Photoinduced, Ionic Meerwein Arylation of Olefins

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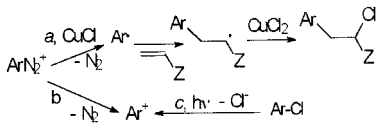
Irradiation of 4-chloroaniline or of its *N*,*N*-dimethyl derivative in polar solvents generates the corresponding triplet phenyl cations. These are trapped by alkenes yielding arylated products in medium to good yields. B3LYP calculations show that the triplet cation slides with negligible activation energy to a bonded adduct with ethylene, whereas it forms only a marginally stabilized CT complex with water (chosen as a representative σ nucleophile). The structure of the final products depends on the preferred path from the adduct cation with the alkene. In the case of aryl olefins, this deprotonates to stilbene derivatives, while, from 2,3-dimethyl-2-butene and allytrimethylsilane, allylanilines are obtained by elimination of an electrofugal group in γ. In the case of mono- and disubstituted alkenes the cation adds chloride rather than eliminating and β-chloroalkylanilines are obtained. The regio- and sterochemistry of the addition across the alkene are best understood with a phenonium ion structure for the adduct. The nucleophile entering in β can be varied under conditions in which the adduct cation is trapped more efficiently than the starting phenyl cation. Thus, β-methoxyalkylanilines are formed when the irradiation is carried out in methanol. β-Iodoalkylanilines are obtained in acetonitrile containing iodide and unsubstituted alkylanilines in the presence of sodium borohydride. A case of intramolecular nucleophilic trapping is found with 4-pentenoic acid. The reaction is a wide-scope ionic analogue of the radicalic Meerwin arylation of olefins.

The Meerwein arylation of alkenes[1] involves reduction of diazonium salts, homolytic dediazonation, and addition of the resulting aryl radical onto an olefin activated by an electron-withdrawing group.[2] This is shown in Scheme 1, path a, for a typical example in which the initial reductive step involves a Cu(I) species and the process is terminated by ligand transfer from copper(II) chloride. The process was first proposed to involve heterolytic cleavage (path b)[1] but was subsequently proved to follow the homolytic path.[3] Thus the phenyl radical, not the cation, is involved in the C−C bond-forming step. The latter species has been generated by photolysis of phenyldiazonium salts,[4] but under these conditions only synthetically uninteresting reactions with the solvent (acting as a nucleophile or as a hydrogen donor) have been reported.[4] In fact, C−C bond formation via an aryl cation was not known until recently. In 1998, however, it was reported that phenyl cations formed via photoinduced dediazonization could be trapped by arenes,[5,6] and in the following year, we found a different access to such

Scheme 1



cations, on the basis of the photoinduced heterolysis of 4-chloroanilline and its *N*,*N*-dimethyl derivative. These gave the corresponding 4-aminophenyl cations (Scheme 1, path c), which could be trapped by arenes.[7] This suggested the possibility of a ionic analogue of the Meerwein reaction. As it appears in the following, the expectation was fulfilled and led to an arylation reaction susceptible to several variations of synthetic interest.[8] Indeed, this photochemical method for the generation of phenyl cations showed a limited dependence on experimental parameters and allowed more freedom in directing the ensuing chemistry of such intermediates through the appropriate change in the conditions. Furthermore, B3LYP calculations on the *triplet* 4-aminophenyl cation allowed one to rationalize the mechanism of the addition to alkene as well as the lack of reaction of this cation with neutral σ nucleophiles.

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(6) This differs from the Gomberg−Bachmann arylation of aromatic compounds, which again involves aryl radicals and not cations; see ref 2.

(7) See the accompanying manuscript.

(8) Preliminary communication of part of this work: Fagnoni, M.; Mella, M.; Albini, A. *Org. Lett.* **1999**, *1*, 1299. Coppo, P.; Fagnoni, M.; Albini, A. *Tetrahedron Lett.* **2001**, *42*, 4271.

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Scheme 2

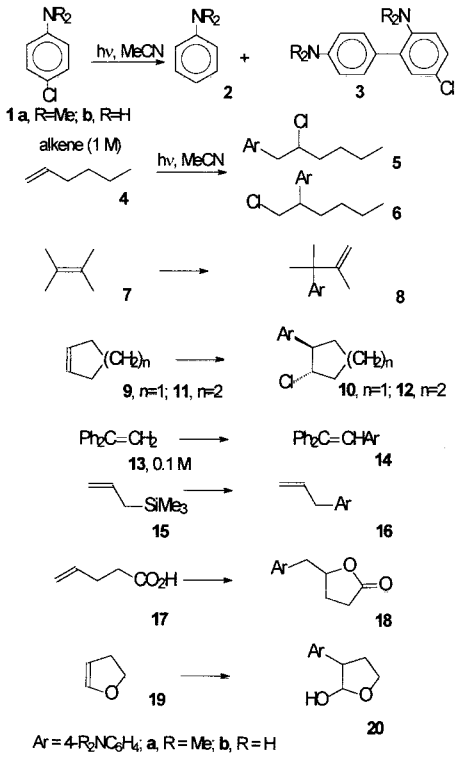


Table 1. Preparation of 4-Alkylanilines by Irradiation of Chloroanilines 1a,b in Acetonitrile in the Presence of Alkenes

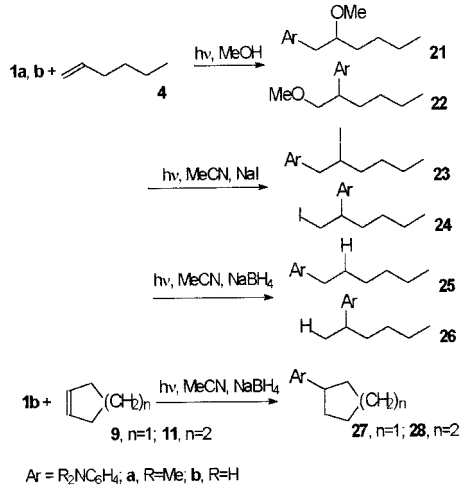
aniline	alkene[a] (1 M)	alkylated aniline	other products (% yield)[b]
1a	**4**	**5a** (35), **6a** (18)	**2a** (20)
1b	**4**	**5b** (35), **6b** (16)	**2b** (23)
1a	**7**	**8a** (64)	**2a** (15)
1b	**7**	**8b** (55)	**2b** (18)
1b	**9**	**10b** (49)	**2b** (29)
1a	**11**	**12a** (42)	**2a** (34)
1b	**11**	**12b** (45)	**2b** (37)
1a	**13**[c]	**14a** (90)	**2a** (3)
1a	**15**	**16a** (81)	**2a** (4)
1a	**17**	**18a** (70)	**2a** (5)
1a	**19**	**20a** (49)	**2a** (13)

[a] 1 M except when noted. [b] In all cases low amounts (up to 5%) of diphenyldiamines **3a,b** were formed. [c] 0.1 M.

Results

Preparative Irradiations in Acetonitrile. In the accompanying paper it has been reported that the irradiation of 4-chloroanilines **1a,b** in acetonitrile caused both reductive dechlorination to the corresponding anilines **2a,b** and coupling to the biphenyldiamines **3a,b** (see Scheme 2).[7] The photochemical reaction was now explored in the presence of alkenes. Thus, a solution containing 0.05 M **1a** and 1 M 1-hexene (**4**) was irradiated and it was observed that the photodecomposition of the chloroanilines occurred at about the same rate as in neat MeCN, but the yields of aniline **2a** and of **3a** dropped to 20 and 5%, respectively, and two new products were formed. These were characterized as the regioisomeric 4-(*β*-chloroalkyl)anilines **5a** and **6a**, formed in 35% and 18% yields, respectively (Scheme 2, Table 1). In the presence of a lower amount of the alkene, e.g. 0.1 M, the main products remained **2a** and **3a** with no preparatively significant formation of the alkylanilines **5a** and **6a**. The

Scheme 3



nonmethylated chloroaniline **1b** was similarly alkylated in the presence of **4** with practically the same yields.

