Photochemical Reaction of *N*,*N*-Dimethyl-4-chloroaniline with Dienes: New Synthetic Paths via a Phenyl Cation

Benedetta Guizzardi, Mariella Mella, Maurizio Fagnoni, and Angelo Albini*[a]

Abstract: The irradiation of *N*,*N*-dimethyl-4-chloroaniline in the presence of open-chain dienes in acetonitrile leads to addition of the aminophenyl and chloro groups across one of the double bonds; transannular cyclization takes place with cyclic dienes, leading to an arylnortricyclene from norbornadiene and to 1-arylbicyclo[3.3.0]octanes from 1,5-cyclooctadiene. The reaction proceeds by photoheterolysis of the chloroaniline to yield the 4-aminophenyl cation and addition to a C=C double bond. The chemistry of the adduct cation depends on structure and medium, involving ion pairs in MeCN and solvated ions in CF_3CH_2OH. In the latter solvent, formation of ethers from open-chain alkenes is accompanied by Wagner–Meerwein hydride shift. In acetonitrile, the cation from cyclooctadiene partitions between deprotonation and Ritter addition, while the one from norbornadiene is reduced; both cations undergo nucleophilic addition in trifluoroethanol. The relevance of these cationic reactions under unusually mild conditions is discussed.

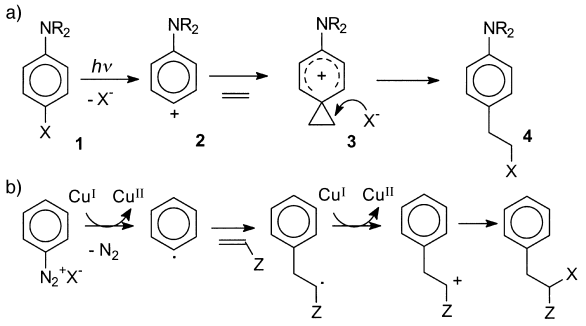
Keywords: alkylation · anilines · carbocations · photochemistry

Introduction

Phenyl cations have not been considered useful intermediates in chemical synthesis due to their difficult accessibility under convenient conditions.[1] These species have been generated in solution only in a few particular cases, allowing for some exploration of the chemistry, such as solvolysis of some perfluoroalkylsulfonic aryl esters,[2] solvolytic cyclization of (trifluoromethanesulfonyl)oxydienynes,[3] and controlled (photo)decomposition of diazonium salts.[4] A large fraction of the reports on aryl cations involves gas-phase studies, in which they arise by decay of tritiated benzenes,[5] or spectroscopic studies in matrix at cryogenic temperatures.[6]

However, a mild entry at least to electron-donating, substituted phenyl cations is offered by the photoheterolysis of haloanilines[7, 8] and halophenols;[9] this occurs efficiently in polar or protic solvents, as has been demonstrated through several pieces of evidence. As an example, 4-*N*,*N*-dimethylchloroaniline (**1**, Scheme 1) gives the substituted phenyl cation **2**.

Under these conditions the cation is formed in the triplet state. This is interesting, because, while singlet phenyl cation usually exhibits unselective attack to the solvent,[4a,f] triplet cation **2** was found to add to alkenes, not to the solvent (acetonitrile).[8b,c] The reaction yields 4-(β-chloroalkyl)anilines **4**, rationalized as arising via phenonium cation **3**. There are several points of interest in the mechanism of the process. One is the unusual selective reaction of the triplet cation with π rather than σ nucleophiles, which is in accord with the prediction by B3LYP calculation.[8b] Another one is the formation along the path of a phenonium ion, another intermediate that has been the subject of a extensive investigation.[10] In this case, the phenonium ion is formed through cationic addition, rather than by the usual path, that is, elimination from a phenethyl derivative.



Scheme 1.

However, the reaction has also a preparative significance. As it appears from Scheme 1, the overall sequence (case a) exactly parallels the Meerwein arylation of alkenes (case b),[11] with the important difference that the key bonding step involves a phenyl *cation* in the former case and a *radical* (formed by metal-induced reductive decomposition of a benzenediazonium cation) in the latter one. The difference

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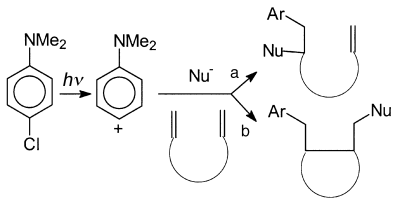
shows up clearly in the fact that the Meerwein arylation is usually carried out with electrophilic alkenes (Z in Scheme 1 is an electron-withdrawing group), while in the above ionic variation nonconjugated, nucleophilic alkenes are used. Furthermore, the cation also adds to aromatic compounds to finally give biaryls in a variation of the Gomberg–Bachmann synthesis;[12] this again proceeds via the phenyl cation rather than the radical.

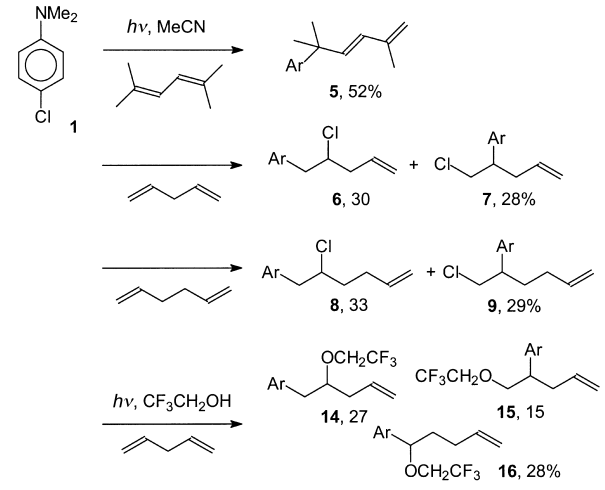
The complementarity with the Meerwein arylation of alkenes encouraged us to further examine this reaction. An appealing extension that we considered was to replicate the reaction and explore whether the first addition step could be followed by a second addition to a π nucleophile and, thus, form two new C–C bonds. Intramolecular attack seemed a reasonable possibility (see Scheme 2, path b vs. a), and accordingly we studied the photogeneration of the 4-*N*,*N*-dimethylaminophenyl cation in the presence of some open-chain, cyclic, and bicyclic dienes. In the event, we found that double attack by path b did take place under precise conditions, and this offered a more detailed rationalization of these cationic reactions.



