JOC Article

Phenonium Ions from the Addition of Phenyl Cations to Alkenes. Photochemical Synthesis of (Rearranged) Aminoalkylanilines from Haloanilines in the Presence of Alkenes and Amines†

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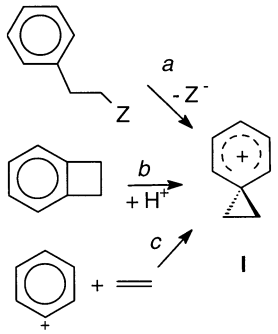
β-Aminoalkylanilines are smoothly obtained by irradiation of 4-chloro- and 4-fluoroanilines (as well as the *N*,*N*-dimethyl derivatives) in the presence of alkenes (1-hexene, cyclohexene) and amines (butylamine, piperidine) in polar, protic solvents such as trifluoroethanol (yield 40−75%). The reaction involves photoheterolysis of the haloaniline, addition of the resulting phenyl cation to the alkene and trapping of the phenonium cation by amine. A fraction (up to ca. 20%) of aminoalkylanilines resulting from Wagner−Meerwein rearrangement of the phenonium cation is obtained in some cases. Reduction and direct trapping of the phenyl cation by the amine compete with the above three-component synthesis in a less stabilizing solvent such as acetonitrile, but not in CF_3CH_2OH.

More than half a century ago, Cram proposed the phenonium ion (spiro[5.2]octa-5,7-diene-4-yl cation, **I**, Scheme 1) as the intermediate in the solvolysis of 3-phenylethyl-2-tosylates.[1] Since then bridged phenonium ions have been extensively investigated from the experimental[2] and computational[3] point of view, also in connection with the so-called classical-nonclassical carbocation debate.[4] The effect of electron-donating substituents on the ring in facilitating participation in the intermediate has been documented.[2d,5] Furthermore, long-lived phenonium ions have been prepared and

SCHEME 1



characterized under superacidic conditions, demonstrating the "classical" spiro-cyclopropane structure of the cation (**I**).[6] In most cases, such ions are generated, as in the original report, through the solvolysis of *β*-arylakyl systems (path *a*), a facts that limits the scope of the reaction. An independent route has been more recently reported through the protonation of benzocyclobutene (path *b*) under superacidic conditions.[7] On the contrary, the seemingly straightforward generation of phenonium ion by addition of a phenyl cation to an alkene (path *c*) is hampered by the inaccessibility of the first intermediate in solution,[8] though this reaction has been studied in the gas phase.[9]

In contrast, it has been recently shown that electron-donating substituted aromatics such as haloanilines[10,11] and halophenols[12] are smoothly dehalogenated by irradiation in a polar medium, thus affording a mild entry

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† Dedicated to Prof. Paola Vita Finzi on occasion of her 70th birthday.

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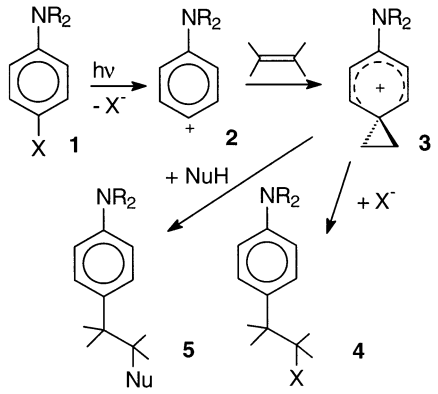
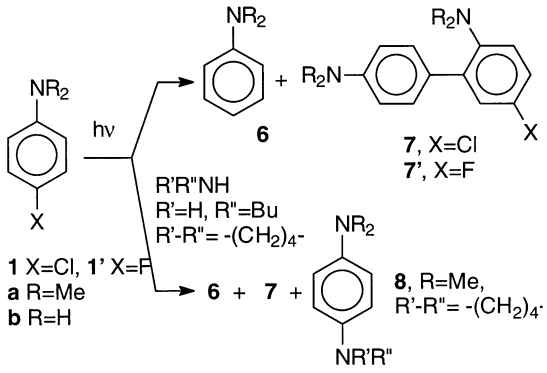
SCHEME 2



to aryl cations. The heterolytic step occurs from the triplet state, and the multiplicity is conserved in the aryl cation generated. This is important for the ensuing reaction, because although a singlet aryl cation reacts unselectively, this is not the case for the triplet. We demonstrated that the latter species adds efficiently to π-nucleophiles but not to σ-nucleophiles, except when charged (e.g., iodide anion). Thus, irradiation of 4-chloroanilines (**1** in Scheme 2) in polar "inert" solvents leads to reductive dechlorination and formation of diaminobiphenyls, both processes occurring via triplet 4-aminophenyl cation (**2**).[11]

SCHEME 3



No alkoxyanilines are formed in alcohols (whereas they would be if singlet phenyl cation were involved).[13]

In the presence of mono- or disubstituted alkenes cation **2** is efficiently trapped to give β-chloroalkylanilines (**4**, X = Cl) via phenoniun cation **3** (in a variation of the process, when using tetraalkyl-substituted as well as aryl alkenes, proton elimination occurs leading to allyl or vinylanilines).[11] We had some indication, however, that a σ-nucleophile adds to the phenonium cation, leaving the first formed phenyl cation unaffected. Thus, carrying out the same photoreaction with alkenes in methanol gives β-methoxyalkylanilines (**5**, Nu = OMe). This was an appealing indication, since it suggested that the scope of this three-component synthesis could be significantly widened by changing the entering nucleophile, and we decided to investigate this issue in some detail. For a more informative investigation, this was done by using nucleophiles better than alcohols, i.e., amines. As will be shown in the following, β-aminoalkylanilines could indeed be obtained in this way. Furthermore, this study offered support and clarification to the proposed mechanism and revealed new facets of the chemistry involving the intermediate phenyl and phenonium cations.