Irradiation of both chloroanilines in the presence of 2,3-dimethyl-2-butene (**7**) gave reasonable yields of chlorine-free products, the trimethylallylanilines **8a,b** (64 and 55%, respectively). The reaction with cyclopentene (**9**) and cyclohexene (**11**) gave again *β*-chloroalkylanilines (**10**, **12**). Yields were lower in these cases (42−49%), and the products were formed in the trans configuration.

1,1-Diphenylethene (**13**) was then tested as a representative aromatic alkene. This was used at a lower concentration (0.1 M) and slowed the photoreaction of **1a** because of competitive absorption in the same wavelength range. It gave a good yield (90%) of the (aminophenyl)diphenylethene **14a**.

The photochemical reaction was then explored in the presence of functionalized alkenes. Allyltrimethylsilane (**15**) was a quite efficient trap giving the allylaniline **16a** (81%). 4-Pentenoic acid (**17**) gave lactone **18** in 70% yield. With enol ether **19** extensive polymerization took place due to catalysis by the hydrochloric acid liberated in the photodecomposition of **1a**. However, stirring solid potassium carbonate in the irradiation vessel during the reaction eliminated this drawback, and under this condition, the aniline was alkylated, giving after chromatography lactol **20a**, obtained as a solid (49%; in solution this hemiacetal was present as a mixture of diastereoisomers).

Solvent Effect and Quantum Yield Measurements. The above photochemical reaction of the anilines with alkenes was explored also in other solvents using 1-hexene. Alkylation was successful also under these conditions, but several changes occurred. These included the following: (i) a change in the structure of the alkylated products, since the irradiation in methanol gave the *β*-methoxyalkylaniline **21**, with a trace of isomeric **22** detected only by GC/MS, rather than the two isomeric *β*-chloroalkylanilines discussed above (see Scheme 3, Table 3); (ii) a variation in the ratio between alkylanilines and other products, in particular reduced anilines **2** (Table 2); (iii) a change in the reaction quantum yield (Table 2); (iv) the formation of additional products when the solvent was itself a trap for the phenyl cation, as it was the case for benzene which gave some biphenylamine (Table 2).

Preparative studies were not extended to all conditions, but points ii and iii were investigated systematically by

Table 2. Reaction Quantum Yield and Percentages of Reduction and Alkylation in the Irradiation of Chloroanilines 1a,b in Various Solvents in the Presence of 1 M 1-Hexene

		1a			1b		
solvent	Φ_r	% redn	% alkyln	% diamine	Φr	% redn	% alkyln[a]
MeCN	0.84	11	70	7	0.44	11	86
MeOH	0.94	26	60	9	0.47	21	76
CF_3CH_2OH	0.55	6	72	12	0.2	9	85
iso-PrOH	0.91	68	21	4	0.39	60	35
tert-BuOH	0.68	11	80	4	0.23	8	84
AcOEt	0.45	11	55	5	0.11	13	80
benzene	0.05		40[b]		0.05		58[c]

[a] A small amount of diphenyldiamine **3b** (up to 5%) is formed also in these cases. [b] 35% of *N*,*N*-dimethyl-4-biphenylamine also formed. [c] 25% of 4-biphenylamine also formed.

Table 3. Products from the Irradiation of 4-chloroanilines 1a,b in the Presence of Alkenes (1 M) under Various Conditions[a]

reagents[b]	conditions	products (% yield)
1a, **4**	MeOH	**2a** (15), **21a** (58), **22a** (tr)
1b, **4**	MeOH[b]	**2b** (12), **21b** (62), **22b** (tr)
1a, **4**	MeCN, 0.015 M NaI[c]	**2a** (2), **23a** (35), **24a** (5), $4\text{-}IC_6H_4NMe_2$ (10)
1b, **4**	MeCN, 0.015 M NaI[c]	**2b** (3), **23** (32), **24** (10), $4\text{-}IC_6H_4NH_2$ (12)
1a, **4**	MeCN, $NaBH_4$[d]	**2a** (33), **5a** (tr), **6a** (tr), **25a** (32), **26a** (21)
1b, **4**	MeCN, $NaBH_4$[d]	**2b** (27), **5b** (2), **6b** (3), **25b** (34), **26b** (17)
1b, **9**	MeCN, $NaBH_4$[d]	**2b** (36), **10** (8), **27** (38)
1b, **11**	MeCN, $NaBH_4$[d]	**2b** (36), **12** (7), **28** (33)

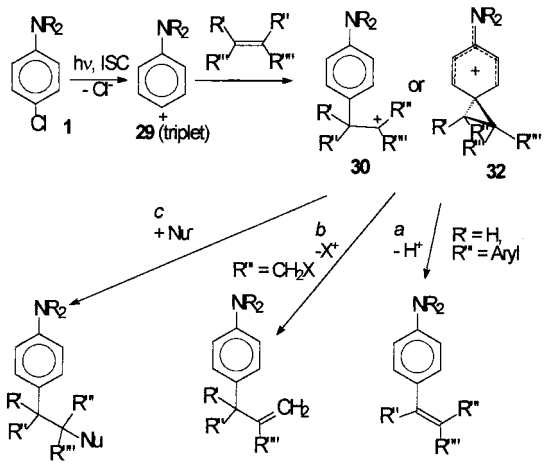
[a] ≥85% conversion except where otherwise noted. [b] 0.05 M **1a,b** except where otherwise noted. [c] 0.02 M **1b**, 60% conversion. [d] A concentrated aqueous solution of $NaBH_4/K_2CO_3$ was drop-by-drop added during the irradiation (see Experimental Section).

measuring the reaction quantum yield of reaction of chloroanilines **1a,b** (Φ_r) and the proportions of reduction to anilines **2a,b** vs that of alkylation in a range of solvents. The results are reported in Table 2.

Trapping by Anions. A previous study[7] had shown that irradiation of the anilines in the presence of iodide led to the corresponding iodoanilines. In view of the present finding that β-chloroalkylanilines were formed in the presence of alkenes, it was explored whether iodide could be incorporated in the alkyl chain. Indeed, irradiation of 0.02 M solution of **1a,b** containing 0.015 M sodium iodide and 1-hexene gave the β-iodoalkylanilines **23** and **24** as the main products at 60% conversion (Scheme 3, Table 3), though at complete conversion some secondary decomposition occurred.

This encouraged us to extend the experiments to conditions devised to modify the nucleophile entering in the β position during the process. The most significant target appeared to be insertion of a nonfunctionalized alkyl chain. A relatively mild reducing agent was used, $NaBH_4$. This was soluble up to 0.03 M in MeCN. Irradiation of chloroanilines **1a,b** under this condition caused almost only reductive dechlorination (93−95%). In the presence of alkenes, however, both anilines and alkylanilines were formed, with a strong reduction of the proportion of the β-chloroanilines. From the preparative point of view, it was found more expedient to drop-by-drop add a concentrated solution of $NaBH_4/K_2CO_3$ during the irradiation to maintain a low steady-state concentration of the reducing agent. Under these conditions the hexylanilines **25a,b** and **26a,b** were obtained from both **1a,b** in 50−55% combined yield along with ca. 30% reduced anilines **2a,b** and ≤5% chloroalkylanilines (**5**, **6**). In a control experiment, it was shown that irradiation under the same conditions of a solution of the β-chlorohexylanilines **5** and **6** in the presence of $NaBH_4/K_2CO_3$ did not cause their reduction.

