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On the addition of 4-(*N*,*N*-dimethylamino)phenyl cation to norbornene†

Mariella Mella, Maurizio Fagnoni and Angelo Albini

Dept. Organic Chemistry, University of Pavia, v. Taramelli 10, 27100, Pavia, Italy.
E-mail: angelo.albini@unipv.it

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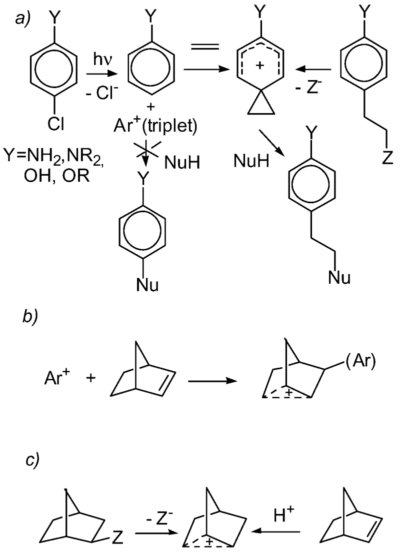
The photochemically generated 4-(*N*,*N*-dimethylamino)phenyl cation adds to norbornene giving a phenylnortricyclene and various 2-*exo* substituted phenylnorbornanes (main isomers, 3-*endo*-, 7-*anti*- and 7-*syn*-phenyl). Acetamides are obtained in MeCN and ethers in alcohols (MeOH, *iso*-PrOH, *tert*-BuOH, CF_3CH_2OH). The product distribution is closely reminiscent of that obtained in the solvolysis of 2-norbornyl derivatives, supporting that the reaction offers a novel access to a 'non classical' 2-norbornyl cation. The fate of this cation is determined by the basicity/nucleophilicity of the solvent.

Introduction

The synthesis of alkylaromatics and of biaryls by electrophilic attack of aryl cations on olefins and arenes is an appealing path that has received virtually no attention, due to the unavailability of the key intermediate.[1] In fact, while in the gas phase phenyl cations have been smoothly generated from tritiated derivatives and demonstrated to add to olefins,[2] there are only a couple of cases where such species have been generated in solution. These are the solvolysis of some perfluoroalkylsulfonic aryl esters,[3] the solvolytic cyclization of (trifluoromethanesulfonyl)oxydienynes[4] and the controlled (photo)decomposition of diazonium salts in the absence of reducing agents.[5] However, it has recently been found that electron-donating substituted phenyl cations can be conveniently generated by photoheterolysis from the corresponding aryl halides (Scheme 1a).[6–8] In this case the photochemical reaction was explored in the presence of alkenes and arenes and it was found that efficient trapping takes place. The resulting processes are ionic analogues of the Meerwein arylation of alkenes or of the Gomberg–Bachmann arylation of arenes and have been characterized for 4-chloroaniline, -phenol, and -anisole.[9,10] The successful arylation was due to the fact that in this case (differently from what happens with most diazonium salts)[5] the phenyl cation was generated in the triplet state. This intermediate selectively attacked π-nucleophiles, while n-nucleophiles such as alcohols or amines only attacked the adduct cation.[9,10] As an example, irradiation of a substituted phenyl halide in alcohol solution in the presence of an alkene gave a β-alkoxyalkylbenzene.

The first intermediate in the addition to alkenes can be envisaged either as a localized alkyl cation or as a bridged phenonium ion (Scheme 1, ethylene is indicated for simplicity). The situation is reminiscent of the extensively investigated solvolysis of β-arylalkyl systems. In that case, it has been shown that a continuous spectrum of species exists, from open-chain to fully bridged ions, depending on the structure of the starting material and on the medium.[11] The phenonium ion (a 'classical' cation) has been characterized in superacid medium, where it slowly rearranged to the more stable methylbenzyl cation.[12]

The structure of the products obtained from the reaction of chloroanilines and alkenes is consistent with a phenonium intermediate[9,10] and depends on the medium. In highly polar solvents, the final adducts to alkenes may involve rearrangement of the carbon skeleton.[13,14]



Scheme 1

We thought that more indications about the intermediates could be obtained from the reaction with norbornene, because addition would lead to an easily rearranging cation, 2-norbornyl cation (Scheme 1b). Furthermore, this species is the prototype of 'non classical' (alkyl bridged) carbocations.[15] The long debate on the structure of this cation has been based on a relatively small number of solvolysis reactions of 2-norbornyl derivatives, besides the characterization in superacid medium (Scheme 1c).[16] Thus, it may be interesting to arrive at the same species through a novel path under the mild conditions of the photochemical method.

