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Smooth Synthesis of Aryl- and Alkylanilines by Photoheterolysis of Haloanilines in the Presence of Aromatics and Alkenes

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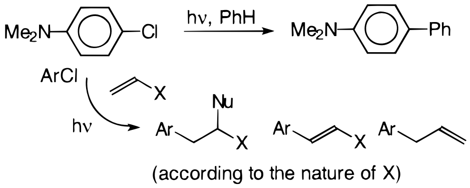
ABSTRACT



Irradiation of 4-chloro-*N,N*-dimethylaniline in acetonitrile in the presence of benzene and of various alkenes leads to heterolytic dehalogenation and trapping of the cation. 4-(Dimethylamino)biphenyl is formed in the first case, while with alkenes *β*-chloroalkylanilines, stilbenes, or allylanilines are obtained depending on the alkene structure. 4-Fluoroaniline is similarly dehalogenated.

Phenyl cations have been the subject of active research from the mechanistic point of view.[1] These are usually generated under proper conditions from diazonium salts[2] and have been spectroscopically characterized both in matrix[3] and in the gas phase.[4] In the few case where the products from the reaction in solution have been characterized, both reduction and addition to O- and N-centered nucleophiles have been found to occur.[2a,5] On the contrary, C−C bond formation does not involve the cation. When biaryls are formed from diazonium salts, as in the Gomberg−Bachmann or in the Pschorr reactions,[6] the actual reacting species is the aryl radical. Recently, however, Steenken and McClelland[7] reported the formation of biphenyls by irradiation of phenyldiazonium salts in the presence of benzene derivatives and showed that the process involved the cation.

We are pleased to report in the following an alternative generation of aryl cations and to show that this gives rise to synthetically useful reactions.

Irradiation of both 4-chloro- and 4-fluoro-*N*,*N*-dimethylaniline (**1a**,**b**) in acetonitrile caused reductive dehalogenation to **2**, but important products were also the corresponding 2,4′-bis(*N*,*N*-dimethylamino)biphenyls **3** (ca. 30%, see Scheme 1). This appeared a clear indication that a phenyl cation was formed under this condition.

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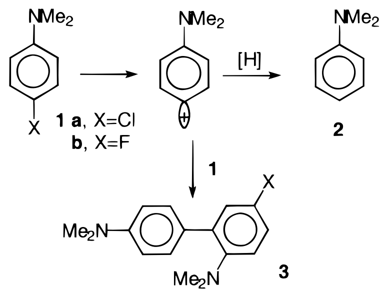
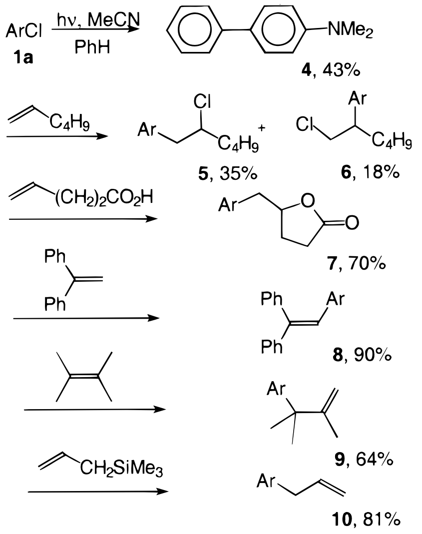
10.1021/ol990982g CCC: $18.00

Scheme 1. Photolysis of 4-Chloro- and 4-Fluoro-*N*,*N*-dimethylaniline in Acetonitrile



Trapping experiments were thus undertaken with **1a**. Photolysis of **1a** in 1 M benzene in acetonitrile gave biphenylamine **4** in a moderate yield. With 0.1 M benzene in MeCN, trapping was partial, while in neat benzene the photolysis of **1a** occurred sluggishly, though actually giving **4** (Scheme 2).

Scheme 2. Photolysis of 4-Chloro-*N*,*N*-dimethylaniline in Acetonitrile in the Presence of Benzene or of Alkenes

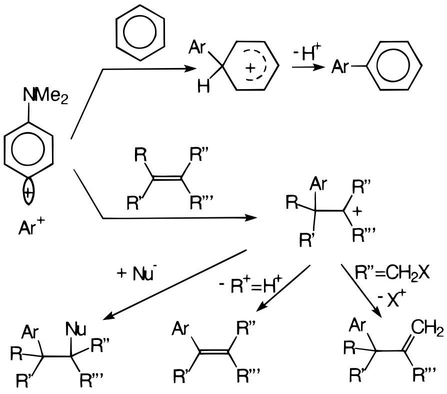


Alkenes were then tested. In the presence of 1 M 1-hexene, **1a** gave the two possible β-chloroalkylanilines **5** and **6**. An experiment of intramolecular nucleophilic trapping was attempted with 4-pentenoic acid, and actually gave lactone **7** in a satisfactory yield.

In the presence of 1,1-diphenylethylene (0.1 M), stilbene **8** was obtained in a good yield. Finally, both 2,3-dimethyl-2-butene and allyltrimethylsilane gave an allyl derivative, respectively compounds **9** and **10**, in good yields.

All of these results are compatible with the generation of the 4-(*N*,*N*-dimethylamino)phenyl cation by heterolysis of the corresponding halide. The reaction is efficient, with the quantum yield for decomposition of **1a** approaching unity, at least in a polar solvent. The cation is in part reduced, consistently with the possible role of a triplet state (radical $\pi^5\sigma^1$ structure, rather than the $\pi^6\sigma^0$ singlet state structure).[8] In the presence of a π nucleophile, however, an efficient electrophilic reaction results. Thus, the cation is trapped either by the starting haloaniline to give products **3a**,**b** or, when this is present, by another aromatic, as is the case here with benzene (Scheme 3). This offers a method for the synthesis of biarylamines.

Scheme 3. Mechanism of the Arylation Reaction



Even more interesting from the preparative point of view is the addition to alkenes. This is not regiospecific, judging from the result with 1-hexene, but has the advantage that it gives the adducts in a clean way, with no significant polymerization, since the cation adduct is efficiently trapped by the chloride anion set free in the photolysis (see Scheme 3). Intramolecular nucleophilic trapping is possible, as shown by the efficient synthesis of lactone **7** (minor amount of the regioisomeric chlorinated pentanoic acids analogous to **5** and **6** were also formed).

Under appropriate conditions, elimination was also effective and depended on thermodynamic or kinetic grounds. Thus, in the case of diphenylethylene, α-deprotonation occurred efficiently and led to the stabilized triarylethylene **8**, while with dimethylbutene β-deprotonation occurred in preference to nucleophile addition at a tertiary center. The presence of a good electrofugal group such as the trimethylsilyl cation likewise directed the reaction toward β elimination to give the 4-allylaniline **10** with allylsilane.

The above smooth method should be compared with alternative syntheses that, when available as for allylaniline **10**[9] and triarylethylene **8**,[10] involve metal complex-catalyzed coupling or multistep procedures.

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Summing up, apart from the mechanistic interest, the smooth generation of phenyl cations from haloanilines is a synthetically promising method. The unconventional alkylation of anilines leads to C−C bond formation via the nearly unprecedented electrophilic addition onto alkenes.[11] The present findings are limited to anilines. However, there is some evidence in the literature that photoinduced heterolytic dehalogenation may take place also with other electron-donating substituted aromatics[12] or heterocycles[13] and it is possible that the synthetic principle illustrated above may be more largely applicable.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of compounds **3a**, **3b**, **5**−**7** and **9** (compounds **4**, **8** and **10** are known). This material is available free of charge via the Internet at http://pubs.acs.org.

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