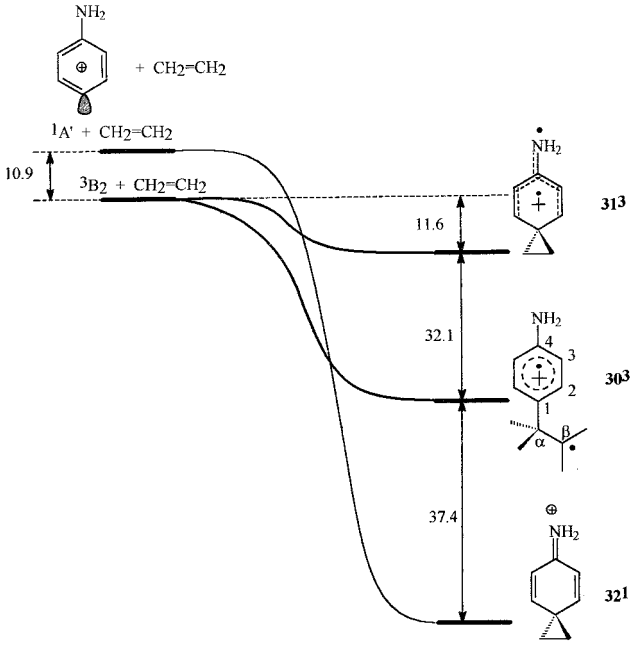
Scheme 4



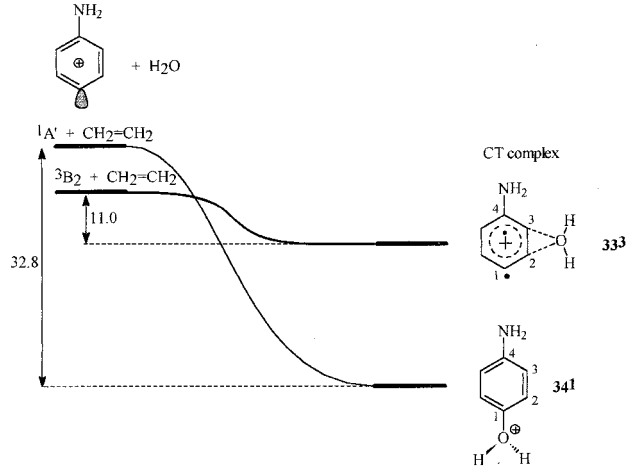
The hexylanilines **25** and **26** were easily freed from the nonalkylated anilines by bulb-to-bulb distillation, and this appeared to be a viable entry to such compounds. Therefore, the experiments were extended to cycloalkenes **9** and **11** and reasonable yields of the 4-cycloalkylanilines **27** and **28** were obtained. In these experiments, as well as in the previous cases, the rate of photochemical reaction of the chloroanilines underwent no major change with respect to the irradiation in a neat solvent, although, as seen above, the product distribution changed deeply. The reaction of **1b** in MeCN containing 0.03 M $NaBH_4$ was somewhat more efficient than in neat MeCN (Φ_r ca. 0.6 vs 0.44) both in the presence and in the absence of the olefins. There was no corresponding increase in the case of **1a**.

Calculations. In the accompanying paper it has been shown that photoheterolysis of chloroanilines **1a,b** led to the corresponding *triplet* phenyl cations (**29**), which is suggested to be the key intermediate in the present reactions (see Scheme 4).[7] This state had an intermediate carbene−diradical at C_1, as evidenced by computational data obtained at the B3LYP/6-31G(d) as well CASSCF-(8,8)/6-31(d) levels of theory. To obtain a mechanistic rationale for the chemistry discussed above, viz. the efficient arylation of alkene as contrasted with the lack of formation of ethers with alcohols, a computational study was carried out. Thus, the PESs (potential energy surfaces) of the 4-aminophenyl cation (both triplet and singlet states) with water and with ethylene (chosen as prototypes of an n nucleophile and π nucleophile, respectively) were investigated in the gas phase. Since our previous work had demonstrated that the B3LYP method

Scheme 5. Potential Energy Surface (B3LYP/6-31G(d)) for Singlet ($^1A'$) and Triplet ($^3B_2$) States of the 4-Aminophenyl Cation with Ethylene



Scheme 6. Potential Energy Surface (B3LYP/6-31G(d)) for Singlet ($^1A'$) and Triplet ($^3B_2$) States of the 4-Aminophenyl Cation with Water



was satisfactory for describing the nature of the triplet state of this cation,[7] this method (with a 6-31G(d) basis set) could be confidently used for locating possible intermediates on the PES in the case of the triplet. In the case of the singlet state, one had to keep in mind that, due to the peculiar nature of the singlet state which is described by *two* electronic configurations ($\pi^6\sigma^0$ and $\pi^4\sigma^2$), a better strategy for a computational investigation on the singlet state reactivity would be using a multiconfigurational approach (CASSCF method). Work is in progress on this issue. However, at the present stage B3LYP data are sufficient for evidencing the contrasting behavior of the two states as far as the location of the intermediates along the PES is concerned.

The results are shown in Scheme 5 for the reaction with ethylene, where two minima were located on the triplet PES (**30**^{3} and **31**^{3}) and one on the singlet PES (**32**^{1}), and in Scheme 6 for the reaction with water, where the minima located were **33**^{3} in the triplet and **34**^{1} on the singlet surface.

Discussion

Main Features and Scope of the Reaction. A parallel mechanistic investigation of the photochemistry of 4-chloroanilines **1a,b**[7] demonstrated that these undergo heterolytic cleavage from the triplet state and give the corresponding phenyl cations. These are formed in the triplet state that in this case (contrary to parent phenyl cation) are the ground states (stabilized by >10 kcal mol^{-1} with respect to the singlet). Such species are trapped by benzene and its methyl derivatives through an electrophilic substitution reaction, but do not form ethers with alcohols.[7] Ethers are on the contrary obtained by photodecomposition of 4-(dialkylamino)phenyldiazonium salts in alcohols, a reaction presumed to involve the singlet phenyl cation.[4d]

The present study confirms the expectation based on the above-mentioned indications about the reactivity of triplet cation, demonstrating that electrophilic addition to alkenes occurs efficiently and that the choice of the medium and of additives allows one to further manipulate the path followed toward a variety of final products. The irradiation of choroanilines in the presence of alkenes can thus be developed into a versatile method for the synthesis of variously functionalized alkylanilines.

Consideration of the quantum yields of reactions of the chloroanilines in the presence of alkenes (Φ_r in Table 2) shows that these little differ from those previously measured in the same solvents in their absence (compare ref 7).[9] This implies that a reactive intermediate is formed upon excitation independently from the additives but with a strongly polarity-dependent efficiency. This is the 4-aminophenyl cation **29**, formed, as previously proposed,[7] from the heterolysis of triplet chloroanilines **1**. The cleavage is due to the internal charge-transfer character of these states and is promoted by a polar medium, as shown by the increase by a factor of 20 in passing from benzene to acetonitrile and alcohols with ethyl acetate in an intermediate position. A more acidic alcohol, on the other hand, depresses Φ_r (see the lower values with CF_3CH_2OH), since in this case hydrogen bonding of the amino group decreases the CT character of the excited state.

As surmised, the cation is trapped by alkenes. That the alkene traps the cation rather than interacting with triplet chloroaniline before the fast fragmentation of the latter ($\tau \ll 100$ ns)[7] is indicated by the above-mentioned invariance of Φ_r in the absence and in the presence of the alkenes which, along with the further evidence below, excludes that a different mechanism, such as photoinduced electron transfer, exciplex formation or $S_{RN}1$, is involved. End products are vinyl-, allyl- or β-chloroalkylanilines, all of which can be rationalized as arising via the intermediate adduct cation. As it will be discussed

(9) (a) An exception is the reaction with 1,1-diphenylethylene, where competitive light absorption by the alkene makes it difficult to evaluate the quantum yield of the reaction via excited chloroaniline and its quantum yield. A recent investigation by Arnold[9b] reports a large number of photoreactions of this alkene with substituted halobenzenes, including methoxychlorobenzenes. Such reaction apparently involve an electron-transfer path or an exciplex. A donating group does not favor that reaction, and we feel that this mechanism does not apply in the present reaction of chloroanilines. (b) Mangion, D.; Arnold, D. R. *Can. J. Chem.* **1999**, *77*, 1655.

in the following, this can be envisaged either as an open-chain or as a phenonium cation (respectively structures **30** and **32** in Scheme 4). Evidence for the structure of such an intermediate and a rationalization of its role in the formation of the final products are presented.