Scheme 2.

Results

Open-chain 1,3-, 1,4-, and 1,5-dienes were tested. Thus, irradiation of a solution of 4-chloro-*N*,*N*-dimethylaniline (0.05 M) in acetonitrile containing 2,5-dimethyl-2,4-hexadiene (1M) gave, beside a small amount of dimethylaniline, a single product. This was identified as the *trans*-pentadienylaniline (**5**: Scheme 3) on the basis of the analytical and spectroscopic properties.

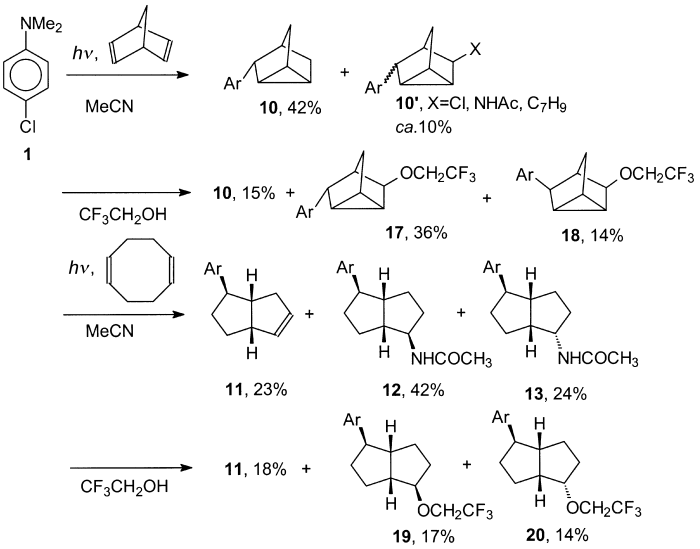


Ar = C_6H_4-4-NMe_2

Scheme 3.

In the case of 1,4-pentadiene, two products were obtained. These were identified as the chlorinated alkenylanilines **6** and **7**, resulting from the two regioisomeric additions of the aryl group and chlorine across one of the double bonds. A similar result was found with 1,5-hexadiene, which gave the corresponding chlorohexenylanilines **8** and **9**.

Cyclic dienes were then explored. Norbornadiene gave a nonchlorinated alkylaniline as the main product. Spectroscopic examination demonstrated the presence of a nortricyclene skeleton, with the aryl residue in the 2-position (product **10**, Scheme 4).



Scheme 4.

With 1,5-cyclooctadiene, three products were obtained, all of them containing a bicyclo[3.3.0]octane skeleton with the aminoaryl group in the 2-position; NOE experiments established that the aryl group was *cis* to the bridgehead hydrogens in every case. Detailed examination showed that one of the products was the arylated bicyclooctene **11**, while the other two, which together accounted for 66% of the reaction, were stereoisomers **12** and **13**, bearing an acetamido group on the same skeleton. Clearly the last reaction resulted from incorporation of the solvent acetonitrile and adventitious water. This encouraged us to carefully examine the reaction with norbornadiene, which revealed the presence of further products. Although we did not obtain a complete characterization, due to the tiny amounts (overall ca. 10%), GC/MS data (see Experimental Section) supported the formation of six further anilines (**10′**), resulting from the incorporation of norbornadiene and 1) a chlorine atom (three isomers), 2) an acetamido group, and 3) a further norbornadiene unit (two isomers).

This suggested testing further solvents, and some of the above reactions were repeated in trifluoroethanol. In this solvent, the reaction with 1,4-pentadiene gave three trifluoroethyl ethers (Scheme 3, bottom). These were the β-arylethyl ethers **14** and **15**, corresponding to the β-chloroalkyl derivatives obtained in acetonitrile, as well as an unexpected isomer, the benzyl ether of structure **16**.

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As for norbornadiene, the above-mentioned product **10** was a minor product in trifluoroethanol, in which the reaction mainly gave two trifluoromethyl ethers, compounds **17** and **18** (Scheme 4), which differ in the stereochemistry of the aryl group. With cyclooctadiene compound **11**, which contains the bicyclooctene moiety, was still formed and was accompanied by two ethers (compounds **19** and **20**) corresponding to the amides obtained in acetonitrile.

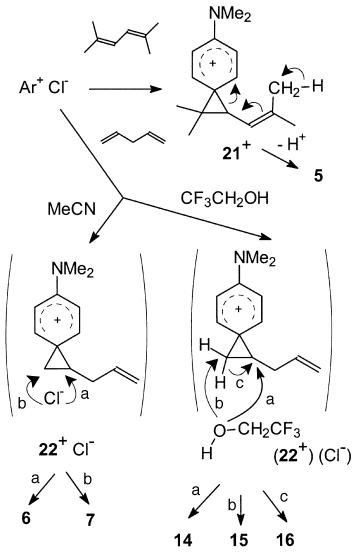
Discussion

The above results show that simple arylation is obtained with open-chain dienes, while arylation is accompanied by intramolecular alkylation forming a second carbon–carbon bond with cyclic dienes. The structure of final products depends on conditions. Thus, the resulting alkyl chain introduced on the aniline bears a chloro atom with open-chain alkenes in MeCN, or a trifluoroethoxy group in CF_3CH_2OH (one of the products has a rearranged chain), no substituent with norbornadiene in MeCN, an acetamido group with cyclooctadiene in the same solvent, and again an alkoxy group with the cyclic dienes in CF_3CH_2OH.