In the following, we report the photoreaction of *N*,*N*-dimethyl-4-chloroaniline with norbornene in various solvents and compare the results with those obtained in the same reaction with other alkenes.[17]

Results

N,*N*-Dimethyl-4-chloroaniline was irradiated in acetonitrile in the presence of 1 M alkenes. With cyclopentene and cyclohexene it had been previously demonstrated[9] that, apart from some reduction to *N*,*N*-dimethylaniline, the virtually exclusive products were the corresponding *trans*-1-(4-*N*,*N*-dimethylaminophenyl)-2-chlorocycloalkanes **1** and **2** (Scheme 2). Competition experiments were now carried out in the presence of an equimolecular

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† Dedicated to Professor Ugo Mazzucato on occasion of his 75th birthday.

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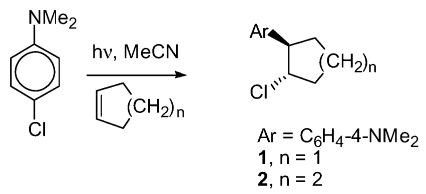
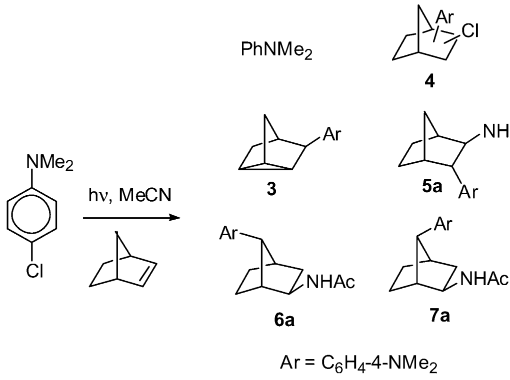


Scheme 2

amount of 2-norbornene (NB) and of one of the above cycloalkenes. The reduction in the formation of products **1** and **2** allowed evaluating the relative reactivity and gave the ratios NB : cyclohexene 67 : 33 and NB : cyclopentene 76 : 24.

The structure of the photoproducts from the chloroaniline and NB was next examined. A trace amount of the product of reductive dechlorination, *N*,*N*-dimethylaniline, was formed also in this case, but most of the products resulted from the combination with NB. Column chromatography gave in the first fractions an alkylated aniline, which was recognized by spectroscopic and analytic determinations to contain the nortricyclene skeleton (compound **3**, Scheme 3, Table 1). A minor product was present that according to GC/MS data resulted from the addition of the fragments of chloroaniline onto NB (generic structure **4**), but its amount was too low for a more detailed identification. The most abundant products, however, were contained in the slowly eluting fractions and were arylated *N*-norbornylacetamides. Three isomers were present in a sufficient amount for structure attribution on the basis of spectroscopic properties, particularly by NOE correlations as indicated in the Experimental section. The structures of 3-*endo*-phenyl-2-*exo*-acetylaminonorbornane (**5a**), 7-*anti*-phenyl-2-*exo*-acetylaminonorbornane (**6a**), and 7-*syn*-phenyl-2-*exo*-acetylaminonorbornane (**7a**) were assigned. Two further isomeric amides were present, as revealed by GC/MS, in too small an amount for allowing structure assignment.

The photochemistry of *N*,*N*-dimethyl-4-chloroaniline in the presence of NB was next examined in methanol (Scheme 4, Table 1). The phenylnortricyclene **3** was formed in a lower amount than in MeCN, while there was more of the aniline and the main products were phenylnorbornyl ethers, among which three main products were separated and identified as the 3-*endo*-phenyl-2-*exo*-methoxy- (**5b**), 7-*anti*-phenyl-2-*exo*- (**6b**) and 7-*syn*-phenyl-2-*exo*-methoxynorbornane (**7b**). These were accompanied by two minor isomers (see Experimental section).

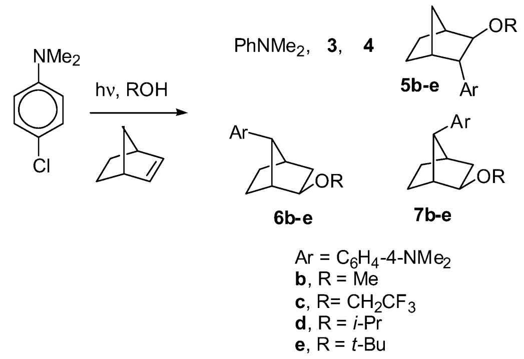


Scheme 3

Table 1 Products from the photolysis of 4-*N*,*N*-dimethyl-4-chloroaniline in the presence of 1 M norbornene

Solvent	Products (% Yield)
MeCN	**3** (33), **5a** (17), **6a** (22), **7a** (11), $PhNMe_2$ (tr)[a,b]
MeOH	**3** (17), **5b** (14), **6b** (27), **7b** (10), $PhNMe_2$ (7)[a]
CF_3CH_2OH	**3** (4), **5c** (18), **6c** (24), **7c** (17)[a]
i-PrOH	**3** (20), **5d–7d** (22), $PhNMe_2$ (16)[a]
t-BuOH	**3** (39), **5e–7e** (12), $PhNMe_2$ (2)[a,b]

[a] GC/MS examination shows that two further isomers of products **5–7** are present (cumulative intensity of the two peaks 8–10% of the sum of other isomers). [b] GC/MS shows a trace amount of a product with a (dimethylaminophenyl)chloronorbornane structure (**4**).