Reactions of the Phenyl Cation. The PES of the reaction between both the triplet (**29**^{3}, $^3B_2$ symmetry) and the singlet (**29**^{1}, $^1A'$ symmetry) states of 4-aminophenyl cation with ethylene (in the gas phase) are depicted in Scheme 5. Both states evolve to further intermediates (**30**−**32** and respectively **33** and **34**) with a negligible electronic energy barrier. The PES appear to be slippery surfaces, and any attempt for locating transition structures connecting the reactants to such intermediates failed. On the other hand, the fact that the activation energy barrier is negligible in the present process, where the 4-aminophenyl cation cleaves no σ bond, comes as no surprise when one considers that for the parent phenyl cation it has been found that hydride anion abstraction from an alkyl C−H group occurs with a very small (1.2 kcal mol^{-1}) electronic activation energy.[11]

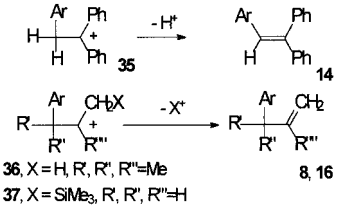
A negligible energy barrier favors the chemical reaction pathway with respect to ISC from triplet **29**^{3} to singlet **29**^{1}. This requires at least 9.1 kcal mol^{-1}, as suggested by the reported computation of the energy difference between the triplet state and the MECP (minimum energy crossing point, between triplet and singlet PESs).[12] Thus, it is reasonable that the 4-aminophenyl cation when generated, as in the present case, in the triplet state, reacts maintaining this multiplicity.

Two minima were located on the triplet PES surface in the reaction with ethylene, viz. cations **30**^{3} and **31**^{3} (see Scheme 5). The latter intermediate has a symmetric spirocyclopropane structure with a delocalized diradical character and the charge likewise delocalized, whereas the latter one is an open-chain structure with a localized alkyl radical character and the aromatic ring as a π radical-cation. **31**^{3} is only 10.6 kcal mol^{-1} more stable than the reactants, but **30**^{3}, which shows a completely formed C_1–C_α bond, lies much more below the reactants (by 43.7 kcal mol^{-1}). Cation **30**^{3} is the most stable open-shell species and is expected to control the reaction of triplet 4-aminophenyl cation with ethylene. This theoretical evidence suggests that it should be possible (at least in an *N*,*N*-dialkylamino derivative of the phenyl cation) to detect such as intermediate by laser flash photolysis and predicts that its spectrum should be quite similar to an *N*,*N*-dialkyl-substituted aniline radical cation. However, the overlap of several intermediates in flash photolysis discouraged for the moment a detailed interpretation.

As for the singlet cation−ethylene system, this evolves to a cationic closed-shell intermediate (**32**^{1}) which is similar in structure to high-energy **31**^{3} but is the most stable of all the adduct cations lying 92.0 kcal mol^{-1} below the reagents.

The PES of the same cations with water are depicted in Scheme 6. The singlet state evolves with no significant energy barrier into a σ intermediate (**34**^{1}), where the oxygen atom is strongly bonded to C_1 (bond length, 1.50 Å), recognizable as 4-aminophenol protonated at the oxygen atom. This is stabilized by 32.8 kcal mol^{-1} with respect to the reagents.

Scheme 7



We were unable to find evidence for a comparable σ intermediate on the triplet PES. However**,** a CT complex (**33**^{3}) was located also in this case, a bare 11 kcal mol^{-1} below the reagents.[13] We define this intermediate a "CT complex" due to very elongated C_2−O and C_3−O bonds (3.19 and 3.04 Å, respectively). The fact that the CT complex lies in a very shallow minimum suggests that the process is reversible and is not a chemical pathway leading to the end products in the reaction of the triplet state with water.

The strikingly different reactivity of singlet and triplet 4-aminophenyl cations discussed above confirm the picture we gave for these species on the basis of CASSCF-(8,8)76-31G(d) results. The triplet has a radical−triplet carbene character well in accord with attack to π nucleophiles, whereas the σ cation−singlet carbene character of the singlet explains the reaction with σ nucleophiles.

Finally, it should be remarked that the reactions of 4-chloroaniline **1b** closely parallel those of the *N*,*N*-dimethyl derivative **1a**. Therefore, all of the present reactions take place via the phenyl cation **29** and do not require previous deprotonation to a neutral carbene **29′** which could be formed only from **1b**. In contrast, previous studies on chlorophenol and chloroaniline, mainly in water, had considered deprotonation as immediately following chloride loss, so that the key intermediate was the neutral carbene.[14]

29′

Reactions of the Adduct Cations. The formation of the end products depends on the alkene structure, and this dependence can be rationalized by considering the paths from adduct cation. With some of the olefins, elimination reactions occurs, and these can be rationalized through the open-chain intermediate **30** (Scheme 4). Thus, in the case of diphenylethylene (**13**) a benzyl cation (**35**) is formed and undergoes, as one may expect, proton loss from the initially attacked position and gives highly conjugated triphenylethylene (**14**) (see Scheme 7 and

(10) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715. Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852.

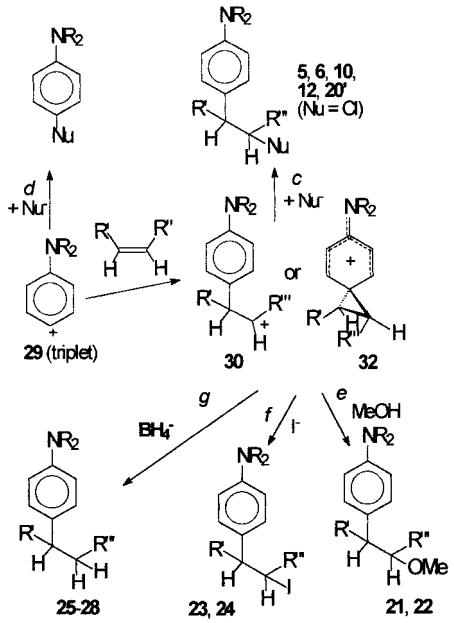
(11) Hory, K.; Sonoda, T.; Harada, M.; Yamanaki-Nishida, S. *Tetrahedron* **2000**, *56*, 1429.

(12) Aschi, M.; Harvey, J. N. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1059.

(13) However, exploration of PES of the triplet state of the parent phenyl cation and water enabled us to locate both a σ-intermediate similar to **34**^{1}, which lay 14.6 kcal mol^{-1} above the reagents, and a CT complex which was slightly more stable than the reagents. Thus, also in the case of parent phenyl cation, formation of an adduct where the oxygen is σ-bonded to the phenyl cation is not energetically favored for the triplet. Computational and experimental findings on this topic will be reported in due course.

(14) Grabner, G.; Richard, C.; Köhler, G. *J. Am. Chem. Soc.* **1994**, *116*, 11470. Durand, A. P.; Brown, R. G.; Worral, D.; Wilkinson, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 365. Othmen, K.; Boule, P.; Szczepanik, B.; Rotkiewicz, K. *J. Phys. Chem. A* **2000**, *104*, 9525

Scheme 8

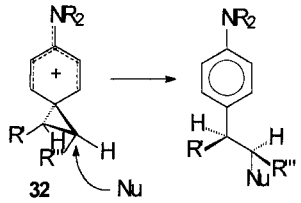


path a in Scheme 4). In the case of tertiary alkyl cation **36** deprotonation is only possible from the terminal position and gives the allylaniline **8**. With the β-silyl cation **37** (where the silicon atom β-stabilization is operating),[10] elimination of a good electrofugal group such as the trimethylsilyl cation is preferred to formation of a phenylalkene by proton loss and gives allylaniline **16** (Scheme 7 and path b in Scheme 4). All of these paths involve elimination of a good electrofugal group, strengthening the notion that the entire reaction evolves via cationic intermediates, even if strongly delocalized.