Results

The study was carried out by using primary and secondary alkenes and primary and secondary amines as traps. We considered both 4-fluoro- and 4-chloroanilines as precursors of the aryl cation. As previously reported, chloroanilines (**1a**,**b**) are efficiently photodecomposed in a polar solvent such as acetonitrile and undergo reduction to **6a**,**b**, as well as coupling to chlorodiphenyldiamine **7a**,**b** (Scheme 3). The reaction occurred similarly in other polar solvents, with considerable variation in the product ratio (e.g., hydrogen-donating MeOH favored reduction).[11]

Photoreaction of Haloanilines in the Presence of Amines. The effect on the photoreaction of the presence of amines was first explored (Scheme 3). Representative results are reported in Table 1, and the key features are listed in the following. With the chloro-*N*,*N*-dimethylaniline **1a** in MeCN, 0.5 M butylamine increased the yield of **6a** and decreased that of **7a**; the accumulation of amine **6a** resulted in the formation of a certain amount of chlorine-free diphenyldiamines (2,4′ and 4,4′). Other

(8) (a) Phenylium cations (ref 8b,c) have been obtained in solution only under particular conditions, allowing for little exploration of the chemistry, such as solvolysis of some perfluoroalkylsulfonic aryl esters (ref 8d−g), by solvolytic cyclization of (trifluoromethanesulfonyl)-oxydienynes (ref 8h−j), and by controlled (photo)decomposition af diazonium salts (ref 8k−q). (b) Stang, P. J. In *Dicordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: New York, 1997; p 451. (c) Hanack, M.; Subramanian, L. R. In *Methoden Organische Chemie*; Hanack, M., Ed.; Thieme: Stuttgart, 1990; Vol. E19C, p 249. (d) Himeshima, Y.; Kobayashi, H.; Sonoda, T. *J. Am. Chem. Soc.* **1985**, *107*, 5286. (e) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, *107*, 5285. (f) Subramanian, L. R.; Hanack, M.; Chang, L. W.; Imhoff, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099. (g) Laali, K.; Szele, I.; Yoshida, K. *Helv. Chim. Acta* **1983**, *66*, 1710. (h) Holweger, W.; Hanack, M. *Chem. Ber.* **1984**, *117*, 7, 3004. (i) Bleckmann, W.; Hanack, M. *Chem. Ber.* **1984**, *117*, 3021. (j) Hanack, M.; Rieth, R. *Chem. Ber.* **1987**, *120*, 1659. (k) Romsted, L. S.; Zhang, J.; Zhang, L. *J. Am. Chem. Soc.* **1998**, *120*, 10046. (l) Chauduri, A.; Loughlin, J. A.; Romsted, L. S.; Yao, J. *J. Am. Chem. Soc.* **1993**, *115*, 8351. (m) Swain, C. G.; Sheats, J. E.; Harbison, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 783. (n) Bergstrom, R. G.; Landells, R. G. M.; Wahl, G. W.; Zollinger, H. *J. Am. Chem. Soc.* **1976**, *98*, 3301. (o) Zollinger, H. *Diazochemistry I*; VCH: New York, 1995. (p) Gasper, S. M.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 5206. (q) Steenken, S.; Askokkuna, M.; Maruthamuthu, P.; McClelland, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 11925.

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TABLE 1. Products from Irradiation of Haloanilines 1 and 1′ in the Presence of Amines

haloaniline	solvent	amine, 0.5 M	products (% yield)
1a	MeCN	none	**6a** (47), **7a** (30)
1b	MeCN	none	**6b** (45), **7b** (31)
1a	MeCN	$BuNH_2$	**6a** (59), **7a** (9)[a]
1a	MeCN	piperidine	**6a** (45), **7a** (tr), **8** (28)
1a	MeOH	piperidine	**6a** (68), **7a** (6), **8** (3)[b]
1a	CF_3CH_2OH	piperidine	**6a** (33), **7a** (6)[c]
1b	MeCN	$BuNH_2$	**6b** (95)
1b	MeCN	piperidine	**6b** (87)
1′a	MeOH	piperidine	**6a** (71), **7a′** (12), **8** (10)
1′b	MeOH	piperidine	**6b** (80)

[a] 2,4- and 4,4-*N*,*N*′-tetramethyldiphenyldiamine also formed, 5%. [b] 7%. [c] 4%.

primary amines (e.g., *iso*-propylamine) had a similar effect. With piperidine in MeCN, however, substitution to form the piperidinoaniline **8** took place (28% yield), though reduction remained the main path. The proportion of **8** dropped strongly in protic solvents such as methanol and trifluoroethanol. The trend was similar with other secondary amines, such as diethylamine and pyrrolidine. The nonmethylated chloroaniline **1b** did not undergo significant substitution under any of the conditions tested, though the amine considerably favored reduction (see Table 1).

Fluoroanilines **1′a**,**b** were likewise photodecomposed in acetonitrile, giving products **6** and **7′**;[11d] however, the photoreaction was quite slow and made preparative experiments inconvenient in this case. An efficient defluorination was found to require a protic solvent, such as methanol or trifluoroethanol, where the reaction was about half as fast as with the chlorinated analogues. The addition of amines had a similar effect, with a little substitution to give **8** being observed only in the photoreaction of the *N*,*N*-dimethyl derivative **1′a** in the presence of secondary amines in methanol (not in CF_3CH_2-OH), while an increase of the reduction to **6** took place in the other cases (Table 1).

Photoreaction of Haloanilines in the Presence of Alkenes and Amines. The photoreaction was then carried out with alkenes (1 M) and amines simultaneously present. Low amine concentration (≤0.1 M) did not affect the course of the reaction of chloroanilines **1**, which in acetonitrile gave the previously reported *β*-chloroalkylanilines (products **4** in Scheme 2, X = Cl). At higher amine content (0.5−0.7 M), however, aminoalkylanilines were obtained instead, and the product distribution depended on the starting haloaniline and on the solvent. The key results are shown in Table 2 and Scheme 4 and indicated in the following.

The structure of products obtained was in part unexpected. Thus, with both chloro- and fluorodimethylanilines (**1a** and **1′a**) and 1-hexene, *three* adducts were obtained with both butylamine and piperidine (see Scheme 4). These were identified (see Experimental Section) as the 4-(2-alkylaminohexyl)anilines (**9a** and **12a**, respectively, from the two amines) and 4-[1-(alkylaminomethyl)pentyl]anilines (**10a** and **13a**), resulting from the two alternative regiochemical additions of the aryl and the amino group across the double bond, accompanied by a third type of products bearing both groups on the same atom, viz., the 4-(1-alkylaminohexyl)-anilines (**11a** and **14a**).

From the nonmethylated chloro- and fluoroanilines (**1b**, **1′b**), however, only the first two types of regioisomeric adducts (**9b** and **10b** with butylamine and **12b** and **13b** with piperidine) were obtained.

As for the reaction with cyclohexene, the *trans*-4-[(2-alkyamino)cyclohexyl]anilines **15a** and **17a** were the main products from both **1a** and **1′a** in the presence of butylamine and piperidine, respectively. These were accompanied by a significant amount of isomeric adducts. Spectroscopic examination (see Experimental Section) demonstrated that in these compounds the alkyl group had rearranged with ring contraction, and the structure was that of the cyclopentylmethylanilines **16a** and **18a**.

Nonrearranged alkylaminocyclohexylanilines (**15b** and **17b**, respectively) were obtained when the nonmethylated haloaniline **1′b** was the reagent, and there were no analogues of compounds **16** or **18** in this case. However, a certain amount of a further product identified as *trans*-4-(2-phenylamino)cyclohexylaniline **19** was formed in both experiments.