Scheme 4

The reaction in trifluoroethanol gave none of the aniline and very little of nortricyclene **3**. The predominating products were five arylnorbornyl trifluoroethyl ethers, of which the three main ones were characterized. These were the 3-*endo*-phenyl-2-*exo*- (**5c**), 7-*anti*-phenyl-2-*exo*- (**6c**) and 7-*syn*-phenyl-2-*exo*- (**7c**) norbornyl ethers.

Irradiation in *iso*-PrOH and, even more markedly, in *tert*-BuOH gave nortricyclene **3** as the major product. GC/MS indicated the presence of five isomeric ethers in each case, with a distribution pattern similar to the previous alcohols, but we did not succeed in separating and characterizing the single products. The overall yield of the ethers is reported in Table 1.

Discussion

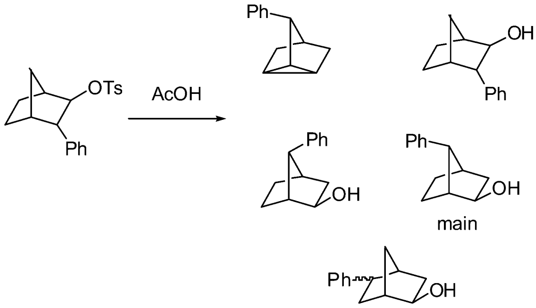
General mechanism of the addition to alkenes

It has been previously established that triplet 4-aminophenyl cation is formed under these conditions.[7,8] This species is remarkable for its non-reactivity with n-nucleophiles, which allows the study of the addition to alkenes with no competitive trapping by the solvent, even when this is a nucleophile. Competition experiments show that the cation reacts with NB 2 to 3 times faster than with monocyclic alkenes. Thus, the triplet aryl cation exhibits little discrimination among alkenes, in contrast with what has been observed with extensively delocalized cations, such as benzhydryl cations, for which the ratio is much higher.[18,19] This suggests that the phenyl cation reacts too rapidly for discriminating and leads to a similar adduct cation (phenonium) with all of the alkenes. Inspection of the previously calculated potential energy surface for the reaction with ethylene[9] suggests that intersystem crossing to the singlet state takes place at the phenonium ion configuration and at this stage reaction with n-nucleophiles ensues.

Product structures

Although NB appears not to differ from other alkenes in the first step of the reaction with dimethylaminophenyl cation, the end products have a different structure than those obtained from monocyclic alkenes. Considering the results in MeCN, there are two differences. First, the last alkenes undergo addition of the 4-aminophenyl group and of a chlorine atom across the double bond and no products from solvent trapping are obtained, while with NB a chlorinated adduct is formed only in traces. Indeed, cyclization to nortricyclene **3** and trapping by MeCN to finally yield acetamides (Ritter reaction) account for *ca.* 40 and 60% of the products, respectively. Second, the trapping products from NB involve a rearrangement. The three main isomers bear the phenyl group in 3-*endo*-, 7-*syn*, 7-*anti*- and the acetyl amino group in every case in 2-*exo*.

Carrying out the irradiation of NB in alcohols leads to the same chemistry. Nortricyclene **3** is formed again and is accompanied by norbornyl ethers, which replace the amides. Chloronorbornane (**4**) is a minor product in *tert*-butanol. The distribution of the ethers remains essentially the same with all of the alcohols tested and is similar to that of the amides in MeCN. What changes is the ratio between elimination, leading to **3**, and nucleophile addition, leading to isomeric norbornyl derivatives (**5**–**7**, besides two further isomers in a minor amount). The **3**/(**5**–**7**) ratios vary from 0.07 in trifluoroethanol to 0.3, 1 and 3.2 in methanol, *iso*-propanol and *tert*-butanol, respectively; the ratio is 0.65 in MeCN. The distribution is reminiscent of that obtained in nucleophile substitution reactions from 2-norbornyl derivatives (see *e.g.* the solvolysis of 3-phenyl-2-norbornyl tosylate in Scheme 5)[20] and in part of the addition of diarylmethyl cations (from the diarylmethyl halides with $ZnCl_2$ in ether) to NB, which gives the 7-*syn*- (main) and 7-*anti*-benzyl-2-*exo*-chloronorbornane.[21]