This demands a detailed rationalization and more precise definition of the scope of the arylation reaction via photogenerated aryl cations. As previously demonstrated, photolysis of chloroanilines occurs from the triplet state and yields the triplet cation. B3LYP calculations showed that this species is not a localized σ cation, but rather the charge is delocalized over the π system and the divalent carbon resembles a triplet carbene. More importantly, calculations showed that the triplet does not react with a σ nucleophile such as water, while it adds to an alkene forming an adduct still of triplet multiplicity.[8b] The lowest lying adduct cation is a singlet phenonium cation to which the previous species intersystem crosses. In full agreement, it was found that arylation of alkenes occurs under these conditions yielding β-choroalkylanilines (Scheme 1).

In the present reaction, the photoproduced aryl cation adds to dienes as it does to alkenes. The ensuing chemistry depends on the structure of the diene and on the reaction conditions. With open-chain dienes in acetonitrile, the pattern is essentially the same as with alkenes and can again be rationalized by the intermediacy of a phenonium cation. In the case of the conjugate diene that we investigated (2,5-dimethyl-2,4-hexadiene), an allylic proton acts as an electrofugal group, and deprotonation from intermediate $\mathbf{21}^+$ gives the observed (*trans*) pentadienyl aniline (Scheme 5), in the same way as an allylaniline was obtained with 2,3-dimetyl-2-butene, to which this diene is equivalent with the interposition of a further double bond.

With nonconjugated dienes, a chloride ion acts as a nucleophile yielding β-chloroalkyl derivatives, as with simple alkenes, with no interference by the second double bond. This is reasonable, because a solvent such as acetonitrile moderately stabilizes the ions formed from the photofragmentation and oppositely charged ions are expected to remain paired ($Ar^+ Cl^-$). Therefore, insertion of the cation into the alkene to give the ion pair $\mathbf{22}^+ Cl^-$ is immediately followed by addition



Scheme 5.

of closely lying chloride (Scheme 5). The remaining double bond has some effect on the regioselectivity in the adduct cation reaction, since with alkenes we found attack at the methine predominating by about 2 to 1 with Cl^- in MeCN (and 95 to 5 with MeOH as neat solvent),[8a] and in general some selectivity is expected with phenonium ions, whereas here there is no selectivity in the pairs **6**/**7** and **8**/**9**.

Changing the medium causes a drastic change on the reaction course, as shown in the experiments in trifloroethanol. Solvation of the ions here is much more important, and it is expected that free ions are involved ($(\mathbf{22}^+)(Cl^-)$, see Scheme 5). The intermediacy of the free cation is apparent through a diagnostic reaction, the Wagner–Meerwein rearrangement,[13] of the alkyl cation to form a benzyl cation (path c in Scheme 5). Thus, under these conditions both the non-rearranged β-alkoxyalkylanilines **14** and **15** (with moderate regioselectivity) and the rearranged α-alkoxyalkylaniline **16** are formed. The last compound accounts for about 40% of the alkylated anilines formed.

Contrary to the case of freely rotating open-chain dienes, the second double bond is directly involved in the addition with the cyclic derivatives, apparently due to entropic reasons. Thus, with norbornadiene attack by the phenyl cation is immediately followed (or accompanied, we have no evidence for the role of a phenonium intermediate) by interaction with the second double bond. This leads to a nortricyclene cation ($\mathbf{23}^+$, Scheme 6), as often observed with norbornadiene under acidic conditions.[14] Formation of the transannular bond moves the cationic site away from the counterion, and the interception of $Ar^+ Cl^-$ in MeCN is not followed by recombination with chloride. Product **10′** (X = Cl, three isomers) is formed only in traces and further products arise from addition of different nucleophiles, namely, acetonitrile (to form a ylide and the acetamide from it) or a further molecule of norbornadiene (products **10′**, X = NHAc, C_7H_9).

The major process in this solvent, however, is reduction to the alkane (product **10** is present in four times as much as the sum of products **10′**). We see no evident path for intermolecular reduction. A possible rationalization is that ion $\mathbf{23}^+$

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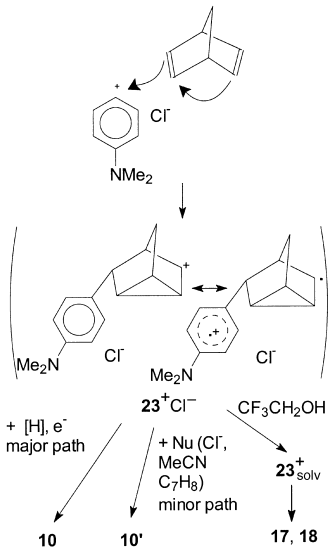
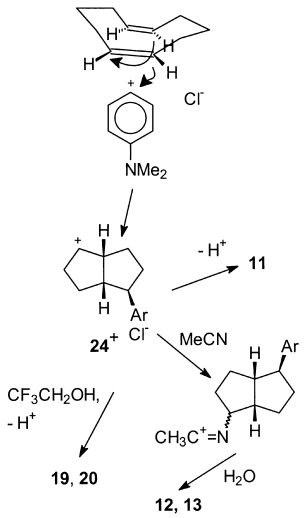


Scheme 6.

obtains some stabilization through intramolecular electron transfer from the aniline moiety to the cationic site in front of it (Scheme 6) and that this facilitates hydrogen abstraction from the medium. This path is important only in moderately polar MeCN, and in the better ion-solvating trifluoroethanol the stabilized ion $\mathbf{23}^{+}_{solv}$ mainly undergoes nucleophile addition to yield ethers **17** and **18**, with **10** as a minor product.

