benzene. [g] Not determined.

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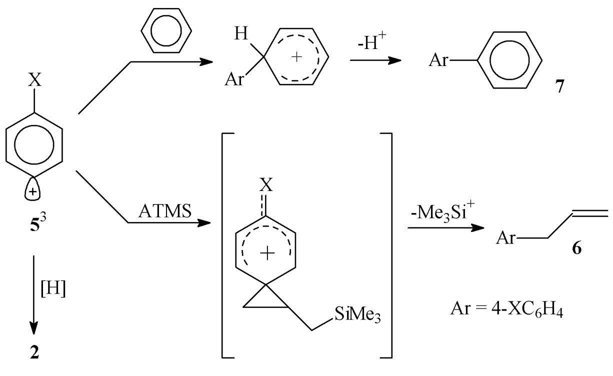
Since direct irradiation led to singlet chemistry almost exclusively with salts **1c–e** and for a large part with **1b**, we turned to sensitisation and used xanthone, because diazonium salts are known as ketone triplet quenchers.[12] In all cases, formation of the acetanilides was greatly reduced or eliminated and reduction to compounds **2** became the major pathway in neat MeCN. In the presence of ATMS or benzene, arylated products **6** and respectively **7** became in most cases the main products. Clearly, a different chemistry was occurring and involved reduction and addition to π nucleophiles, *viz* the reactions expected from the triplet phenyl cation.

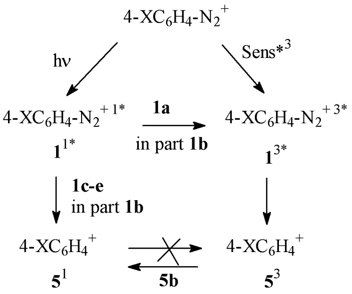
Thus, sensitisation leads to triplet diazonium salt, fragmentation occurs in this manifold and the thus formed triplet phenyl cation (**5**^{3}) reacts before ISC to the singlet takes place, even when the latter spin state is the lowest one, as it is the case for all the compounds examined except the amino substituted **1e**. The triplet abstracts hydrogen even from a poor donor such as acetonitrile rather than forming an ylide as the singlet does, and reacts with π nucleophiles *via* an addition–elimination mechanism as represented in Scheme 2 (the adduct with ATMS is indicated as a phenonium cation, probably the most stable configuration).[9]

The material balance is satisfactory and, except in the case of **1d** (X = *tert*-butyl), where reduction remains the main path also in the presence of benzene, reaction with π nucleophiles is efficient and the synthetically interesting products **6** and **7** are formed in good yield. These reactions are ionic analogues of the Meerwein and Gomberg–Bachmann arylations and are clearly distinguished from them, which, as it is well known, involve the aryl radical. In fact the present arylations are not chain reactions (Φ = 0.5 for **1c–e**, 0.25 for **1b** and $\leq$0.1 for **1a**). Photoinitiated chain reactions are known for easily reducible diazonium salts such as **1a** in the presence of good hydrogen donors, *e.g.* aqueous methanol as the solvent, where reduction occurs with $\Phi \approx 3.5$–8.[13] Furthermore, the present reactions involve attack to nucleophilic, not electrophilic, olefins. We checked that generating the 4-nitrophenyl radical from **1a** under the classical Meerwein conditions ($CuCl_2$) leads to arylation of acrylonitrile (forming the 3-phenyl-2-chloropropionitrile) but not of ATMS (product **6a** 10%) and conversely photodecomposition of **1a** in the presence of acrylonitrile does not lead to arylation, contrary to the case of ATMS. At any rate, it may prove difficult to exclude some participation of a phenyl radical in the case of the easily reduced **1a**, but this does not applies to the other salts.

Thus, photosensitisation is a general method for arriving at the *triplet* phenyl cation, when, as occurs with most diazonium salts, direct irradiation yields the singlet. In contrast, the nitro-substituted **1a**^{1*} apparently undergoes ISC to the diazonium triplet before decomposition and generates the phenyl cation in the triplet state also upon direct irradiation. The same behavior has been previously found for the 4-benzoyl derivative[8] and is not surprising in view of the fast ISC generally occurring with nitroaromatics.[14] The case of cyano derivative **1b** is somewhat more complicated, in that some arylation products **6b**, **7b** are found also upon direct irradiation, and the sensitised reaction differs essentially in the non-formation of acetanilides. The simplest explanation is that ISC from the excited diazonium singlet **1b**^{1*} competes to some degree with fragmentation and the phenyl cation is formed in both spin states. However, the triplet cation **5b**^{3} seems to be a poor hydrogen abstracting species, and in neat MeCN it intersystem crosses to the lower-lying singlet, although the presence of π traps such as ATMS or benzene reveals its presence (Scheme 3).



Scheme 2



Scheme 3

Summing up, a rivisitation of the direct and sensitized photochemistry of diazonium salts suggests that controlled conditions may be found for the generation of phenyl cations in either spin state each of which have a distintive chemistry. These as yet elusive species may develop from spectroscopic curiosities to synthetically useful intermediates, in particular with regard to the triplet states which lend themselves to C–C bond forming reactions.

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