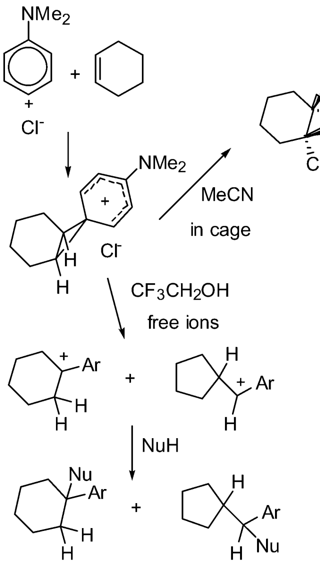


Scheme 5

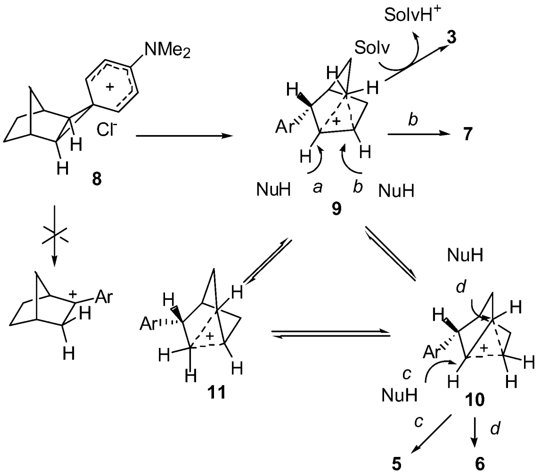
In cage *vs.* out of cage reactions

With monocyclic alkenes the structure of the products depends on the medium, however. As shown in Scheme 6 for cyclohexene, the products in trifluoroethanol have a different structure than those in MeCN. These contain a nucleophile different from chloride and a rearranged skeleton, resulting from hydride and alkyl Wagner–Meerwein rearrangement in the adduct cation to yield the more stabilized benzyl cations. Acetonitrile is likewise a nucleophile and it has been demonstrated that it traps phenonium ions.[22] Thus, the fact that no acetamide is formed from cyclohexene in MeCN and addition of chloride to give product **2** rather takes place in this solvent supports that the phenyl cation adds to the alkene when still paired with the counterion, so that C–C bond formation is immediately followed by chloride addition. Charge stabilization by trifluoroethanol, on the other hand, favors dissociation of the ion pair to free ions and under these conditions rearrangement of the cation occurs.[9]

In contrast, with NB, chlorinated adducts are in all cases formed in $\ll 5\%$, showing that no reaction occurs in the initial ion pair, apparently due to collapse of the cation to a more stable structure where the cationic site is away from the chloride anion. The results can be rationalized with reference to Scheme 7. The initial phenonium ion **8**, reasonably resulting from attack at the *exo* side, as it is generally observed with NB, rearranges before trapping to phenylated non-classical 2-norbornyl cation **9**.[23] Cyclization and deprotonation of this intermediate yields **3**. Nucleophile trapping (mainly by the solvent, since the chloride ion is not close by) occurs along path *b*, since path *a* is hindered by the phenyl group, and gives **7**. Degenerate equilibria are known to be fast in 2-norbornyl cation,[16] and amides or ethers of structure **5** and **6** result from the trapping of form **10** (paths *c*, *d*), with the nucleophile entering in *exo*-position. The products expected from the trapping of form **11** (2-*exo*-substituted 5-(*exo* or *endo*)-phenylnorbornanes) have not been isolated. On the basis of the observed fragmentation pattern in the mass spectrum, we hypothesize that these correspond to the two isomers detected in all cases as minor components by GC/MS. Compounds of such structure have actually been isolated as minor products in the solvolysis of 3-phenyl-2-norbornyl tosylate, see Scheme 5). Summing up, with NB the stabilization as a non-classical cation prevents in cage recombination with chloride occurring with simple olefins in a moderately polar solvent such as MeCN, and rearrangement occurs under all of the conditions tested.



Scheme 6



Scheme 7

Reactions of the phenylnorbornyl cation with bases/nucleophiles

As mentioned above, the elimination/addition ratio depends on the solvent. Importantly, in the series MeOH, *iso*-PrOH, *tert*-BuOH basicity increases (pK_b 2.95, 1.87 and 0.75 in CBr_2F_2)[24] and nucleophilicity decreases.[25] As an example, the rate of reaction of a delocalized cation such as Ph_2CH^+ decreases by a factor of 20 in going from methanol to *tert*-butanol (MeOH, 1.2×10^9; *iso*-PrOH, 3.1×10^8; *tert*-BuOH, 6.9×10^7 mol^{-1} s^{-1}).[26] This is consistent with the fact that deprotonation to yield **3** progressively overcomes nucleophile trapping along this series (Table 1).