One may think that steric constraints are essential in facilitating transannular bonding in norbornadiene. However, the same chemistry is observed with cyclooctadiene, in which attack by the aryl cation is followed by intramolecular C–C bond formation leading to two fused five-membered rings (ion $\mathbf{24}^{+}$ in Scheme 7). The charge is now further removed from the counterion, no alkyl chloride is detected, and the cation partitions, as one may expect, between deprotonation to yield alkene **11** and addition to acetonitrile to yield acetamides **12** and **13**. This clearly involves a Ritter reaction via the corresponding ylides, a process as yet known to occur only under strongly acidic conditions,[15] including the case of transannular bonding in cyclic dienes.[15c] Since the cationic site is not protected by the counterion, there is no difference between the reaction in the two solvents MeCN and CF_3CH_2OH, the respective solvent-trapping products being obtained in each case (Scheme 7).



Scheme 7.

The steric arrangement of the aryl group is consistently *cis* to the bridgehead protons. This configuration has been calculated to be the most stable among the phenylbicyclo[3.3.0]octyl cations formed from acid-catalyzed reactions between cyclooctadiene and benzene,[16] apart from those implying hydride transfer, which are not observed here.

In conclusion, the present results widen the scope of the photoinduced preparation of alkyanilines starting from chloroanilines. The photochemical step leads to highly functionalized products that would otherwise require multistep procedures. With open-chain dienes an alkenyl chain susceptible of further elaboration is introduced and with cyclic dienes transannular cyclization occurs under appropriate conditions, leading,for example, to bicyclo[3.3.0]octane derivatives, a frequent structure fragment among natural products.[17] From the mechanistic point of view, this works reiterates the characteristic selectivity for reactions with π nucleophiles of the 4-aminophenyl cation (and presumably of other phenyl cations) in the *triplet* state. The adduct cation formed undergoes intersystem crossing to the singlet state, and the "classic" carbocation chemistry appears in the ensuing reactions. Clear examples have been found with cyclic dienes, namely, the transannular cyclization and the Ritter reaction with acetonitrile. Furthermore, the difference between paired ions and free ions has been evidenced with the study in an ion-stabilizing medium such as trifluoroethanol, for example, in the increased nucleophilic trapping with norbornadiene and in the Wagner–Meerwein rearrangement observed with 1,4-pentadiene. One should point out that alkylation of aromatics can be also obtained from olefins and benzene derivatives, but only under strongly acidic conditions,[14, 18] while in the present case the reaction occurs under extremely mild conditions. This allows us to control the course of the reaction, as already apparent from the few examples presented. This ongoing work, as well as different approaches from other laboratories,[4f,g, 7, 9, 19] suggests that photochemistry may be the suitable way for generating phenyl cations in solution and that the little investigated chemistry of this species may turn out to be rich and rewarding.

Experimental Section

General: *N,N*-Dimethyl-4-chloroaniline was prepared by methylation of the aniline and recrystallized. The dienes were commercial products. For the irradiations, spectroscopic grade solvents were used as received.

Preparative irradiations: In a typical experiment a solution of aniline **1** (780 mg, 0.05 M) in acetonitrile or trifluoroethanol (100 mL) was subdivided into five quartz tubes and flushed with argon for 15 min. The dienes (1 M) were added, flushing resumed for further 5 min, and the tubes were tightly capped. These were externally irradiated by means of 6×15 W (centre of emission, 310 nm) phosphor-coated lamps for 3 hours 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 purified by chromatog-

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raphy on silica gel 60 HR (Millipore) by eluting with cyclohexane/ethyl acetate or cyclohexane/toluene mixtures, which contained 0.01% of 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 details below) were contaminated by one of their isomers. The products were characterized by elemental analysis, GC/MS, and IR and NMR spectroscopy 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 by using a HP-5MS column (30 m × 0.25 mm with film thickness 0.25 μm) and helium as carrier (0.6 mL min^{-1}). The total run time was 30 min with the initial oven temperature 100 °C (4 min), rising at a rate of 10 °C min^{-1} to 250 °C. The structures of new compounds were deduced from the results of ^{1}H, ^{13}C, DEPT-135, and 2D correlated NMR experiments.

Irradiation of aniline 1 in the presence of 1,5-dimethyl-2,4-hexadiene in MeCN: Chromatography on silica gel eluting with cyclohexane/toluene (1:1) gave 52% of product **5**.

***trans*-*N*,*N*-Dimethyl-4-(1,1,4-trimethyl-2,4-pentadienyl)aniline (5)**: Elemental analysis calcd (%) for $C_{16}H_{23}N$: C 83.79, H 10.11, N 6.11; found: C 83.9, H 10.2, N 6.0; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.4$ (s, 6H; 1′-Me_2), 1.8 (s, 3H; 4′-Me), 2.9 (s, 6H; NMe_2), 4.9 (AB, 2H; 5′-H_2), 5.8 (d, ^3J(H,H) = 16 Hz, 1H; 3′-H), 6.1 (d, ^3J(H,H) = 16 Hz, 1H; 2′-H), 6.7, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.7$ (CH_3), 26.8 (CH_3), 39.4 (C), 40.6 (CH_3), 112.5 (CH), 114.6 (CH_2), 126.7 (CH), 128.1 (CH), 128.9 (CH), 140.7 (CH), 148.7 ppm (C); IR (neat): $\nu = 1615$, 1515 cm^{-1}.