In all of the above reactions, formation of the above aminoalkylanilines competed with straightforward reduction to anilines (**6**) and, with piperidine under some conditions, with formal substitution to give phenylendiamine **8**. The competition was strongly solvent-dependent. As can be seen from Table 2, both reduction and substitution (the latter process occurring only with piperidine and starting from the dimethylaniline **1a**) were favored in acetonitrile, where however only the chloroanilines **1a**,**b** reacted at a convenient rate. Methanol as solvent allowed use also of the fluroaniline, but in this case reduction to **6** was too efficient (not reported in the table). Changing the solvent to trifluoroethanol eliminated product **8** and gave a much higher proportion of adducts both from the chloroanilines **1** and from the fluoroanilines **1′**, with little difference in the product distribution when using either reagent and with the peculiarity that aminoalkylanilines containing a rearranged alkyl chain were obtained to some extent from the dimethylanilines. The *β*-chloroalkylanilines (**4**) obtained by irradiation of **1a**,**b** in the absence of amine were reduced to traces under the present conditions. Of the possible products from solvent trapping, trifluoroethoxyanilines were never detected, while there was some evidence for the presence of 4-(2-trifluoroethoxyalkyl)-anilines (**5**, Nu = OCH_2CF_3) from GC−MS examination. These, however, were minor products.

Discussion

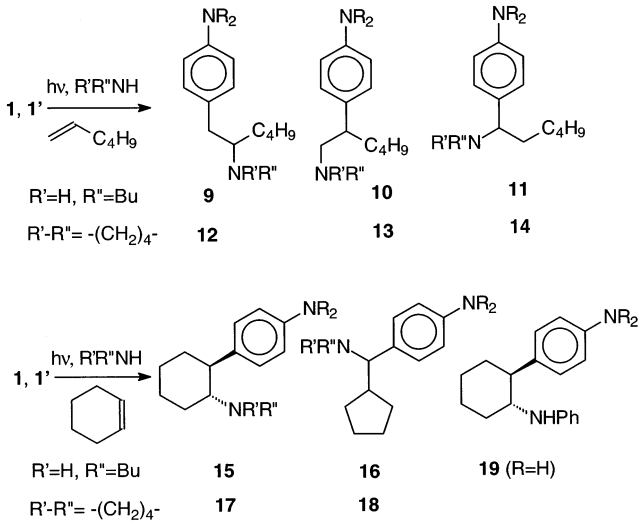
The present work confirms that the photoheterolysis of 4-chloro- and 4-fluoroanilines affords a viable path for the generation of the 4-aminophenyl cation (**2**, Scheme 2) under mild conditions. The time required for photolyzing these compounds in a given neat solvent is little affected by the presence of either amines or alkenes or of both traps. This fits with the previously obtained evidence that the photochemical step involves unimolecular fragmentation. This has been shown to occur from the short-lived (in polar solvents) triplet state of the aniline yielding triplet 4-aminophenyl cation ($^3B_2$, eq 1):[11a]

$$4R_2NC_6H_4X^{3}* \rightarrow 4R_2NC_6H_4^{+}\,(\text{triplet}) + X^{-} \quad (1)$$

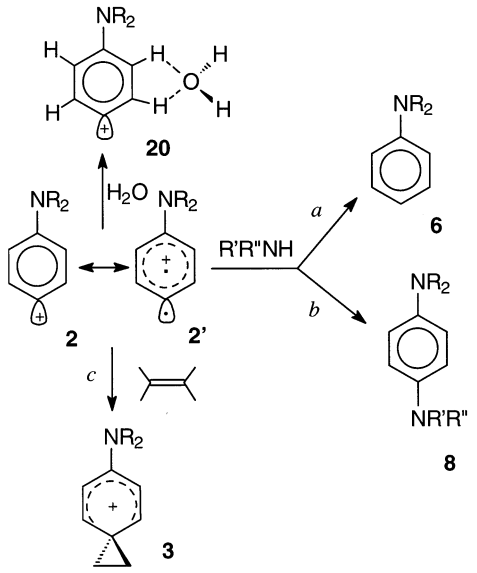
TABLE 2. Products from Irradiation of Haloanilines 1 and 1′ in the Presence of Alkenes and Amines

haloaniline	solvent	alkene	amine	products (% yield)
1a	MeCN	1-hexene	$BuNH_2$	**6a** (38), **9a** (7), **10a** (6), **11a** (1)
1a	CF_3CH_2OH	1-hexene	$BuNH_2$	**6a** (29), **9a** (12), **10a**(13), **11a** (13)
1′a	CF_3CH_2OH	1-hexene	$BuNH_2$	**6a** (9), **9a** (18), **10a** (13), **11a** (9)
1a	MeCN	1-hexene	piperidine	**6a** (33), **8** (17), **9a** (7), **10a** (8)
1a	CF_3CH_2OH	1-hexene	piperidine	**6a** (8), **12a** (20), **13a** (20), **14a** (7)
1′a	CF_3CH_2OH	1-hexene	piperidine	**6a** (18), **12a** (15), **13a**(15), **14a** (10)
1′a	CF_3CH_2OH	cyclohexene	$BuNH_2$	**6a** (22), **15a** (61), **16a** (14)
1a	MeCN	cyclohexene	piperidine	**6a** (39), **8** (17), **17a** (7)
1a	CF_3CH_2OH	cyclohexene	piperidine	**6a** (20), **17a** (45), **18a** (12)
1′a	CF_3CH_2OH	cyclohexene	piperidine	**6a** (18), **17a** (56), **18a** (14)
1′b	CF_3CH_2OH	1-hexene	$BuNH_2$	**6b** (29), **9b** (33), **10b** (21)
1b	MeCN	1-hexene	piperidine	**6b** (51), **12b** (20), **13b** (20)
1b	CF_3CH_2OH	1-hexene	piperidine	**6b** (18), **12b** (22), **13b** (16)
1′b	CF_3CH_2OH	cyclohexene	$BuNH_2$	**6b** (36), **15b** (34), **19** (16)
1′b	CF_3CH_2OH	cyclohexene	piperidine	**6b** (36), **17b** (40), **19** (12)

SCHEME 4



SCHEME 5



The latter intermediate, contrary to what happens with parent phenyl cation, is the lowest state in this case. Computational data obtained at the B3LYP/6-31G(d) and CASSCF-(8,8)/6-31(d) levels of theory evidenced that in 4-aminophenyl cation the σ and the π orbital are both singly occupied, so that the charge is delocalized over the ring and the divalent carbon is best envisaged as triplet carbene (with one of the unpaired electron delocalized in the π system) rather than a localized σ carbocation (see mesomeric formula **2′** in Scheme 5). Furthermore, the above calculations showed that, contrary to the singlet state, triplet **2**[3] develops *no* bonding interaction with nucleophiles such as water or methanol, while forming a slightly stabilized CT complex in which such solvents behave as Lewis bases and are located at the side of the ring, not in the vicinity of the divalent carbon (see formula **20**).[11b] With methanol, hydrogen transfer finally leading to reduced aniline **6** was an easy path.