The other two solvents tested, MeCN and CF_3CH_2OH, are much less effective *both* as bases and as nucleophiles.[25,27] Taking again Ph_2CH^+ as a model, trifluoroethanol[28] is only slightly more nucleophilic than acetonitrile[29] (3.2×10^6 *vs.* 2.5×10^6 mol^{-1} s^{-1}), both reacting much more slowly than the alcohols. Since MeCN is not a better base, the lower **3**/(**5**–**7**) ratio with TFE is reasonably due to the better solvation of the cation in the latter solvent, known for the high ionizing power.[27,30] This results in a better opportunity for trapping the cation even by a poor nucleophile.

While the reactivity order of norbornyl cation **8** with nucleophiles parallels that of benzylic cations, an important difference is that more stable products are formed. As an example, in the photolysis of benzhydryl chloride in MeCN, flash photolysis reveals fast addition of the cation to the solvent to give an iminium cation, but the actually isolated product is diphenylcarbinol, which cannot be due to direct trapping by water ($\leq$2 mM).[29] This shows that the reaction with MeCN is reversible in that case [eqn. (1)]. On the contrary, the present norbornyl cations ($\mathrm{ArNB^+}$) clearly give iminium cations stable enough to add moisture and give the Ritter amides [eqn. (2)] as the final products. Clearly, the stability attained by alkyl bridging in the non-classical cation can't be compared with the delocalization in a benzylic cation.

$$\mathrm{Ph_2CH^+ + MeCN \rightleftharpoons Ph_2CH\text{-}N{=}C^+\text{-}Me} \qquad (1)$$

$$\mathrm{ArNB^+ + MeCN \rightarrow ArNB\text{-}N{=}C^+\text{-}Me + H_2O \rightarrow ArNB\text{-}NHCOMe} \qquad (2)$$

Noteworthy is also the fact that neither a phenylnorbornene nor any 2-substituted 2-phenylnorbornane were obtained, or at least not in an amount sufficient for identification. These compounds would be expected if 2,3-hydride shift had occurred to give the 2-phenyl-2-norbornyl cation (see Scheme 7, left-hand). This is another indication that the initial phenonium ion rapidly collapses to the nonclassical structure, and is again reminiscent of the solvolysis of 2-*exo*-norbornyl derivatives, where such a shift does not take place.[20] By contrast, norbornene is a main product when the 2-norbornyl cation is generated *via* a SNi mechanism, such as the decomposition of (*exo* and *endo*) 2-norbornyloxychlorocarbene.[31]

Competing paths from the dimethylaminophenyl cation

Finally, an accompanying product in these reactions is *N*,*N*-dimethylaniline. It has been shown that triplet dimethylaminophenyl cation abstracts hydrogen efficiently.[7] Indeed, photodecomposition of *N*,*N*-dimethyl-4-chloroaniline in neat MeCN leads to 47% reduction and in MeOH or *iso*-PrOH the yield grows to 90%. Trapping by 1 M NB is overwhelming, but some aniline is formed in proportion to the hydrogen donating ability of the solvent, reaching 16% in *iso*-PrOH.

Conclusion

Summing up, a product distribution closely matching that obtained by solvolysis of phenylnorbornyl derivatives has been found when generating the key intermediate cation through a different path, addition of triplet 4-dimethylaminophenyl cation to norbornene. The selective reaction of this species with alkenes offers a novel access to a 2-norbornyl cation under mild non-acidic conditions. This allows the exploration (and to some degree the control) of the reaction of this non-classical intermediate in solvents of different basicity and nucleophilicity.

Experimental

Preparative irradiations in neat solvent

A solution of 195 mg *N*,*N*-dimethyl-4-chloroaniline (5×10^{-2} M) in 25 mL acetonitrile, methanol or other alcohols in a quartz tube was flushed with argon for 15 min. Norbornene (2.35 g, 1 M) was added, the flushing resumed for further 5 min and the tube was tightly capped. This was externally irradiated by means of 6 × 15 W (center 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.

Comparison of the alkenes

The irradiations were carried out as above in MeCN in the presence of cyclohexene and cyclopentene. Further experiments were carried out in the presence of equimolecular amounts of the previous cycloalkenes and NB. The ratio of the amounts of arylchlorocycloalkanes **1** and **2** in the presence and in the absence of NB was gas chromatographically determined

Product 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 containing 0.1% 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 a 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 $\mathrm{min^{-1}}$). The total run time was 30 min with the initial oven temperature 80 °C (4 min), rising at a rate of 10 °C $\mathrm{min^{-1}}$ to 250 °C. The structures of new compounds were assigned mainly on the basis of ^{1}H, ^{13}C, DEPT-135, HSQC and 2D-COSY and NOESY experiments. The characterization of nortricyclene **3** has been previously reported[14] and was recognized by comparison with an authentic sample. NMR, IR (where relevant) and MS data of new compounds are listed below. In ^{1}H NMR, the δ values of hydrogen atoms correlating with the same carbon are listed consecutively and connected by 'and'.