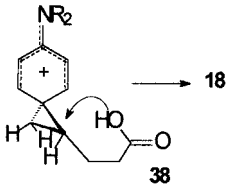
Nucleophile addition to the adduct cation is the predominating process with other substrates. This is the case with less stabilized alkyl cation such as the primary or secondary cations arising from 1-hexene, cyclopentene, and cyclohexene (see path c in both Schemes 4 and 8, $Nu^- = Cl^-$). In these cases, elimination is not competitive and chloride addition leads to the observed β-chloroalkylanilines. Scheme 5 indicates that the open-chain cation **30**[3] is first formed from triplet phenyl cation. However, it is possible that this open-shell species undergoes intersystem crossing to a closed-shell species before further reacting. Scheme 5 indeed shows that a strongly stabilized singlet cation is available, viz. phenonium ion **32**[1]. Thus it is likely that, unless a very fast different process competes, structure **32** is achieved. This intermediate is well suited for explaining some features of the reactions by attributing the regio- and stereoselectivity observed in the final products to the nucleophile attack to the phenonium ion rather than to the previous attack of the phenyl cation to the alkene. In particular the trans structure of the adducts from cyclic alkenes (**10** and **12**, $R'-R''' = (CH_2)_{3,4}$ in Scheme 9) is well explained on this basis, as is the fact that only a moderate Markovnikov regioselectivity is observed with 1-hexene (preferred attack for $R' = H$, $R''' = C_4H_9$; see Scheme 9) when the entering nucleophile is highly reactive chloride, whereas the selectivity is much stronger with a weaker nucleophile such as methanol (the ratio **5**/**6** is 2 to 1, while the ratio **21**/**22** is 95 to 5).[15]

On the other hand, the strongly stabilized cation

Scheme 9



Scheme 10



formed from enol ether **19** does not eliminate and gives hemiacetal **20**, apparently resulting from addition of moisture present in the solvent to the cation (see Schemes 2 and 8, path c, Nu = OH).

Synthetic Variations. The key features of the present reaction are that the initial *triplet* phenyl cation formed by photoheterolysis of the chloroaniline (**29**[3]; see Scheme 5) has no cationic character at C_1 and does not react with σ nucleophiles, whereas the adduct cation formed with alkenes, whether having a open-chain structure or that of a phenoniun ion (**30** and respectively **32** in Scheme 8) does react with σ nucleophiles, charged (Cl^-) or uncharged (MeOH). This allows for a considerable degree of synthetic variations, since, in the presence of a high enough concentration of the alkene, trapping of the 4-aminophenyl cation **29** occurs undisturbed by the additive present, which may however effectively trap the adduct cation, therefore offering a method for choosing the group entering in β (path c in Scheme 8).

Thus, a direct entry to β-alkoxyanilines is available by simply carrying out the irradiation in alcohols, where, as previously mentioned, no alkoxyanilines (expected from the trapping of the phenyl cation) are formed. In methanol, products **21** and **22** are formed with incorporation of the solvent (see Scheme 8, path e). As mentioned above, this is accompanied by a much increased bias toward the Markovnikov product, consistently with the formulation of the adduct cation as phenonium ion **32**. An intramolecular version of nucleophilic trapping is that observed with pentenoic acid, where cation **38** undergoes ring closure by attack of the carboxylic group and gives the observed lactone **18** (Scheme 10).

The above results encouraged us to test the versatility of the method by introducing further functionalities in the entering alkyl group by the appropriately directing the nucleophile trapping of the adduct cation. In particular, the use of charged nucleophiles was appealing but presented the problem that in this case direct reaction of phenyl cation with the nucleophile according to path d was efficient (see Scheme 8). As an example, irradiation of chloroanilines in acetonitrile containing sodium iodide or sodium borohydride gave iodoanilines

(15) (a) We are highly indepted to a reviewer for pointing out the implication of the phenonium pathway. (b) For indications about the phenonium path, see: Lancelot, C. J.; Schleyer, P. v. R *J. Am. Chem. Soc.* **1969**, *91*, 4291. Lancelot, C. J.; Hayer, I. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 4294. Schleyer, P. v. R.; Lancelot, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 4297. Diaz, A. F.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 4300.

or respectively anilines in an almost quantitative yield through direct trapping of **29**. To our delight, we found however that when a low concentration of the nucleophile was used, phenyl cation **29** was still trapped by 1 M alkene with a reasonable efficiency and thus β-iodoalkyl- as well as alkylanilines could be obtained in a decent yield through nucleophile trapping of **30**−**32** (paths f and g, Scheme 8).

The reaction in the presence of $NaBH_4$ was explored in some degree depth, since alkylanilines are of practical significance both as strong and selective aromatase inhibitors[16] and as liquid crystals components[17] but are presently prepared through multistep procedures such as the nitration of alkylbenzenes. The present method, based on the slow addition of $NaBH_4$ to the irradiated solution to maintain a constant steady-state concentration of the reducing agent, gave encouraging results with all of the alkenes tested. The ratio of alkylated anilines vs reduced anilines was 1.1 to 2.1, and within the first group the ratio of alkylanilines vs β-chloroalkylanilines was 5 to >10. This demonstrates the possibility of differentiating the trapping of phenyl cation **29** and of the adducts **30**−**32**, since control experiments showed that the products did not arise from a subsequent reduction of the chloroalkylanilines.

Furthermore, this procedure may have some preparative significance in view of the fact that it leads in a single step to the desired alkylanilines and these are easily separated from the main byproducts, nonalkylated anilines **2**, and purified by bulb-to-bulb distillation.

Conclusion

The smooth generation of *triplet* 4-aminophenyl cations by photolysis of the corresponding chloroanilines in moderately polar solvents offers the possibility of exploiting the selective electrophilic reactions of such species, in particular the propensity for attack to π, rather than σ, nucleophiles. In this way, a ionic analogue of the Meerwein arylation of alkenes has been found, which has a different scope (electron-rich rather than electron-poor olefins are attacked) and, judging from the results presented here, a large application. The versatile photochemical generation of the intermediate phenyl cation, requiring only that a moderately polar to polar medium is used, allows for a considerable degree of variations. These are based on the characteristic selectivity of triplet phenyl cations. As demonstrated both by B3LYP analysis and by experiments, these behave as electrophilic diradical and add efficiently to alkenes but not to neutral σ nucleophiles, whereas the thus resulting adduct cations react unselectively with nucleophiles. In this way, a range of alkyl- and β-substituted alkylanilines are obtained in a single step from chloroanilines. In view of the simplicity of the method, these synthesis may have some preparative value. Explorative studies are under way to more fully develop both the generation of the phenyl cation, by extending the method to other electron-donating substituted haloaromatics, and the exploitation of intermediate alkyl cations such as **30**−**32,** through further selective trappings.

(16) Hartmann, R. W.; Batzl, C. *Eur. J. Med. Chem.* **1992**, *27*, 537.
(17) Byron, D. J.; Matharn, A. S.; Rees, M.; Wilson, R. C. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1995**, *258*, 229.

Experimental Section

General Methods. *N*,*N*-dimethyl-4-chloroaniline (**1a**, prepared by methylation of aniline **1b**) and the other reagents (of commercial origin) were distilled or recrystallized before use. For the irradiations, spectroscopic grade solvents were used as received.

Preparative Irradiations in Neat Solvent. In a typical experiment a solution of 780 mg of aniline **1a** or 625 mg of aniline **1b** (0.05 M) in 100 mL of acetonitrile or in methanol was irradiated for 1.5 or 3 h in an immersion well apparatus fitted with an high-pressure mercury arc (125 W, water-cooled through a quartz jacket) after 15 min of flushing with argon and maintaining a slow gas flux during the irradiation. With acid-sensitive substrates (in particular in the experiments with the nonmethylated aniline **1b**) anhydrous potassium carbonate (2 g) was added and the solution magnetically stirred during the experiment. In an alternative procedure, irradiations were carried out by using 20 mL portions of the same solutions in a number of quartz tubes which were capped after flushing with argon for 15 min and externally irradiated by means of 6 × 15 W phosphor-coated lamps for 3 or 6 h in a merry-go-round apparatus. In this case, the solution was made 0.1 M in triethylamine when buffering the acidity was desired. Experiments in methanol were similarly carried out. The progress of the reaction was monitored by GC and GC/MS. Experiments in the presence of the various alkenes listed in Table 1 were carried out in the same way.

Products Isolation and Identification. The irradiated solution was evaporated under reduced pressure and the residue chromatographed on silica gel 60 HR (Millipore) by eluting with cyclohexane−ethyl acetate mixtures. The products were obtained as solids or oils from the fractions (by repeating the chromatography in the case of unsatisfactory separation) and characterized by elemental analysis, GC/MS, and NMR as detailed in the following. The structures of new compounds were deduced from the results of ^{1}H, ^{13}C, DEPT-135, and 2D-correlated experiments. Triphenylethylene **14a**,[12] allylaniline **16a,**[13] and cyclohexylaniline **28b**[14] have been previously reported and fully characterized. NMR and GC/MS data are listed also for compounds previously incompletely characterized.