Irradiation of aniline 1 in the presence of 1,4-pentadiene in MeCN: Chromatography on silica gel eluting with cyclohexane/toluene (1:1) gave a fraction that contained the isomeric products **6** (30%) and **7** (28%); IR (neat): $\nu = 1615$, 1520 cm^{-1}.

***N*,*N*-Dimethyl-4-(2-chloro-4-pentenyl)aniline (6)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.65$ (m, 2H; 4′-H_2), 2.95 (s, 6H; NMe_2), 3.0 (m, 2H; 1′-H_2), 4.1 (tt, ^3J(H,H) = 7, 5 Hz, 1H; 2′-H), 5.17 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5 Hz, 1H; 5′-H *trans*), 5.19 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10.5, ^4J(H,H) = 1.5 Hz, 1H; 5′-H *cis*), 5.8 (ddt, ^3J(H,H) = 17, 10.5, 7 Hz, 1H; 4′-H), 6.75, 7.16 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 40.2$ (CH_3), 41.0 (CH_2), 42.9 (CH_2), 62.7 (CH), 112.2 (CH), 117.5 (CH_2), 125.2, 129.6 (CH), 133.8 (CH), 149.1; GC/MS: *m*/*z* (%): 223 (20) [M^+], 134 (100).

***N*,*N*-Dimethyl-4-(1-chloromethyl-3-butenyl)aniline (7)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.45$, 2.7 (2m, 2H; 2′-H_2), 2.95 (s, 6H; NMe_2), 2.97 (m, 1H; 1′-CH), 3.71 (d, ^3J(H,H) = 6.5 Hz, 2H; CH_2Cl), 5.02 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10.5, ^4J(H,H) = 1.5 Hz, 1H; 4′-H *cis*), 5.1 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5 Hz, 1H; 4′-H *trans*), 5.74 (ddt, ^3J(H,H) = 17, 10.5, 7 Hz, 1H; 3′-H), 6.75, 7.15 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 36.9$ (CH_2), 40.2 (CH_3), 46.3 (CH), 49.0 (CH_2), 112.1 (CH), 116.3 (CH_2), 127.9 (CH), 128.7, 135.5 (CH), 149.2 ppm; GC/MS: *m*/*z* (%): 223 (23) [M^+], 182 (48), 147 (55), 134 (100).

Irradiation of aniline 1 in the presence of 1,5-hexadiene in MeCN: Chromatography on silica gel eluting with cyclohexane/ethyl acetate (95:5) gave a fraction that contained the isomeric products **8** (33%) and **9** (29%); IR (neat): $\nu = 1615$, 1520 cm^{-1}.

***N*,*N*-Dimethyl-4-(2-chloro-5-hexenyl)aniline (8)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.8$–2.0 (m, 2H), 2.2–2.4 (m, 2H), 2.95 (s, 6H; NMe_2), 3.0 (AB part of an ABX system, ^2J(H,H) = 14 Hz, 2H; 1′-H_2), 4.9 (ddt, ^3J(H,H) = 9, 4, 7 Hz, 1H; 2′-H), 5.0 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10.5, ^4J(H,H) = 1.5 Hz, 1H; 6′-H *cis*), 5.1 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5 Hz, 1H; 6′-H *trans*), 5.8 (ddt, ^3J(H,H) = 17, 10.5, 7 Hz, 1H; 5′-H), 6.75, 7.15 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 30.5$ (CH_2), 36.3 (CH_2), 40.6 (CH_3), 44.0 (CH_2), 63.7 (CH), 112.5 (CH), 115.3 (CH_2), 125.7, 129.9 (CH), 137.2 (CH), 149.3 ppm; GC/MS: *m*/*z* (%): 237 (13) [M^+], 134 (100).

***N*,*N*-Dimethyl-4-(1-chloromethyl-4-pentenyl)aniline (9)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.7$–1.8 (m, 2H), 1.9–2.1 (m, 2H), 2.85 (m, 1H; 1′-H), 2.95 (s, 6H; NMe_2), 3.65 (AB part of an ABX system, ^2J(H,H) = 12 Hz, 2H; CH_2Cl), 4.98 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10.5, ^4J(H,H) = 1.5 Hz, 1H; 5′-H *cis*), 5.1 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5 Hz, 1H; 5′-H *trans*), 5.77 (ddt, ^3J(H,H) = 17, 10.5, 7 Hz, 1H; 4′-H), 6.75, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.2$ (CH_2), 31.9 (CH_2), 40.5 (CH_3), 46.4 (CH), 50.0 (CH_2), 112.6 (CH), 114.6 (CH_2), 128.3 (CH), 129.2, 138.9 (CH), 149.5 ppm; GC/MS: *m*/*z* (%): 237 (18) [M^+], 147 (20), 134 (100).

Irradiation of aniline 1 in the presence of 2,5-norbornadiene in MeCN: Chromatography on silica gel eluting with cyclohexane/ethyl acetate (95:5) gave a fraction that contained product **10** (42%). A GC/MS analysis revealed several other peaks, in an overall amount of ca. 10%, as listed below.