Irradiation in acetonitrile

3-*endo*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-acetylaminonorbornane (5a). (Found: C, 75.0; H, 8.9; N, 10.0. $\mathrm{C_{17}H_{24}N_2O}$ requires C, 74.96; H, 8.88, N, 10.28%); $\nu_{\max}$ (film)/cm^{-1} 3250, 1660; δ_{H} ($\mathrm{CDCl_3}$) 1.3 (m, 2H), 1.35 (m, 2H), 1.45 and 1.62 (two m, 2H), 1.96 (s, 3H), 2.31 (m, 1H), 2.47 (m, 1H), 2.71 (br t, J = 3.5 Hz, 1H), 2.92 (s, 6H), 3.98 (dt, J = 3.5, 2 Hz, 1H), 5.5 (br d, J = 3.5 Hz, exchanges with $\mathrm{D_2O}$, 1H), 6.70 and 7.08 (AA′BB′, 4H); δ_{C} ($\mathrm{CDCl_3}$) 21.5 ($\mathrm{CH_2}$), 23.4 ($\mathrm{CH_3}$), 26.9 ($\mathrm{CH_2}$), 37.2 ($\mathrm{CH_2}$), 40.6 ($\mathrm{CH_3}$), 41.7 (CH), 43.7 (CH), 55.7 (CH), 56.7 (CH), 112.6 (CH), 128.4 (CH), 127.8, 149.1, 162.0; *m*/*z* 272. Structure attribution supported by NOE between H-2 at δ 3.98 and aromatic protons at 7.08 and between H-3 at 2.47 and NH at 5.5 as well as one of the protons in 7 at 1.62.

7-*anti*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-acetylaminonorbornane (6a). (Found: C, 74.9; H, 9.0; N, 10.0. $\mathrm{C_{17}H_{24}N_2O}$ requires C, 74.96; H, 8.88, N, 10.28%); $\nu_{\max}$ (film)/cm^{-1} 3260, 1650; δ_{H} ($\mathrm{CDCl_3}$) 1.15 and 1.55 (two m, 2H), 1.25 and 1.58 (two m, 2H), 1.95 (s, 3H), 1.41 and 1.96 (two m, 2H), 2.55 (m, 1H), 2.58 (m, 1H), 2.85 (br s, 1H), 2.92 (s, 6H), 3.82 (m, 1H), 5.52 (br s, exchanges with $\mathrm{D_2O}$, 1H), 6.68 and 7.08 (AA′BB′, 4H); δ_{C} ($\mathrm{CDCl_3}$) 23.4 ($\mathrm{CH_3}$), 24.3 ($\mathrm{CH_2}$), 25.6 ($\mathrm{CH_2}$), 38.7 (CH), 40.6 ($\mathrm{CH_3}$), 40.7 ($\mathrm{CH_2}$), 45.3 (CH), 49.6 (CH), 53.1 (CH), 112.5 (CH), 128.1 (CH), 128.5, 148.7, 169.1; *m*/*z* 272. Structure attribution based on NOE between NH at δ 5.52 and H-7 and 2.85, H-2 at 3.82 and one of the protons in 3 at 1.96.

7-*syn*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-acetylaminonorbornane (7a). (Fraction containing some **6a**) (Found: C, 75.2; H, 9.1; N, 10.0. $\mathrm{C_{17}H_{24}N_2O}$ requires C, 74.96; H, 8.88, N, 10.28%); $\nu_{\max}$ (film)/cm^{-1} 3280, 1650; δ_{H} ($\mathrm{CDCl_3}$) 1.22 and 1.72 (two m, 2H), 1.30 and 1.70 (two m, 2H), 1.50 and 1.83 (two m, 2H), 1.58 (s, 3H), 2.62 (m, 1H), 2.72 (m, 1H), 2.92 (m, 1H), 2.95

(s, 6H), 3.85 (m, 1H), 4.7 (br s, exchanges with D_2O, 1H), 6.7 and 7.15 (AA′BB′, 4H); δ_C ($CDCl_3$) 23.2 (CH_3), 27.7 (CH_2), 28.5 (CH_2), 37.6 (CH), 37.9 (CH_2), 40.7 (CH_3), 46.5 (CH), 51.6 (CH), 52.9 (CH), 112.6 (CH), 127.9, 128.5 (CH), 149.0, 168.3; *m/z* 272. Structure attribution, in particular with regard to the *syn* arrangement of the phenyl ring based on the absence of NOE between H-2 at δ 3.85 and H-7 at 2.72 and on a weak cross peak between NH at 4.7 and the aromatic protons at 7.15. GC/MS of the photolyzed mixture showed two further peaks isomeric with **5a–7a** (*m/z* 272) and a minor chlorine-containing peak (*m/z* 249), attributed to an aminophenylchloronorbornane of generic structure **4**.