***N*,*N*-Dimethyl-4-(2-chlorohexyl)aniline (5a) and *N*,*N*-dimethyl-4-(1-(chloromethyl)pentyl)aniline (6a)** were obtained as a mixture (oil), to which the NMR characterization is referred. Satisfactory separation and characterization was obtained by GC/MS. Anal. Found: C, 70.22; H, 9.32; N, 5.74. Calcd for $C_{14}H_{22}NCl$: C, 70.13; H, 9.25; N, 5.84. **5a**: ^{1}H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.3−1.6 (m, 6H), 2.9 (s, 6H), 2.95 (AB part of an ABX system, 2H), 4.0 (X part, 1H), 6.75 and 7.05 (AA′BB′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.1 (CH_2), 28.5 (CH_2), 37.0 (CH_2), 40.5 (NCH_3), 44.1 (CH_2), 64.6 (CH−Cl), 112.5 (CH), 129.9 (CH), 132.1, 149.3; GC/MS *m*/*z* 239 (18, Cl contg), 134 (100). **6a**: ^{1}H NMR δ ($CDCl_3$) 0.85 (t, 3H, J = 7 Hz), 1.3−1.6 (m, 6H), 2.9 (s, 6H), 2.78 (m, 1H), 3.6 (AB part of an ABX system, 2H), 6.75 and 7.05 (AA′BB′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.5 (CH_2), 29.5 (CH_2), 32.5 (CH_2), 40.5 (CH_3), 47.1 (CH), 50.1 (CH_2), 113.5 (CH), 126.2 (CH), 133.2, 149.4; GC/MS *m*/*z* 241 (13), 239 (25, Cl contg), 190 (70), 182 (20, Cl contg), 134 (100), 120 (30).

4-(2-Chlorohexyl)aniline (5b) and 4-(1-chloromethylpentyl)aniline (6b) were obtained as a mixture (oil), to which the NMR characterization is referred. Satisfactory separation and characterization was obtained by GC/MS. Anal. Found: C, 67.85; H, 8.40; N, 6.72. Calcd for $C_{12}H_{18}$ NCl: C, 68.07; H, 8.57; N, 6.62. **5b**: ^{1}H NMR δ ($CDCl_3$) 0.95 (t, 3H, J = 7 Hz), 1.2−2.0 (m, 6H), 2.96 (AB part of an ABX system, 2H), 3.7 (broad, 2H, exch), 4.1 (X part, 1H), 6.73 and 7.05 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.1 (CH_2), 28.5 (CH_2), 37.0 (CH_2), 44.2 (CH_2), 64.6 (CH−Cl), 115.1 (CH), 130.1 (CH), 132.0, 144.8; GC/MS *m*/*z* 211 (10, Cl contg), 106 (100). **6b**: ^{1}H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.3−2.0 (m, 6H), 2.8 (m, 1H), 3.6 (AB part of an ABX system, 2H), 3.7 (broad, 2H, exch), 6.8 and 7.01 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.5 (CH_2), 29.4 (CH_2), 32.7 (CH_2), 47.3 (CH), 50.2 (CH_2), 115.2

(CH), 128.5 (CH), 133.5, 144.9; GC/MS *m*/*z* 211 (18, Cl contg), 162 (60), 154 (28, Cl contg), 19 (38), 106 (100), 91 (12).

***N,N*-Dimethyl-4-(1,1,2-trimethyl-2-propenyl)aniline (8a)** was obtained as an oil. Anal. Found: C, 65.85; H, 5.10; N, 12.72. Calcd for $C_{14}H_{21}$ N: C, 82.70; H, 10.41; N, 6.89. Data: ^{1}H NMR δ ($CDCl_3$) 1.45 (s, 6H), 1.6 (s, 3H), 2.95 (s, 6H), 4.85 (bs, 1H), 4.97 (bs, 1H), 6.7 and 7.2 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 20.0 (CH_3), 28.3 (CH_3), 40.5 (CH_3), 42.3, 108.7 (CH_2), 112.3 (CH), 126.6 (CH), 136.3, 148.5, 155.2.

4-(1,1,2-Trimethyl-2-propenyl)aniline (8b) was obtained as an oil. Anal. Found: C, 65.85; H, 5.10; N, 12.72. Calcd for $C_{12}H_{17}$ N: C, 82.23; H, 9.78; N, 7.99. Data: ^{1}H NMR δ ($CDCl_3$) 1.4 (s, 6H), 1.54 (bs, 3H), 3.0 (broad, 2H, exch), 4.85 (bs, 1H), 4.95 (bs, 1H), 6.65 and 7.1 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 20.0 (CH_3), 28.4 (CH_3), 42.9, 108.9 (CH_2), 114.5 (CH), 126.8 (CH), 138.5, 143.7, 148.5, 153.1.

***trans*-2-Chloro-1-(4-aminophenyl)cyclopentane (10b)** was obtained as an oil. Anal. Found: C, 67.80; H, 7.35; N, 7.05. Calcd for $C_{11}H_{14}$ NCl: C, 67.51; H, 7.21; N, 7.16. Data: ^{1}H NMR δ ($CDCl_3$) 1.7−2.4 (m, 6H), 3.15 (m, 1H, H-1), 3.7 (broad, 2H, exch), 4.12 (m, 1H, H-2), 6.7 and 7.05 (AA′XX′, 4H). The NOE difference spectra supported the trans spatial relationship between H-2 and H-1: the irradiation of H-1 caused a weak signal enhancement for H-2 due to coupling not to spatial proximity. ^{13}C NMR: δ ($CDCl_3$) 22.4 (CH_2), 32.0 (CH_2), 36.1 (CH_2), 54.6 (CH), 66.4 (CH), 115.2 (CH), 127.9 (CH), 132.1, 144.9. GC/MS: *m*/*z* 195 (40, Cl contg), 160 (25), 132 (100).

***trans*-2-Chloro-1-(N,N-dimethyl-4-aminophenyl)cyclohexane (12a)** was obtained as an oil. Anal. Found: C, 70.90; H, 8.55; N, 5.75. Calcd for $C_{14}H_{20}$NCl: C, 70.72; H, 8.48; N, 5.89. Data: ^{1}H NMR δ ($CDCl_3$) 1.4−1.6 (m, 4H), 1.7−2.0 (m, 3H), 2.4 (m, 1H), 2.62 (dt, J = 11, 4 Hz, 1H, H-1), 2.95 (s, 6H), 4.0 (dt, J = 11, 4 Hz, 1H, H-2), 6.75 and 7.05 (AA′XX′, 4H). The large coupling constant between H-1 and H-2 (11 Hz) proved their trans spatial relationship. ^{13}C NMR: δ ($CDCl_3$) 25.8 (CH_2), 26.5 (CH_2), 35.6 (CH_2), 37.9 (CH_2), 40.5 (CH_3), 52.5 (CH), 65.1 (CH), 112.4 (CH), 127,8 (CH), 131.9, 149.3. GC/MS: *m*/*z* 209 (60, Cl contg), 174 (10), 132 (100).

***trans*-2-Chloro-1-(4-aminophenyl)cyclohexane (12b)** was obtained as an oil. Anal. Found: C, 68.65; H, 7.60; N, 6.55. Calcd for $C_{12}H_{16}$NCl: C, 68.73; H, 7.69; N, 6.68. Data: ^{1}H NMR δ ($CDCl_3$) 1.3−2.4 (m, 8H), 2.6 (dt, J = 11, 4 Hz, 1H, H-1), 3.65 (broad, 2H, exch), 3.95 (dt, J = 11, 4 Hz, 1H, H-2), 6.7 and 7.02 (AA′XX′, 4H). The large coupling constant between H-1 and H-2 (11 Hz) proved their trans spatial relationship. ^{13}C NMR: δ ($CDCl_3$) 25.8 (CH_2), 26.5 (CH_2), 35.6 (CH_2), 37.9 (CH_2), 52.6 (CH), 64.9 (CH), 115.1 (CH), 128.4 (CH), 134.1, 144.8.