We carried out preliminary calculations for ammonia and found that also in this case neither bond formation (eq 2) nor single electron transfer (eq 3) were favored.[14]

$$4H_2NC_6H_4^+ + NH_3 \rightarrow 4H_2NC_6H_4\text{-}NH_3^+ \quad (2)$$

$$4H_2NC_6H_4^+ + NH_3 \rightarrow 4H_2NC_6H_4^{\cdot} + NH_3^{\cdot +} \quad (3)$$

On the contrary, we had previously demonstrated that the triplet aminophenyl cation−ethylene system smoothly evolves to a bonded state with negligible activation energy. An open-shell species is first formed still with triplet multiplicity, but intersystem crossing to the most stable adduct, ring-closed phenonium cation **3** (lying 92.0 kcal mol below the reagents), is strongly exothermic and expected to be facile.[11b] Indeed, arylation of alkenes occurred under these conditions, as shown in Scheme 2.

The experimental data conforms to what is predicted by calculations and evidences that also with amines triplet phenyl cation undergoes reduction in preference to addition, though these are better nucleophiles than alcohols. With the secondary amines indeed addition takes place under some conditions and some phenylendiamine **8** is obtained with piperidine, but reduction remains the main path (Table 1, paths *a*, *b* in Scheme 5). With 0.5 M piperidine, the ratio reduction/amination

(14) Computation performed by Dr: M. Freccero in this Department; see Experimental Section.

is 1.75 in acetonitrile but it grows to >20 in methanol, and no significant amount of diamine **8** is formed in trifluoroethanol, a solvent known for its effect of stabilizing cations.[2h] Apparently, stabilization of the cation suppresses the tendency to react with a σ nucleophile. Furthermore, the reaction with piperidine occurs only with the *N*,*N*-dimethylaniline **1a** and not with the nonmethylated **1b** derivative, for which reduction is the only path observed, possibly because the protolytic equilibrium of the NH_2 group makes the reaction of the phenyl cation as C-electrophile less effective.

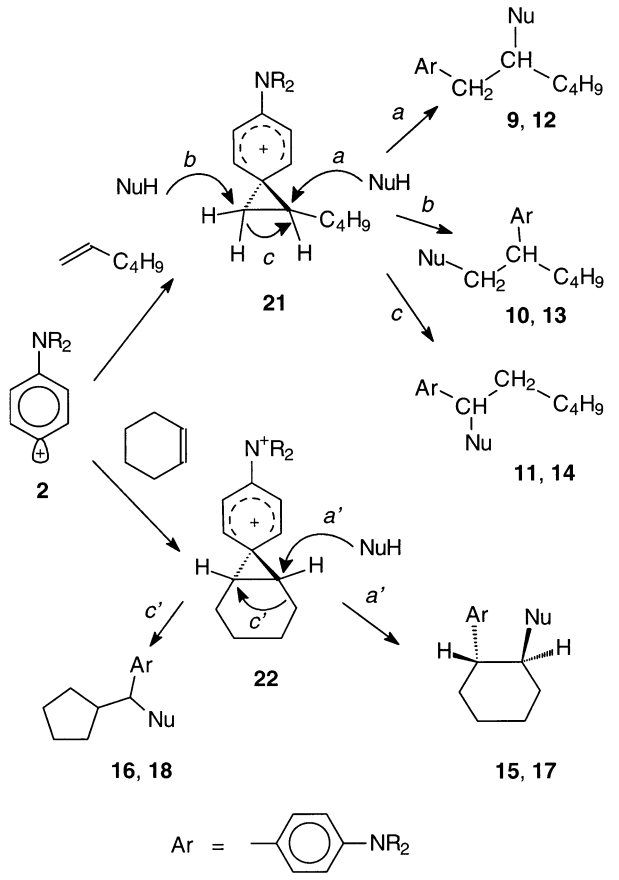
The limited or negligible reaction with σ nucleophiles leaves the field open for the reaction with π nucleophiles leading to adduct cation (phenonium) **3** even in the presence of amines (path *c* in Scheme 5).

This is a singlet cation and there is no hindering toward reaction with σ nucleophiles, as apparent here from the reaction with amines. In fact, particularly in cation-stabilizing trifluoroethanol, the main products are 4-(2-aminoalkyl)anilines resulting from the nucleophilic trapping of phenonium ion. This is a result of some synthetic interest in view of the fact that reaction via this cation, even formed via solvolysis, has been scarcely used for synthetic purposes,[2h] whereas in this case the ion is generated via C−C bond formation and then reacts. Also, the aminoalkylanilines obtained are useful as intermediates, in particular for drugs and dyes and for the preparation of various heterocycles.[15]Considering the simplicity of this three-component, one-step synthesis, yields are of some value at least with a symmetric olefin such as cyclohexene, where the yields of the adducts range between 33% and 61% (only *trans* stereochemistry observed), although regioisomeric adducts are formed with an unsymmetrical olefin such as 1-hexene (overall yield 35% to 54% in CF_3CH_2OH; see further below).

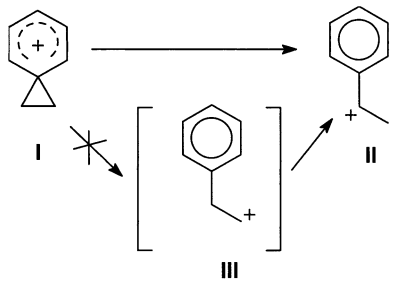
From the mechanistic point of view, the key result is more detailed evidence about the reactivity of phenonium cation **3**, which had previously been suggested as an intermediate in the photoreaction of chloroanilines with alkenes. This comes from the regiochemistry of the final products. In previous work with 1-hexene, we had observed a moderate preference for attack at the more substituted carbon in the alkyl-substituted phenonium ion **21** (see Scheme 6) when the entering nucleophile was a charged species such as chloride (ca. 2 :1, see the β-chloroethylanilines formed in MeCN) and a much stronger selectively with a uncharged nucleophile such as methanol (ca. 95:5 in neat MeOH).[11b] In the present reaction, amines behave, as one may expect, as stronger nucleophiles compared to alcohols and paths *a* and *b* leading, respectively, to amines **9**, **12** and **10**, **13** (Scheme 6) both contribute (in a ratio ranging from 1:1 to 1:2.1).