3-(4-*N*,*N*-Dimethylaminophenyl)tricyclo[2.2.1.0^{2,6}]heptane (10): Elemental analysis calcd (%) for $C_{15}H_{19}N$: C 84.46, H 8.98, N 6.57; found: C 84.5, H 9.1, N 6.4; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.1$ (ABX, ^2J(H,H) = 10.5 Hz, 1H; 5-H *endo*), 1.2–1.3 (m, 3H; H-1, H-2, H-6), 1.3 (ABX, ^2J(H,H) = 10.5 Hz; 5-H *exo*), 1.45 (ABXY, ^2J(H,H) = 10 Hz, 1H; 7-H), 1.55 (ABXY, ^2J(H,H) = 10 Hz, 1H; 7-H), 1.9 (brs, 1H; 4-H), 2.8 (brs, 1H; 3-H), 3.0 (s, 6H; NMe_2), 6.75, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.1$ (CH), 11.3 (CH), 13.7 (CH), 28.7 (CH_2), 34.5 (CH_2), 36.0 (CH), 40.7 (CH_3), 48.4 (CH), 112.5 (CH), 128.3 (CH), 136.6, 148.9 ppm; NOE effects between 3-H (2.8) and 7-H (1.55) and between both 2′-H and 6′-H (7.1) and 3-H (2.8) and 4-H (1.9); IR: $\nu = 1615$, 1515 cm^{-1}; GC/MS: *m*/*z* (%): 213 (100) [M^+].

Minor peaks, GC/MS: *m*/*z* (%): $t_R = 13.25$ min (**10′**, X = Cl) 247 (52) [M^+], 212 (100); $t_R = 13.28$ min (**10′**, X = Cl) 247 (45) [M^+], 212 (100); $t_R = 13.40$ min (**10′**, X = Cl) 247 (48) [M^+], 212 (100); $t_R = 16.30$ min (**10′**, X = NHCOMe) 270 (100) [M^+], 210 (80); $t_R = 17.05$ min (**10′**, X = C_7H_9) 305 (100) [M^+], 212 (100); $t_R = 17.05$ min (**10′**, X = C_7H_9) 305 (95) [M^+], 212 (100).

Irradiation of aniline 1 in the presence of 1,5-cyclooctadiene in MeCN: Chromatography on silica gel eluting with cyclohexane/ethyl acetate (from 95:5 to 7:3) gave a fraction that contained product **11** (23%) and a fraction that contained products **12** (42%) and **13** (24%). IR (neat): $\nu = 1680$ cm^{-1}.

6-(*exo*)-(4-*N*,*N*-Dimethylaminophenyl)bicyclo[3.3.0]oct-2-ene (11): Elemental analysis calcd (%) for $C_{16}H_{21}N$: C 84.53, H 9.31, N 6.16; found: C 84.4, H 9.2, N 6.0; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.6$, 2.1 (2m, 2H; 7-H_2), 1.95–2.0 (m, 2H; 8-H_2), 2.2 and 2.5 (2m, 2H; 4-H_2), 2.5 (m, 1H; 5-H), 2.6 (m, 1H; 6-H), 2.95 (s, 6H; NMe_2), 3.3 (m, 1H; 1-H), 5.6 (m, 1H; 3-H), 5.68 (m, 1H; 2-H), 6.75, 7.2 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 31.6$ (CH_2), 35.6 (CH_2), 37.8 (CH_2), 40.9 (CH_3), 48.8 (CH), 50.5 (CH), 52.6 (CH), 113.0 (CH), 127.7 (CH), 128.7 (CH), 133.5, 135.2 (CH), 149.0 ppm; NOE effects: 3-H (5.6) with 4-H (2.2 and 2.5), 2′-H and 6′-H with 5-H (2.6) and 6-H (2.5), 1-H (3.3) with 5-H; IR (neat): $\nu = 1615$, 1525 cm^{-1}; GC/MS: *m*/*z* (%): 227 (90) [M^+], 160 (100), 147 (88), 134 (45).

***cis*-2-(4-*N*,*N*-Dimethylaminophenyl)-6-acetamidobicyclo[3.3.0]octane (12)**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.4$–1.9 (m, 6H), 2.0–2.25 (m, 2H), 1.97 (s, 3H; $COCH_3$), 2.3–2.6 (m, 3H; 1-H, 2-H, 5-H), 2.9 (s, 6H; NMe_2), 4.0 (m, 1H; 6-H), 5.8 (brs, 1H; NH), 6.7, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 23.3$ (CH_3), 29.4 (CH_2), 31.4 (CH_2), 32.1 (CH_2), 36.1 (CH_2), 40.7 (CH_3), 50.3 (CH), 51.0 (CH), 52.2 (CH), 57.5 (CH), 112.8 (CH), 127.6 (CH), 132.9, 148.9, 169.5 ppm; NOE effects: 1-H (2.3–2.6) with 5-H (2.3–2.6) and with 2′-H, 6′-H (7.1); GC/MS *m*/*z* (%): 286 (100) [M^+].

***trans*-2-(4-*N*,*N*-Dimethylaminophenyl)-6-acetamidobicyclo[3.3.0]octane (13)**: ^{1}H NMR (300 MHz, ($CDCl_3$): $\delta = 1.3$–1.7 (m, 6H), 1.5–1.8 (m, 2H), 1.95 (s, 3H; $COCH_3$), 2.25 (m, 1H; 1-H), 2.35 (m, 1H; 2-H), 2.7 (quint, ^2J(H,H) = 8 Hz; 5-H), 2.9 (s, 6H; NMe_2), 3.85 (m, 1H; 6-H), 6.7, 7.0 (AA′BB′, 4H; aromatics), 8.0 ppm (brs, 1H; NH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 23.1$ (CH_3), 27.5 (CH_2), 28.2 (CH_2), 29.1 (CH_2), 35.6 (CH_2), 40.7 (CH_3), 44.9 (CH), 50.0 (CH), 53.1 (CH), 53.7 (CH), 112.8 (CH), 127.6 (CH), 132.7, 148.9, 169.7 ppm; NOE effects: 6-H (3.35) with 5-H (2.7), 5-H with 1-H (2.25), 2′-H and 6′-H (7.0) with 2-H (2.35) and 1-H (2.25), NH (8.0) with 5-H (2.35); GC/MS: *m*/*z* (%): 286 (100) [M^+].