5-((*N,N*-Dimethyl-4-aminophenyl)methyl)-2,3,4,5-tetrahydro-2-furanone (18a) was obtained as an oil. Anal. Found: C, 71.20; H, 7.75; N, 6.30. Calcd for $C_{13}H_{17}O_2N$: C, 71.21; H, 7.81; N, 6.39. Data: ^{1}H NMR δ ($CDCl_3$) 2.0 (m, 1H), 2.1−2.5 (m, 3H), 2.85 and 3.0 (AB part of an ABX system, 2H), 2.95 (s, 6H), 4.7 (qui, J = 7 Hz, 1H, H-5), 6.65 and 7.05 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 26.8 (CH_2), 28.5 (CH_2), 40.1 (CH_2), 40.6 (NCH_3), 81.1 (CH-5), 112.8 (CH), 130.0 (CH), 134.3, 149.5, 177.1.

3-(*N,N*-Dimethyl-4-aminophenyl)-2-hydroxy-2,3,4,5-tetrahydrofuran (20a) was obtained as colorless crystals, mp 98−100 °C. Anal. Found: C, 69.75; H, 8.35; N 6.40. Calcd for $C_{12}H_{17}O_2N$: C, 69.54; H, 8.27; N, 6.76. Data: GC/MS *m*/*z* 207 (60), 189 (30), 178 (40), 160 (100). This hemiacetal is present in solution as a mixture of the trans (**20a**) and cis (**20a′**) diastereoisomers, their proportion being solvent dependent. The former isomer was in every case the main one, but in $CDCl_3$ solution the trans/cis ratio was 4:1, while in DMSO or CD_3COCD_3 it became 8:1. In the proton spectrum the respective H-2 signals fell very close (5.42 and 5.46 ppm) so that a NOE experiment to verify the relative configuration was precluded. The two isomers were distinguished on the basis of the carbon chemical shifts, with reference to the known fact that, in 1,2-disubstituted cyclopentane derivatives, the cis spatial arrangement causes shielding of the two carbon involved compared with the trans arrangement (CH-2 appeared at δ 104.1 in **20a** and at δ 98.5 in **20a′**; CH-3 appeared at 51.1 in **20a** and at 49.0 in **20a′**). With DMSO as the solvent the OH signal was apparent in the ^{1}H NMR spectrum (6.12 ppm), while in $CDCl_3$ it was too broadened for a unambiguous identification. **20a**: ^{1}H NMR δ ($CDCl_3$) 2.0 and 2.5 (m, 2H), 2.88 (s, 6H), 3.25 (m, 1H, H-3), 4.1−4.2 (m, 2H, H-5), 5.42 (d, J = 2.5 Hz, 1H, H-2), 6.7 and 7.03 (AA′XX′, 4H);^{13}C NMR δ ($CDCl_3$) 32.7 (CH_2), 40.6 (CH_3), 51.3 (CH-3), 67.4 (CH_2), 104.1 (CH-2), 112.8 (CH), 127.7 (CH), 129.5, 149.4. **20a′**: ^{1}H NMR δ ($CDCl_3$) 2.1 and 2.5 (m, 2H), 2.93 (s, 6H), 3.25 (m, 1H, H-3), 4.0 and 4.3 (m, 2H, H-5), 5.46 (d, J = 4 Hz, 1H, H-2), 6.75 and 7.05 (AA′XX′, 4H);^{13}C NMR δ ($CDCl_3$) 28.1 (CH_2), 40.6 (CH_3), 49.0 (CH-3), 67.1 (CH_2), 98.5 (CH-2), 112.6 (CH), 129.2 (CH), 129.5, 149.7.

***N,N*-Dimethyl-4-(2-methoxyhexyl)aniline (21a)** was obtained as an oil. Anal. Found: C, 76.15; H, 10.95; N, 5.70. Calcd for $C_{15}H_{25}ON$: C, 76.54; H, 10.71; N, 5.95. Data: ^{1}H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.2−1.5 (m, 6H), 2.7 and 2.8 (AB part of an ABX system, 2H), 2.95 (s, 6H), 3.35 (m, 1H, H-2), 3.38 (s, 3H, OMe), 6.7 and 7.05 (AA′X′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.7 (CH_2), 27.4 (CH_2), 33.0 (CH_2), 38.9 (CH_2), 41.0 (NCH_3), 56.8 (OMe), 82.5 (CH-2), 113.1 (CH), 129.9 (CH), 133.9, 144.2; GC/MS *m*/*z* 235 (10), 134 (100). GC/MS analysis of the raw photolyzate showed a peak at a slightly lower t_R compatible with the structure of ***N,N*-dimethyl-4-(1-methoxymethylpentyl)aniline (22a)**: *m*/*z* 235 (12), 203 (15), 164 (100), 149 (25).

4-(2-Methoxyhexyl)aniline (21b). Anal. Found: C, 75.15; H, 10.40; N, 6.50. Calcd for $C_{13}H_{21}ON$: C, 75.31; H, 10.21; N, 6.76. Data: ^{1}H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.2−1.5 (m, 6H), 2.7 (AB part of an ABX system, 2H), 3.3 (m, 1H, H-2), 3.35 (s, 3H, OMe), 3.7 (broad, 2H, exch), 6.73 and 7.03 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 14.0 (CH_3), 22.7 (CH_2), 27.5 (CH_2), 31.7 (CH_2), 39.1 (CH_2), 56.8 (OMe), 82.5 (CH-2), 115.1 (CH), 130.1 (CH), 133.9, 144.2; GC/MS *m*/*z*: 207 (25), 106 (100). GC/MS analysis of the raw photolyzate showed a peak at a slightly lower t_R compatible with the structure of **4-(1-methoxymethylpentyl)aniline (22b)**: *m*/*z* 207 (6), 136 (100).

Preparative Experiments in the Presence of Sodium Iodide. A solution of *N*,*N*-dimethyl-4-chloroaniline (**1a**, 94 mg, 0.02 M) or of **1b** (76 mg) in 30 mL of acetonitrile containing 0.015 M sodium iodide and 1 M 1-hexene was subdivided in two quartz tubes, flushed with argon for 15 min, and irradiated in a merry-go-round apparatus by means of 6 external 15 W phosphor-coated lamps (center of emission 310 nm) for 25 or 50 min (this limited the conversion to ca. 60%). Work up was as above.

***N,N*-Dimethyl-4-(2-iodohexyl)aniline (23a) and *N,N*-dimethyl-4-(1-(iodomethyl)pentyl)aniline (24a)** were obtained as a mixture to which the NMR characterization and elemental analysis are referred. The former was predominant. Anal. Found: C, 50.55; H, 6.40; N, 4.10. Calcd for $C_{14}H_{22}$ NI: C, 50.77; H, 6.69; N, 4.23. The 2D-HSQC experiment identified the carbon to which the iodine was bonded. In detail the proton at 4.27 ppm correlated with the carbon at 40.1 in the main isomer while the methylene group at 3.35 ppm correlated with the carbon at 15.9 ppm in the minor one. **23a**: ^{1}H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.3−1.6 (m, 6H), 2.9 (s, 6H), 3.25 and 3.09 (AB part of an ABX system, J_{gem} = 14 Hz, 2H, CH_2I), 4.27 (m, X part, 1H, H-2), 6.7 and 7.05 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 14.4 (CH_3), 22.3 (CH_2), 32.3 (CH_2), 39.3 (CH_2), 40.9 (CHI), 41.2 (NCH_3), 47.1 (CH_2), 113.1 (CH), 130.1 (CH), 134.0, 149.4; GC/MS *m*/*z* 331 (35), 204 (60), 134 (100). **24a**: ^{1}H NMR δ ($CDCl_3$) 0.88 (t, 3H, J = 7 Hz), 1.2−1.8 (m, 6H), 2.8 (m, H-1) 2.95 (s, 6H), 3.35 (d, J = 7 Hz, 2H, H-1), 6.7 and 7.05 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 14.4 (CH_3), 15.9 (CH_2I), 22.6 (CH_2), 29.7 (CH_2), 33.1 (CH_2), 41.1 (CH_3), 47.7 (CH), 113.1 (CH), 128.4 (CH), 133.3, 148.4; GC/MS *m*/*z* 331 (25), 204 (85), 134 (100).