Irradiation in methanol

3-*endo*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-methoxynorbornane (5b). (Fraction containing some **6b**) (Found: C, 78.0; H, 9.5; N, 5.5. $C_{16}H_{23}NO$ requires C, 78.32; H, 9.45, N, 5.71%); δ_H ($CDCl_3$) 1.15 and 1.65 (two m, 2H), 1.25 (m, 2H), 1.38 (dq, J = 10 and 1.5 Hz, 1H), 1.80 (dt, J = 10 and 1.5 Hz, 1H), 2.38 (br s, 1H), 2.42 (br d, J = 4 Hz, 1H), 2.91 (br t, J = 3.5 Hz, 1H), 2.94 (s, 6H), 3.29 (s, 3H), 3.44 (dd, J = 3.5, 1.5, 1H), 6.70 and 7.10 (AA′BB′, 4H); δ_C ($CDCl_3$) 22.1 (CH_2), 25.1 (CH_2), 37.1 (CH_2), 40.9 (CH_3), 42.0 (CH), 41.8 (CH), 55.0 (CH), 56.1 (CH_3), 88.2 (CH), 112.8 (CH), 128.5 (CH), 129.6, 148.5; *m/z* 245. Structure attribution based on NOE between H-2 at δ 3.44 and aromatic protons at 7.10, H-3 at 2.91 and one of the protons in 7 at 1.80.

7-*anti*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-methoxynorbornane (6b). (Found: C, 78.2; H, 9.5; N, 5.5. $C_{16}H_{23}NO$ requires C, 78.32; H, 9.45, N, 5.71%); δ_H ($CDCl_3$) 1.00 and 1.58 (two m, 2H), 1.05 and 1.50 (two m, 2H), 1.65 (m, 2H), 2.54 (br t, J = 3.5 Hz, 1H), 2.68 (br d, J = 4 Hz, 1H), 2.95 (s, 6H), 3.11 (br s, 1H), 3.35 (s, 3H), 3.40 (dd, J = 7, 2.5, 1H), 6.7 and 7.15 (AA′BB′, 4H); δ_C ($CDCl_3$) 22.7 (CH_2), 26.0 (CH_2), 38.2 (CH), 39.9 (CH_2), 41.0 (CH_3), 43.1 (CH), 48.6 (CH), 55.9 (CH_3), 84.3 (CH), 112.8 (CH), 128.3 (CH), 129.9, 148.1; *m/z* 245. The structure assignment is based on the comparison with isomer **7b** and the fact that no NOE correlation between H-7 at δ 3.11 and H-2 at 3.40 was found. The absorption of H-7 was too close to that of the methoxy group to allow an NOE test.

7-*syn*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-methoxynorbornane (7b). (Found: C, 78.2; H, 9.5; N, 5.5. $C_{16}H_{23}NO$ requires C, 78.32; H, 9.45, N, 5.71%); δ_H ($CDCl_3$) 1.10 (m, 1H) and 1.27 (m, 1H), 1.60 and 1.70 (two m, 4H), 2.65 (br s, 1H), 2.83 (br s, 1H), 2.85 (br d, J = 4 Hz, 1H), 2.92 (s, 6H), 3.12 (s, 3H), 3.36 (ddd, J = 6, 4, 2 Hz, 1H), 6.70 and 7.10 (AA′BB′, 4H); δ_C ($CDCl_3$) 26.6 (CH_2), 28.5 (CH_2), 37.5 (CH_2), 38.1 (CH), 40.9 (CH_3), 42.1 (CH), 51.8 (CH), 55.9 (CH_3), 85.4 (CH), 112.5 (CH), 128.4 (CH), 129.5, 148.1; *m/z* 245. The *syn* arrangement was supported by NOE between the methoxy group at δ 3.12 and aromatic protons at 7.10 as well as between H-2 at 3.36 and both H-5 at 1.10 and H-6 at 1.27. A support was also the large coupling constant between H-7 at 2.85 and H-2 at 3.36 (J = 4 Hz). GC/MS of the photolyzed mixture showed two further peaks isomeric with **5b–7b** (*m/z* 245).