Irradiation of aniline 1 in the presence of 1,4-pentadiene in CF_3CH_2OH: Chromatography on silica gel eluting with cyclohexane/ethyl acetate (9:1) mixture gave, in the following order, fractions that contained products **16** (28%, slight impurity of **6** and **7**), **14** (27%), and **15** (15%, impurity of **14**).

***N*,*N*-Dimethyl-4-[2-(2,2,2-trifluoroethoxy)-4-pentenyl]aniline (14)**: Elemental analysis calcd (%) for $C_{15}H_{20}NF_3O$: C 62.70, H 7.02, N 4.87; found: C 63.0, H 6.9, N 4.5; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.3$ (m, 2H; 3′-H), 2.75 (AB part of an ABX system, ^2J(H,H) = 14, ^3J(H,H) = 6 Hz, 2H; 1′-H_2), 2.98 (s, 6H; NMe_2), 3.63 (quint, ^3J(H,H) = 6 Hz, 1H; 2′-H), 3.73 (m,

^3J(H, F) = 9 Hz, 2H; OCH_2), 5.1 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10.5, ^4J(H,H) = 1.5 Hz, 1H; 5′-H *cis*), 5.13 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5 Hz, 1H; 5′-H *trans*), 5.84 (ddt, ^3J(H,H) = 17, 10.5, 7 Hz, 1H; 43′-H), 6.75, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.2 (CH_2), 39.5 (CH_2), 40.5 (CH_3), 67.3 (q, ^2J(C, F) = 35 Hz; CH_2O), 83.2 (CH), 112.8 (CH), 117.5 (CH_2), 123.8 (q, ^1J(C,F) = 275 Hz; CF_3), 126.2, 130.0 (CH), 134.1 (CH), 149.1 ppm; IR (neat): ν = 1625, 1515, 1160 cm^{-1}.

***N,N*-Dimethyl-4-[1-(2,2,2-trifluoroethoxymethyl)-3-butenyl]aniline (15)**: Elemental analysis calcd (%) for $C_{15}H_{20}NF_3O$: C 62.70, H 7.02, N 4.87; found: C 62.3, H 6.9, N 4.4; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.4, 2.54 (2m, 2H; 2′-H), 2.96 (m, 1H; 1′-H), 3.0 (s, 6H; NMe_2), 3.74 (m, 2H; CH_2O), 3.76 (m, ^3J(H,F) = 9 Hz, 2H; OCH_2CF_3), 5.0 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10, ^4J(H,H) = 1.5 Hz, 1H; 4′-H *cis*), 5.03 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5 Hz, 1H; 4′-H *trans*), 5.73 (ddt, ^3J(H,H) = 17, 10, 7 Hz, 1H; 3′-H), 6.75, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.6 (CH_2), 40.7 (CH_3), 44.6 (CH), 68.4 (q, ^2J(C,F) = 35 Hz; CH_2), 76.7 (CH_2) 112.7 (CH), 116.1 (CH_2), 124.0 (q, ^1J(C,F) = 275 Hz; CF_3), 128.3 (CH), 129.5, 136.3 (CH), 149.2 ppm; IR (neat): ν = 1615, 1515, 1160 cm^{-1}; GC/MS: *m*/*z* (%): 237 (10) [M^+], 134 (100).

***N,N*-Dimethyl-4-[1-(2,2,2-trifluoroethoxymethyl)-4-pentenyl]aniline (16)**: Elemental analysis calcd (%) for $C_{15}H_{20}NF_3O$: C 62.70, H 7.02, N 4.87; found: C 63.2, H 7.2, N 5.0; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.75, 2.0 (2m, 2H; 2′-H), 2.1 – 2.2 (m, 2H; 3′-H), 3.0 (s, 6H; NMe_2), 3.5 – 3.7 (m, ^3J(H, F) = 9 Hz, 2H; OCH_2), 4.3 (dd, ^3J(H,H) = 7, 6 Hz, 1H; 1′-H), 5.0 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 10.5, ^4J(H,H) = 1.5, 1H; 5′-H *cis*), 5.05 (dq, ^2J(H,H) = 1.5, ^3J(H,H) = 17, ^4J(H,H) = 1.5, 1H; 5′-H *trans*), 5.85 (ddt, ^3J(H,H) = 17, 10.5, 7, 1H; 4′-H), 6.75, 7.2 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.9 (CH_2), 36.7 (CH_2), 40.4 (CH_3), 65.3 (q, ^2J(C,F) = 35 Hz; CH_2O), 82.6 (CH), 112.3 (CH), 114.8 (CH_2), 124.1 (q, ^1J(C,F) = 275 Hz; CF_3), 125.8, 127.7 (CH), 137.9 (CH), 150.4 ppm; IR (neat): ν = 1615, 1515, 1170 cm^{-1}; GC/MS: *m*/*z* (%): 237 (13) [M^+], 134 (100).

Irradiation of aniline 1 in the presence of 2,5-norbornadiene in CF_3CH_2OH: Chromatography on silica gel eluting with cyclohexane/ethyl acetate (95:5 to 8:2) gave a fraction that contained product **10** (15%) and one that contained products **17** (36%) and **18** (14%). IR (neat): ν = 1615, 1515, 1160 cm^{-1}.