Furthermore, a third path comes into play under this condition and involves hydrogen shift concurrently with (or previous to) nucleophilic addition (path *c* yielding rearranged benzylamines **11**, **14**). A Wagner−Meerwein rearrangement of this type had been previously observed in solvolytic reactions to a degree dependent on the

SCHEME 6



SCHEME 7



structure. Thus, hydrogen shift is a very minor process in the solvolysis of β-methyl-β-phenylethyl systems, whereas it becomes important with β,β-dimethyl-β-phenylethyl or β-methoxy-β-phenylethyl systems.[4d,5b,16]Under superacid conditions, as mentioned in the Introduction, phenonium ion **I** has been generated via two independent pathways and characterized as a "classical" spirocyclopropyl carbonium ion (Scheme 1).[6,7] This species has been found to slowly rearrange to the stable α-methylbenzyl cation **II** over a barrier of 13 kcal/mol (Scheme 7). Recent calculations have indicated that such a rearrangement is a one-step process, open chain cation **III** not being an intermediate.[2g] This conversion occurs over a barrier of 26.6 kcal/mol in the gas phase, reduced to 18.7 when the electrostatic solute−solvent interaction is taken into account.

(15) See, e.g.: Sharpe, C. J.; Palmer, P. J.; Evans, D. E.; Brown, G. R.; King, G.; Shadholt, R. S.; Trigg, R. B.; Ward, R. J.; Ashford, A.; Ross, J. W. *J. Med. Chem.* **1972**, *15*, 523. Milligan, B.; Holt, L. A. *J. Soc. Dyers Colour.* **1978**, *94*, 352. Mathison, I. W.; Solomon, W. E. In *Isoquinolines*; Kathawala, F. G., Coppola, G. M., Schuster, H. F., Eds; Wiley: New York, 1990; Vol. 2, p 367.

(16) (a) Saunders, W. H.; Paine, P. H. *J. Am. Chem. Soc.* **1961**, *83*, 882. (b) Tanida, H.; Tsuji, T.; Ishitobi, H.; Irie, T. *J. Org. Chem.* **1969**, *34*, 1086. (c) Kirmse, W.; Plath, P.; Schaffrodt, H. *Chem. Ber.* **1975**, *108*, 79.

In our case the rearrangement is observed under unprecedented mild conditions (neat CF_3CH_2OH, room temperature), where the rearranged products **11** or **14** account for 15−27% of the total weight of adducts. The rearrangement is minimal or unobserved in a solvent less able to stabilize the intermediate cation, such as MeCN, as well as with the nonmethylated anilines, once again probably as a result of protic equilibriums in that case. The rearrangement further supports the cationic path of the reaction. In the present case the phenonium ion results from the strongly exothermic aryl cation−alkene addition, but the fact that the rearrangement is observed only under cation stabilizing conditions supports that at least in CF_3CH_2OH the intermediate thermalizes before reacting and hydrogen shift encounters a small barrier. The presence of an amino group on the phenyl ring may considerably lower the barrier for such a process in the present case.

As for the addition to cyclohexene, we had previously noted in the absence of amines that attack of the nucleophile (chloride) onto disubstituted phenonium ion **22** occurred, as expected from such species, in *anti* fashion, giving *trans* chloroarylcyclohexanes.[11b] Amines behave in the same way and give *trans* adducts **15** and **17** (see path *a′* in Scheme 6). A slight complication is the formation of a certain amount of another *trans* cyclohexene adduct, 4-(*β*-phenylaminoalkyl)aniline **19**, in the reaction of nonmethylated aniline **1′b**, but this is simply due to the competition by reasonably nucleophilic aniline **6b** (formed in the reduction of the haloaniline) with the aliphatic amine in trapping the phenonium ion.

More importantly, a cationic rearrangement occurs also in this case, again in trifluoroethanol and only with the dimethylaniline, and yields as further products benzylamines **16** and **18** (path *c′* in Scheme 6). The rearranged product accounts for 19−23% of the total adducts). The cyclohexyl-cyclopentylmethyl ring contraction apparently results from an alkyl shift similar to the above hydrogen shifts (compare path *c* in Scheme 6 and **I** → **III** in Scheme 7), which although well-documented from cyclohexane and some of its derivatives under superacid conditions,[17] has to our knowledge not been previously reported for phenonium cations. (However, methyl migration has been observed as a minor path in the solvolysis of some *β*,*β*-dimethyl-*β*-phenylethyl brosilates.)[16b,c]

In summary, the medium has a significant effect on product distribution. Stabilization of the cation by a solvent such as trifluoroethanol favors attack to alkenes over the at any rate inefficient trapping by a *σ* nucleophile such as piperidine and further allows for the occurring of diagnostic rearrangements at the cation stage.

The present access to phenonium cation through the photochemical generation of aryl cations and their addition to alkenes in solution appears to offer an unprecedented mild and versatile access to such species, and thus both open new synthetic pathways and make possible mechanistic studies under a larger variety of conditions. The competing paths can to some degree be controlled through the appropriate choice of conditions. Furthermore, there is indication that the key step, the photoheterolysis of the aryl-halogen bond, is not restricted to the case of anilines,[11a,12] and it may be surmised that the scope of photoinduced cationic arylation reactions related to those discussed above can be significantly widened.

Experimental Section

General. 4-Chloro- and 4-fluoroaniline (**1b**, **1′b**) were commercial products, the corresponding *N*,*N*-dimethyl derivatives (**1a**, **1′a**) were prepared from the former by conventional techniques, and the other reagents (of commercial origin) were distilled or recrystallized before use. For the irradiations, spectroscopic grade solvents were used as received. B3LYP/6-31G(d) calculations on the 4-aminophenyl cation−ammonia system were carried out by Dr. M. Freccero as illustrated in ref 11a.

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) (or the corresponding amount of the fluoroanilines **1′**) in 100 mL of acetonitrile, methanol, or trifluoroethanol was subdivided in five quartz tubes and flushed with argon for 15 min. The additives (alkenes 1 M and/or amines 0.5 M) were added, the flushing was resumed for a further 5 min, and the tubes were tightly capped. These were externally irradiated by means of 615-W (center of emission, 310 nm) phosphor coated lamps for 3 or 6 h in a merry-go-round apparatus. The progress of the reaction was monitored by GC and GC−MS.