Irradiation in trifluoroethanol

3-*endo*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-(2,2,2-trifluoroethoxy)norbornane (5c). (Found: C, 65.4; H, 7.3; N, 4.3. $C_{17}H_{22}F_3NO$ requires C, 65.16; H, 7.08, N, 4.47%); δ_H [$(CD_3)_2CO$] 1.20 and 1.61 (two m, 2H), 1.23 (m, 2H), 1.45 and 1.80 (two m, J_{AB} = 10.5 Hz, 2H), 2.45 (br s, 1H), 2.50 (br s, 1H), 2.98 (s, 6H), 3.02 (br s, 1H), 3.85 (br s, 1H), 4.01 (m, 2H), 6.75 and 7.8 (AA′BB′, 4H); δ_H ($CDCl_3$) 21.9 (CH_2), 24.8 (CH_2), 36.9 (CH_2), 41.6 (CH), 41.7 (CH), 54.8 (CH), 65.9 (CH_2, q, J = 32 Hz), 88.1 (CH), 113.2 (CH), 123.2 (q, J = 250 Hz), 128.5 (CH), 135.8, 148.4; *m/z* 313. Structure attribution based on NOE between H-3 at δ 3.02 and one of the protons in 7 at 1.80 as well as between H-2 at 3.85 and the aromatic protons at 7.08. Moreover, a long-range correlation between H-2 at one of the H-7 at 1.45 was evidenced by H,H DQF-COSY.

7-*anti*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-(2,2,2-trifluoroethoxy)norbornane (6c). (Found: C, 65.1; H, 7.3; N, 4.2. $C_{17}H_{22}F_3NO$ requires C, 65.16; H, 7.08, N, 4.47%); δ_H ($CDCl_3$) 1.12 and 1.40 (two m, 2H), 1.19 and 1.61 (two m, 2H), 1.8 (m, 2H), 2.63 (br s, 1H), 2.75 (br s, 1H), 2.90 (s 6H), 3.11 (br s, 1H), 3.73 (m, 1H), 3.75 (m, 2H), 6.80 and 7.05 (AA 'BB', 4H); δ_C ($CDCl_3$) 22.9 (CH_2), 26.3 (CH_2), 38.7 (CH), 40.3 (CH_2), 41.5 (CH_3), 44.0 (CH), 48.9 (CH), 66.0 (CH_2, q, J = 32 Hz), 85.0 (CH), 113.3 (CH), 123.2 (q, J = 250 Hz), 128.7 (CH), 135.5, 149.1; *m/z* 313. The *anti* arrangement was attributed on the base of the close similarity with analogous compounds **6a** and **6b** and by the fact that no NOE was observed either between H-2 at δ 3.73 and H-7 at 3.11 or between H-2 at 3.75 and the aromatic protons at 7.05.

7-*syn*-(4-*N*,*N*-Dimethylaminophenyl)-2-*exo*-(2,2,2-trifluoroethoxy)norbornane (7c). (Found: C, 65.2; H, 7.3; N, 4.2. $C_{17}H_{22}F_3NO$ requires C, 65.16; H, 7.08, N, 4.47%); δ_H ($CDCl_3$) 1.15 and 1.71 (two m, 2H), 1.20 and 1.60 (two m 2H), 1.75 (m, 2H), 2.71 (br s, 1H), 2.80 (br s, 1H), 2.88 (br s, 1H), 2.91 (s, 6H), 3.65 (m, 1H), 3.75 (m, 2H), 6.81 ad 7.15 (AA′BB′, 4H); δ_C ($CDCl_3$) 26.9 (CH_2), 28.9 (CH_2), 37.8 (CH_2), 38.8 (CH), 41.2 (CH_3), 43.7 (CH), 52.3 (CH), 66.5 (CH_2, q, J = 32 Hz), 85.7 (CH), 113.2 (CH), 123.2 (q, J = 250 Hz), 129.0 (CH), 136.1, 149.5; *m/z* 313. The structure attribution was supported by a weak NOE between the ether CH_2 at 3.75 and the aromatic protons at δ 7.15, absent in **6c**. GC/MS of the photolyzed mixture showed two further peaks isomeric with **5c–7c** (*m/z* 313).

Irradiation in other alcohols

GC/MS of the photolyzed mixture in *iso*-PrOH showed, beside the aniline and **3**, five peaks attributable to formula $C_{18}H_{27}NO$ (*m/z* 273), with a distribution pattern similar to the previous cases (two of them in a minor amount). However, chromatographic separation gave, apart from **3**, a single fraction containing all of the isomers and we did not succeed in characterizing the individual compounds. The same held for the irradiation in *tert*-BuOH, where five peaks attributable to formula $C_{19}H_{29}NO$ (*m/z* 287) were detected along with a large amount of **3** and a small peak corresponding to the chlorinated peak observed in MeCN (see above).

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