3-*endo*-(4-*N*,*N*-Dimethylaminophenyl)-5-*exo*-(2′,2′,2′-trifluoroethoxy)tricyclo[2.2.1.0^{2,6}]heptane (17): ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ = 1.4 – 1.6 (m, 3H; 1-H, 2-H, 6-H), 1.55 (br d, ^2J(H,H) = 10.5 Hz, 1H; 7-H), 1.95 (br d, ^2J(H,H) = 10.5 Hz, 1H; 7-H), 2.1 (br s, 1H; 4-H), 2.88 (br s, 1H; 3-H), 2.9 (s, 6H; NMe_2), 3.7 (br s, 1H; 5-H), 3.8 (m, ^3J(H,F) = 9 Hz, 2H; CH_2O), 6.8, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5 (CH), 14.2 (CH), 16.7 (CH), 31.1 (CH_2); 38.8 (CH), 40.7 (CH_3), 47.7 (CH), 66.7 (q, ^2J(C, F) = 35 Hz; CH_2O), 84.3 (CH), 112.5 (CH), 123.2 (q, ^1J(C, F) = 275 Hz; CF_3), 128.1 (CH), 135.5, 149.1 ppm; NOE effects: 2′-H and 6′-H (7.1) with 5-H (3.7), 4-H (2.1), 2-H (1.4 – 1.6), 1-H (1.4 – 1.6); 3-H (2.88) with 2′-H, 6′-H, 4-H and 7-H (1.55); 5-H with 1-H; GC/MS: *m*/*z* (%): 311 (88) [M^+], 212 (30), 134 (42), 121 (100).

2-*exo*-(4-*N*,*N*-Dimethylaminophenyl)-5-*exo*-(2′,2′,2′-trifluoroethoxy)tricyclo[2.2.1.0^{2,6}]heptane (18): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.2 (m, 1H;7-H), 1.4 – 1.6 (m, 3H; 1-H, 2-H, 6-H), 1.6 (m, 1-H, 7-H), 2.2 (br s, 1H; 4-H), 2.85 (br s, 1H; 3-H), 2.88 (s, 6H; NMe_2), 3.85 (m, 1H; 5-H), 4.0 (m, ^3J(H,F) = 9 Hz, 2H; CH_2O), 6.78, 7.1 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5 (CH), 15.6 (CH), 16.8 (CH), 25.4 (CH_2), 39.3 (CH), 40.6 (CH_3), 44.7 (CH), 66.6 (q, ^2J(C, F) = 35 Hz, 2H; OCH_2), 86.6 (CH), 112.5 (CH), 123.2 (q, ^1J(C, F) = 275 Hz; CF_3), 128.1 (CH), 135.5, 149.1 ppm; NOE effects: 5-H (3.85) with 3-H (2.85), 2′-H and 6′-H (7.1) with 3-H and 7-H (1.2) ; GC/MS: *m*/*z* (%): 311 (98) [M^+], 212 (35), 134 (38), 121 (100).

Irradiation of aniline 1 in the presence of 1,5-cyclooctadiene in CF_3CH_2OH: Chromatography on silica gel eluting with cyclohexane/ethyl acetate (95:5 to 8:2) gave a fraction that contained product **11** (18%) and one that contained products **19** (17%) and **20** (14%). IR (neat): ν = 1615, 1515 , 1160 cm^{-1}.

***cis*-2-(4-*N*,*N*-Dimethylaminophenyl)-6-(2,2,2-trifluoroethoxyethyl)bicyclo[3.3.0]octane (19)**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.5 – 2.2 (m, 8H), 2.6 – 2.8 (m, 2H), 2.85 (m, 1H), 2.95 (s, 6H; NMe_2), 3.85 (m, ^3J(H,F) = 9 Hz, 2H; OCH_2), 6.7.5, 7.17 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.7 (CH_2), 26.8 (CH_2), 29.6 (CH_2), 36.2 (CH_2), 41.3 (CH_3), 45.1 (CH), 50.5 (CH), 53.3 (CH), 66.6 (q, ^2J(C, F) = 35 Hz, 2H; OCH_2), 84.0 (CH), 113.5 (CH), 124.0 (q, ^1J(C, F) = 275 Hz; CF_3), 127.8 (CH), 132.5, 148.1 ppm; no NOE effect between 6-H (3.95) and 5-H (2.8); GC/MS: *m*/*z* (%): 327 (76) [M^+], 228 (41), 160 (70), 147 (38), 134 (100).

***trans*-2-(4-*N*,*N*-Dimethylaminophenyl)-6-(2,2,2-trifluoroethoxyethyl)bicyclo[3.3.0]octane (20)**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.2 and 2.15 (m, 2H), 1.4 and 1.8 (m, 2H), 1.7 and 2.0 (m, 2H) 1.8 – 1.9 (m, 2H), 2.45 – 2 – 8 (m, 3H; 1,2,5-H), 2.95 (s, 6H; NMe_2), 3.75 – 3.85 (m, ^3J(H,F) = 9 Hz, 2H; OCH_2), 3.8 (m, 1H; 6-H), 6.75, 7.07 ppm (AA′BB′, 4H; aromatics); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.5 (CH_2), 29.7 (CH_2), 31.3 (CH_2), 36.3 (CH_2), 41.2 (CH_3), 49.8 (CH), 50.2 (CH), 52.1 (CH), 65.9 (q, ^2J(C, F) = 35 Hz, 2H; OCH_2), 89.1 (CH), 113.5 (CH), 124.2(q, ^1J(C, F) = 275 Hz; CF_3), 127.9 (CH), 132.7, 148.3 ppm; NOE effect between 6-H (3.8) and 5-H (2.8); GC/MS: *m*/*z* (%): 327 (98) [M^+], 160 (95), 147 (55), 134(100).

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