Products Isolation and Identification. The irradiated solution was evaporated under reduced pressure, and the residue was chromatographed on silica gel 60 HR by eluting with cyclohexane−ethyl acetate mixtures containing 0.01% triethylamine to avoid product decomposition due to silica gel acidity. The products were obtained as oils or glassy solids from the fractions. Chromatography was repeated on some fractions for increased separation. However, in some cases we did not obtain complete purification and some of the products (see detail below) were contaminated by one of their isomers. The products were characterized by elemental analysis, GC−MS and NMR as detailed in the following. The NMR spectra were recorded on a 300-MHz spectrometer, and the chemical shifts were reported relative to TMS. The GC−MS analyses were performed using a HP-5MS column (30 m × 0.25 mm with film thickness 0.25 μm) and helium as carrier (0.6 mL/min). The total run time was 30 min with the initial oven temperature 8 (4 min), rising at a rate of 10 °C/min to 250 °C. The structures of new compounds were deduced from the results of ^{1}H and ^{13}C NMR, DEPT-135 and 2D correlated experiments. 2,2- and 2,4-Diphenyldiamines ant their *N*,*N*,*N′*,*N′*-tetramethyl derivatives, the halogenated diphenyldiamines **7** and **7′**,[11d] and 4-(1-pyperidinyl)-*N*,*N*-dimethylaniline (**8**)[18] have been previously reported and were recognized by comparison with authentic samples. NMR and GC−MS data of new compounds are listed below.

***N*,*N*-Dimethyl-4-(2-butylaminohexyl)aniline (9a)** and ***N*,*N*-dimethyl-4-(1-butylaminohexyl) aniline (11a)** were obtained as a mixture to which the NMR characterization and elemental analysis were referred. The former compound was predominant. In the ^{13}C NMR, the signals of the two isomers were separated and 2D-HSQC experiments identified the proton signals of each one. The structures were unambiguously attributed considering the long-range C, H correlations in 2D-HMBC spectra; in particular the position of both the aromatic ring and the amine on the aliphatic chain could be demonstrated. In detail for **9a** isomer, cross-peaks between the aromatic hydrogens at 7.01 ppm and the benzylic carbon at

(17) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173; *Angew. Chem.* **1973**, *85*, 183. Olah, G. A. *Carbocations and Electrophilic Reactions*; Verlag Chemie: Weinheim, New York, 1974.

(18) Christensen, J. B.; Schioedt, N. C.; Bechgaard, K.; Buch-Rasmunssen, T. *Acta Chem. Scand.* **1996**, *11*, 1013.

39.5 ppm, as well as between CH-2′ at 59.3 ppm and the benzylic hydrogens (2.6−2.75 ppm), were evidenced. In the case of compound **11a**, the aromatic ring and the amine were bonded to the same carbon in the hexane chain. Thus, CH-1′ (62.8 ppm) gave a cross-peak with the aromatic hydrogens at 7.05 ppm as well as with the amine methylene group at 2.45 ppm; H-1′ at 3.45 ppm gave a cross-peak with CH_2N at 47.3 ppm. Anal. Found: C, 77.9; H, 11.8; N, 10.1. Calcd for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67; N, 10.13. **Data for 9a:** ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3H, J = 7 Hz), 0.9 (t, 3H, J = 7 Hz), 1.2−1.5 (m, 10H), 2.5−2.7 (m, 2H), 2.6−2.75 (m, 2H, H-1), 2.8 (m, 1H, H-2), 2.93 (s, 6H), 6.65 and 7.01 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 14.0 (CH_3), 20.3 (CH_2), 22.9 (CH_2), 28.0 (CH_2), 32.3 (CH_2), 33.4 (CH_2), 39.5 (CH_2-1), 40.7 (NCH_3), 46.8 (CH_2N), 59.3 (CH-2), 112.8 (CH), 127.8, 129.8 (CH), 149.1. **Data for 11a:** ^{1}H NMR δ ($CDCl_3$) 0.87 (t, J = 7 Hz, 3H), 0.9 (t, J = 7 Hz, 3H), 1.25−1.75 (m, 12H), 2.45 (t, J = 7 Hz, 2H, CH_2N), 2.98 (s, 6H), 3.45 (dd, J = 8, 6 Hz, 1H, H-1), 6.7 and 7.05 (AA′BB′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.95 (CH_3), 13.98 (CH_3), 20.4 (CH_2), 22.5 (CH_2), 26.1 (CH_2), 31.8 (CH_2), 32.3 (CH_2), 38.1 (CH_2), 40.6 (NCH_3), 47.3 (CH_2N), 62.8 (CH-1), 112.5 (CH), 127.8 (CH), 132.5, 149.5.

***N,N*-Dimethyl-4-[1-(butylaminomethyl)pentyl]-aniline (10a).** Anal. Found: C, 78.0; H, 11.7; N, 10.0. Calcd for $C_{18}H_{32}N_2$: C, 78.20; H, 11.67; N, 10.13. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 0.9 (t, 3H, J = 7 Hz), 1.1−1.65 (m, 10H), 2.4−2.6 (m, 2H), 2.7 (m, 1H, H-1), 2.7−2.9 (m, 2H), 2.95 (s, 6H), 6.7 and 7.05 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 14.0 (CH_3), 20.4 (CH_2), 22.6 (CH_2), 29.6 (CH_2), 32.0 (CH_2), 34.4 (CH_2), 40.6 (NCH_3), 44.7 (CH-1), 49.6 (CH_2N), 56.0 (CH_2N), 112.8 (CH), 128.2 (CH), 131.8, 149.1.

***N,N*-Dimethyl-4-(2-piperidinohexyl)aniline (12a).** Anal. Found: C, 78.9; H, 11.2; N, 9.6. Calcd for $C_{19}H_{32}N_2$: C, 79.11; H, 11.18; N, 9.71.^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.2−1.6 (m, 12H), 2.25 (dd, 1H, J = 13, 8.5 Hz, H-1), 2.45−2.74 (m, 4H, CH_2N), 2.65 (m, 1H, H-2), 2.89 (dd, 1H, J = 13, 4.5 Hz, H-1), 2.95 (s, 6H), 6.7 and 7.05 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 22.7 (CH_2), 25.1 (CH_2), 26.6 (CH_2), 29.2 (CH_2), 30.1 (CH_2), 34.4 (CH_2-1), 40.8 (NMe), 49.5 (CH_2N), 66.9 (CH-2), 112.8 (CH), 129.6 (CH), 130.1, 148.7. GC−MS *m*/*z* 288.