4-(2-Iodohexyl)aniline (23b) and 4-(1-(iodomethyl)-pentyl)aniline (24b) were obtained as a mixture to which the NMR characterization and elemental analysis are referred. Satisfactory separation and characterization was obtained by GC/MS analysis. Anal. Found: C, 47.35; H, 6.10; N, 4.55. Calcd for $C_{12}H_{18}$ NI: C, 47.54; H, 5.98; N, 4.62. **23b**: ^{1}H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.2−1.8 (m, 6H), 3.05 and 3.2

(AB part of an ABX system, J_{gem} = 14 Hz, 2H, CH_2I), 3.6−3.7 (broad, 2H, exch), 4.2 (m, X part, 1H, H-2), 6.8 and 7.0 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.8 (CH_3), 21.8 (CH_2), 31.7 (CH_2), 38.8 (CH_2), 40.2 (CHI), 46.6 (CH_2), 115.2 (CH), 129.8 (CH), 133.3, 144.6; GC/MS *m*/*z* 303 (10), 176 (30), 106 (100). **24b**: ^1H NMR δ ($CDCl_3$) 0.85 (t, 3H, J = 7 Hz), 1.2−1.8 (m, 6H), 2.75 (m, H-1), 3.3 (AB part, 2H, H-1), 3.6−3.7 (broad, 2H, exch), 6.7 and 6.95 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.8 (CH_3), 15.1 (CH_2I), 22.4 (CH_2), 29.7 (CH_2), 33.2 (CH_2), 47.3 (CH), 115.1 (CH), 128.1 (CH), 133.3, 148.4; GC/MS *m*/*z* 303 (10), 176 (40), 106 (100).

Preparative Experiments in the Presence of Sodium Borohydride. A solution of *N*,*N*-dimethyl-4-chloroaniline (**1a**, 1.09 g, 0.05 M) or of **1b** (0.89 g) in 140 mL of acetonitrile containing 17.5 mL of 1-hexene (1 M), 100 mg of sodium borohydride (0.019 M), and 200 mg of potassium carbonate (0.01 M) was irradiated for 3 or 6 h in an immersion well apparatus fitted with an high-pressure mercury arc (125 W, water-cooled through a quartz jacket) after 15 min of flushing with argon and maintaining a slow gas flux during the irradiation. A solution of 300 mg of $NaBH_4$ and 200 mg of K_2CO_3 in 15 mL of water was slowly added during the irradiation period. The reaction was followed by GC, showing that the proportion of alkylanilines **25a,b** with respect to reacted **1a** remained constant except for some decrease in favor of aniline **2a** and chloroalkylanilines **5a** and **6a** above 70% conversion. Work up was as above.

***N,N*-Dimethyl-4-hexylaniline (25a)[15] and N,N-dimethyl-4-(1-methylpentyl)aniline (26a)** were obtained as a mixture to which the NMR characterization and elemental analysis are referred. Satisfactory separation and characterization were obtained by GC/MS analysis. Anal. Found: C, 81.75; H, 11.15; N, 6.75. Calcd for $C_{14}H_{23}$ N: C, 81.89; H, 11.29; N, 6.82. **25a**: ^1H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.2−1.7 (m, 8H), 2.53 (t, J = 7 Hz, 2H, H-1), 2.93 (s, 6H), 6.72 and 7.08 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 14.0 (CH_3), 22.5 (CH_2), 26.8 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 34.8 (CH_2), 38.2 (CH_2), 40.8 (NCH_3), 112.9 (CH), 128.8 (CH), 131.2, 148.8; GC/MS *m*/*z* 205 (38), 134 (100). **26a**: ^1H NMR δ ($CDCl_3$) 0.88 (t, 3H, J = 7 Hz), 1.23 (d, J = 7 Hz, 3H), 1.5−1.7 (m, 6H), 2.62 (m, 2H, H-1), 2.95 (s, 6H), 6.74 and 7.08 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.4 (CH_2), 22.7 (CH_2), 29.9 (CH_2), 31.7 (CH_2), 38.7 (CH), 40.8 (NCH_3), 112.7 (CH), 127.4 (CH), 136.2, 148.8; GC/MS *m*/*z* 205 (32), 148 (100).

4-Hexylaniline (25b)[16] and 4-(1-methylpentyl)aniline (26b)[17] were obtained as a mixture to which the NMR characterization and elemental analysis are referred. Satisfactory separation and characterization were obtained by GC/MS analysis. Anal. Found: C, 81.15; H, 10.90; N, 7.85. Calcd for $C_{12}H_{19}$ N: C, 81.30; H, 10.80; N, 7.90. **25b:** ^1H NMR δ ($CDCl_3$) 0.85 (t, 3H, J = 7 Hz), 1.2−1.7 (m, 8H), 2.55 (t, J = 7 Hz, 2H, H-1), 3.6 (broad, 2H, exch), 6.67 and 7.1 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 14.0 (CH_3), 22.5 (CH_2), 26.8 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 34.9 (CH_2), 38.2 (CH_2), 115.2 (CH), 129.0 (CH), 133.1, 143.9; GC/MS *m*/*z* 177 (20), 106 (100). **26b**: ^1H NMR δ ($CDCl_3$) 0.9 (t, 3H, J = 7 Hz), 1.23 (d, J = 7 Hz, 3H), 1.2−1.7 (m, 6H), 2.85 (sext, J = 7 Hz, 2H), 3.6 (broad, 2H, exch), 6.68 and 7.01 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.5 (CH_2), 22.7 (CH_2), 29.9 (CH_2), 31.6 (CH_2), 38.9 (CH), 115.2 (CH), 127.6 (CH), 138.2, 143.8; GC/MS *m*/*z* 177 (20), 120 (100).

4-Cyclopentylaniline (27b)[10] was obtained as an oil. Data: ^1H NMR: δ ($CDCl_3$) 1.5−2.1 (m, 8H), 2.9 (qui, J = 8 Hz, 1H), 3.5 (broad, 2H, exch), 6.65 and 7.05 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 20.9 (CH_2), 34.5 (CH_2), 45.1 (CH), 115.0 (CH), 127.7 (CH), 136.4, 144.0; GC/MS *m*/*z* 175 (50), 132 (100), 106 (45).

***N,N*-Dimethyl-4-cyclohexylaniline (28a)** was obtained as an oil. Anal. Found: C, 82.35; H, 10.20; N, 6.50. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Data: ^1H NMR δ ($CDCl_3$) 1.3−2.0 (m, 10H), 2.5 (m, 1H), 2.95 (s, 6H), 6.75 and 7.03 (AA′XX′, 4H); ^{13}C NMR δ ($CDCl_3$) 26.1 (CH_2), 26.9 (CH_2), 34.6 (CH_2), 40.8 (NCH_3), 43.4 (CH), 112.8 (CH), 127.2 (CH), 136.5, 148.9.

Low-Conversion Experiments. Low conversion experiments were carried out for quantum yields measurements (Table 2) and competition experiments (Table 3). The solutions (5 mL) were prepared and irradiated under the same conditions as in the preparative experiments. Alternatively, 2 mL portions were irradiated in spectrophotometric couvettes by means of a 200 W focalized high-pressure mercury arc (interference filter, λ_{tr} 313 nm). In every case the conversion was limited to 20%. Product formation was assessed by GC and HPLC. The light flux was measured by ferrioxalate actinometry.

Calculations. The singlet ($^1A'$) and triplet ($^3B_2$) states of the $H_2N-C_6H_4^+$ cation as well as the intermediates arising from the addition reaction to ethylene and water were optimized by the standard (U)B3LYP method by using the 6-31G(d) basis set, as implemented in the Gaussian 94 program.[24] The singlet ($^1A'$) and triplet ($^3B_2$) states of the cation were also optimized at the 6-311+G(d,p) level of theory. Both states were characterized by harmonic frequency calculations at B3LYP/6-31G(d) level. To confirm the nature of the stationary points and to produce theoretical parameters, vibrational frequencies (in the harmonic approximation) were calculated by B3LYP/6-31G(d) and used with no scaling for computing the zero point energies and their contributions to Gibbs free energies.

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Supporting Information Available: Complete computational results in the form of tables of *Z*-matrixes with the computed total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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