***N,N*-Dimethyl-4-[(1-piperidinomethyl)pentyl)aniline (13a)** and ***N,N*-dimethyl-4-(1-piperidinohexyl)aniline (14a)** were obtained as a mixture to which the NMR characterization and elemental analysis are referred. The former was the main one. As for the similar compounds isolated with butylamine, the structure was attributed on the basis of HSQC and HMBC 2D NMR spectra. In particular in the case of **14a** the aromatic hydrogen at 7.05 ppm gave a long-range correlation with CH-1′ at 69.8 ppm, which in turn gave a cross-peak with piperidine hydrogens at 2.4 ppm. For **13a** the expected correlations were observed. Anal. Found: C, 79.0; H, 11.3; N, 9.7. Calcd for $C_{19}H_{32}N_2$: C, 79.11; H, 11.18; N, 9.71. **Data for 13a:** ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.1 (sext, 2H, J = 7 Hz), 1.2−1.85 (m, 10H), 2.25−2.45 (m, 4H, $-CH_2-N$), 2.35 and 2.5 (AB part, 2H, J = 13 Hz), 2.7 (m, 1H, H-1), 2.95 (s, 6H), 6.7 and 7.05 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 22.8 (CH_2), 24.5 (CH_2), 26.0 (CH_2), 26.3 (CH_2), 29.8 (CH_2), 34.1 (CH_2), 40.8 (NCH_3), 42.3 (CH-1), 55.1 (CH_2N), 66.5 (CH_2), 112.9 (CH), 128.2 (CH), 133.3, 148.8. **Data for 14a:** ^{1}H NMR δ ($CDCl_3$) 0.85 (t, 3H, J = 7 Hz), 1.1−1.65 (m, 14H), 2.4 (m, 4H, CH_2N), 2.98 (s, 6H), 3.12 (dd, 1H, J = 9, 4.5 Hz, H-1), 6.7 and 7.05 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 22.5 (CH_2), 24.6 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 32.0 (CH_2), 32.6 (CH_2), 40.5 (NCH_3), 50.6 (CH_2N), 69.8 (CH-1), 111.8 (CH), 127.8, 129.5 (CH), 149.5.

4-(2-Butylaminohexyl)aniline (9b). Anal. Found: C, 77.3; H, 11.4; N, 11.2. Calcd for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J = 7 Hz), 0.9 (t, 3H, J = 7 Hz), 1.2−1.5 (m, 10H), 2.5−2.7 (m, 5H, H-1, H-2 and CH_2N)), 3.5 (broad, 2H, NH_2), 6.6 and 6.9 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 13.8 (CH_3), 14.0 (CH_3), 20.3 (CH_2), 22.9 (CH_2), 27.9 (CH_2), 32.2 (CH_2), 33.3 (CH_2), 39.6 (CH_2-1), 46.7 (CH_2-N), 59.3 (CH-2), 115.2 (CH), 129.5, 129.9 (CH),144.3. GC−MS *m*/*z* 248.

4-[1-(Butylaminomethyl)pentyl]-aniline (10b). Anal. Found: C, 77.2; H, 11.4; N, 11.2. Calcd for $C_{16}H_{28}N_2$: C, 77.36; H, 11.36; N, 11.28. ^{1}H NMR δ ($CDCl_3$) 0.85 (*t*, J = 7 Hz, 3H), 0.95 (t, J = 7 Hz, 3H), 1.2−1.7 (m, 10H), 2.4−2.6 (m, 2H,), 2.65 (m, 1H, H-2), 2.7−2.8 (m, 2H), 3.5 (broad, 2H, NH_2), 6.65 and 6.98 (AA′BB′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.8 (CH_3), 14.0 (CH_3), 20.3 (CH_2), 22.6 (CH_2), 29.5 (CH_2), 31.6 (CH_2), 34.4 (CH_2), 44.7 (CH), 49.3 (CH_2), 57.7 (CH_2N), 115.3 (CH), 128.4 (CH), 133.5, 144.6. GC−MS *m*/*z* 248.

4-(2-Piperidinohexyl)aniline (12b). Anal. Found: C, 78.5; H, 10.8; N, 10.6. Calcd for $C_{17}H_{28}N_2$: C, 78.40; H, 10.84; N, 10.76. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.1−1.7 (m, 12H), 2.25 (dd, 1H, J = 13.5, 8.5 Hz, H-1), 2.4−2.7 (m, 4H, CH_2N), 2.55 (m, 1H, H-2), 2.85 (dd, 1H, J = 13, 4.5, H-1), 3.5 (broad, 2H, exch, NH_2), 6.6 and 6.95 (AA′BB′, 4H); ^{13}C NMR δ ($CDCl_3$) 13.9 (CH_3), 22.6 (CH_2), 24.9 (CH_2), 26.3 (CH_2), 29.2 (CH_2), 30.0 (CH_2), 34.7 (CH_2-1), 49.5 (CH_2N), 66.9 (CH-2), 115.0 (CH), 129.8 (CH), 131.5, 143.8. GC−MS *m*/*z* 260.

4-(1-Piperidinomethyl)pentyl)aniline (13b). Anal. Found: C, 78.4; H, 11.0; N, 10.6. Calcd for $C_{17}H_{28}N_2$: C, 78.40; H, 10.84; N, 10.76. ^{1}H NMR ($CDCl_3$) δ 0.9 (t, 3H, J = 7 Hz), 1.1−1.8 (m, 12H), 2.25−2.4 (m, 4H, CH_2N), 2.4 and 2.5 (AB part, 2H, J = 12.5 Hz), 2.7 (m,1H, H-1), 3.5 (broad, exch, NH_2), 6.7 and 6.95 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3), 22.7 (CH_2), 24.4 (CH_2), 25.8 (CH_2), 29.6 (CH_2), 34.2 (CH_2), 42.5 (CH-1), 54.9 (CH_2N), 66.3 (CH_2), 115.1 (CH), 128.4 (CH), 135.2, 144.2. GC−MS *m*/*z* 260.

***N,N*-Dimethyl-4-(*trans*-2-butylaminocyclohexyl)-aniline (15a).** Anal. Found: C, 78.8; H, 11.1; N, 10.2 Calcd for $C_{18}H_{30}N_2$: C, 78.77; H, 11.02; N, 10.21. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.1−2.1 (m, 12H), 2.3 and 2.63 (m, 2H), 2.35 (dt, 1H, J = 3, 10 Hz, H-2), 2.55 (dt, 1H, J = 3, 10 Hz, H-1), 2.95 (s, 6H), 6.7 and 7.1 (AA′BB′, 4H). The large coupling constants between H-1′ and H-2′ (10 Hz) proved their *trans* spatial relationship. ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 20.2 (CH_2), 25.2 (CH_2), 26.5 (CH_2), 32.0 (CH_2), 32.1 (CH_2), 34.8 (CH_2), 40.6 (NMe), 46.7 (CH_2N), 49.8 (CH-2), 61.4 (CH-1), 113.0 (CH), 128.1 (CH), 132.1, 149.3.

***N,N*-Dimethyl-4-[(1-butylamino-1cyclopentyl)methyl]-aniline (16a).** 2D-TOCSY (120 ms as mixing time) and NOESY supported the structure attribution. In detail, the first experiment identified the proton signals of a buthylamino fragment (2.4, 1.45, 1.3 and 0.85 ppm) and of cyclopentylmethyl moiety (3.12, 2.1, 1.95, 1.6, 1.35 and 1.1 ppm). The NOE correlations found in NOESY experiment between the aromatics at 7.1 ppm and hydrogens at 3.12, 2.1 2.4 ppm confirmed that butylamine and aniline were bonded to the same hexane carbon. Anal. Found: C, 78.6; H, 11.1; N, 10.0. Calcd for $C_{18}H_{30}N_2$: C, 78.77; H, 11.02; N, 10.21. ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7 Hz), 1.05−1.9 (m, 12H), 2.1 (m, 1H), 2.4 (m, 2H), 2.95 (s, 6H), 3.12 (d, 1H, J = 9 Hz, H-1), 6.7 and 7.1 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 13.8 (CH_3), 20.3 (CH_2), 24.8 (CH_2), 25.3 (CH_2), 30.2 (CH_2), 30.6 (CH_2), 32.0 (CH), 40.5 (NMe), 47.2 (CH_2), 47.3 (CH), 68.3 (CH-1), 112.2 (CH), 128.2 (CH), 131.8, 149.4.

***N,N*-Dimethyl-4-(*trans*-2-piperidinocyclohexyl)-aniline (17a).** In the carbon spectrum, the cyclohexane CH-1 and CH-2 were clearly distinguished (68.1 and 46.8 ppm), while the ^{1}H−^{13}C correlations (HSQC experiment) showed that both H-1′ and H-2′ appeared in the proton spectrum at 2.6 ppm, superimposed with two piperidine hydrogens. Their *trans* spatial relationship was attributed by comparison with the analogue compounds obtained with butylamine (**15b** and **15a**). Anal. Found: C, 79.6; H, 10.7; N, 9.7. Calcd for $C_{19}H_{30}N_2$: C, 79.66; H, 10.56; N, 9.78. ^{1}H NMR ($CDCl_3$) δ 1.22−1.4 (m, 10H), 1.7−2.0 (m, 4H), 2.2 and 2.6 (m, 4H, CH_2N), 2.6 (m, 2H), 2.95 (s, 6H, NMe_2), 6.7 and 7.1 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 25.1 (CH_2), 26.3 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 36.4

(CH_2), 40.6 (NMe), 46.8 (CH); 49.8 (CH_2N), 68.1 (CH), 112.5 (CH), 128.1 (CH), 135.0, 148.6.

***N,N*-Dimethyl-4-[(1-piperidino-1-cyclopentyl)methyl]-aniline (18a)** was obtained impure of isomer **17a**. In this case, the low quantity did not allow further chromatographic separation and other 2D NMR investigations However the ^1H and ^{13}C NMR showed a clear similarity with those obtained for the analogue **16a**. The signals at 3.05 ppm in the proton spectrum and at 74.7 ppm in the carbon spectrum were diagnostic for this structure. ^1H NMR ($CDCl_3$) δ 1.1−1.9 (m, 14H), 2.15 (m, 1H), 2.3−2.6 (m, 4H), 2.95 (s, 6H), 3.05 (d, 1H, J = 11 Hz, H-1), 6.7 and 7.1 (AA′BB′, 4H); ^{13}C NMR ($CDCl_3$) δ 24.9 (CH_2), 25.5 (CH_2), 30.1 (CH_2), 30.2 (CH_2), 40.5 (NMe), 50.1 (CH); 51.1 (CH_2N), 74.7 (CH), 112.7 (CH), 128.2 (CH), 131.5, 148.3.

4-(2-*trans*-Butylaminocyclohexyl)aniline (15b). Anal. Found: C, 77.8; H, 10.5; N, 11.1. Calcd for $C_{16}H_{26}N_2$: C, 77.99; H, 10.64; N, 11.37. ^1H NMR ($CDCl_3$) δ 0.8 (t, 3H, J = 7 Hz), 1.15 (sext, 2H), 1.2−2.1 (m, 10H), 2.35 and 2.65 (m, 2H, CH_2N), 2.38 (td, 1H, J = 11, 4 Hz, H-2), 2.65 (td, 1H, J = 12, 4 Hz, H-1), 3.5 (broad, 2H, exch), 6.65 and 7.05 (AA′BB′, 4H). The large coupling constant between H-1′ and H-2′ (11 Hz) proved their *trans* spatial relationship. ^{13}C NMR ($CDCl_3$) δ 13.8 (CH_3), 20.1 (CH_2), 25.1 (CH_2), 31.5 (CH_2), 31.7 (CH_2), 34.6 (CH_2), 46.3 (CH_2N), 49.5 (CH-2), 61.3 (CH-1), 115.4 (CH), 128.3 (CH), 133.8, 144.8. GC−MS *m*/*z* 246.

4-(2-*trans*-2-Piperidinocyclohexyl)aniline (17b). Anal. Found: C, 78.7; H, 10.0; N, 9.5. Calcd for $C_{17}H_{26}N_2$: C, 79.02; H, 10.14; N, 10.84. In this case H-1′ was close to H-2′ in the proton spectrum also when changing solvent (at 2.5 ppm), while C-1′ and C-2′ were well separated (at 46.9 and 68.1 ppm). The *trans* configuration could thus not be deduced from ^1H NMR spectrum but was attributed on the basis of the close analogy of the whole spectra with the corresponding product from butylamine (**15b**, see below). ^1H NMR ($CDCl_3$) δ 1.1−1.6 (m, 10H), 1.7−1.9 (m, 4H), 2.2 and 2.5 (m, 4H), 2.5 (m, 2H), 3.5 (broad, 2H, exch), 6.6 and 6.9 (AA′BB′, 4H); ^{13}C NMR δ ($CDCl_3$) 21.5 (CH_2), 22.2 (CH_2), 26.3 (CH_2), 26.6(CH_2), 26.7 (CH_2), 36.3 (CH_2), 46.9 (CH), 49.7 (CH_2N), 68.1 (CH-2), 114.9 (CH), 128.3 (CH), 136.9, 143.6. GC−MS *m*/*z* 258.

4-(2-*trans*-2-Phenylaminocyclohexyl)aniline (19). Anal. Found: C, 81.0; H, 8.4; N, 10.4. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.33; N, 10.52. ^1H NMR ($CDCl_3$) δ 1.2−2.0 (m, 8H), 2.45 (m, 1H, H-2), 3.27 (dt, J = 10, 3 Hz, 1H, H-1), 6.45 (dd, J = 8, 2 Hz, 2H), 6.65 and 6.95 (AA′BB′, 4H), 6.7 (dt, J = 2, 9 Hz, 1H), 7.1 (dd, J = 9, 8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 25.1 (CH_2), 26.5 (CH_2), 33.6 (CH_2), 35.9 (CH_2), 50.1 (CH-2); 56.5 (CH-1), 113.1 (CH), 115.3 (CH), 116.6 (CH), 128.1 (CH), 128.9 (CH), 133.9, 144.6, 147.7.

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