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# A novel access to 3-aryl-2-norbornyl cation

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**A novel access to a 2-norbornyl cation under mild, non acidic conditions is found in the addition of photochemically generated 4-dimethylaminophenyl cation to 2-norbornene. Deprotonation to nortricyclene or nucleophile addition ensue depending on the solvent characteristics.**

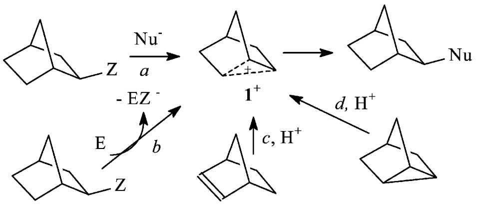
2-Norbornyl cation (**1**$^+$, Scheme 1) is the prototype 'non classical' (alkyl bridged) carbocation and it has been the subject of extensive investigation, with regard both to its role in solvolytic reaction (Scheme 1, path *a*) and to its generation and spectroscopic characterization under 'superacid' conditions (paths *b–d*).[1] The impressive amount of work that has been devoted to this topic over more than four decades has been based upon a small number of reaction types and it appears desirable to explore different paths to such an intermediate.[2]

In this connection, we considered the recent finding that photolysis of 4-chloro (and fluoro) anilines in a polar solvent generates the corresponding phenyl cation (**2**$^+$, Scheme 2),[3] an intermediate otherwise difficult to access in solution,[4] and that this adds to alkenes, not to σ nucleophiles such as alcohols. As an example, irradiation in the presence of alkenes in acetonitrile gives 4-(β-chloroethyl)anilines and in methanol 4-(β-methoxyethyl)anilines (**4**). These were rationalized through the intermediacy of a phenonium cation (**3**$^+$).

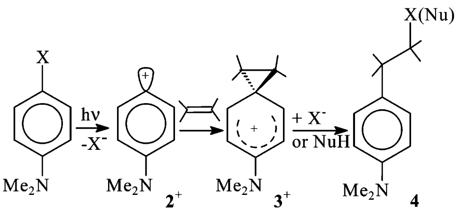
The latter ion pertains to another family of extensively investigated intermediates and, contrary to norbornyl cation, has been characterized as a classical carbocation under superacid conditions.[5] The photolysis of chloroanilines in the presence of norbornene was thus expected to lead to adduct cation(s) under mild, non acidic conditions and we were curious to explore which chemical paths would be followed.

Irradiation of *N*,*N*-dimethyl-4-chloroaniline in acetonitrile containing 1 M norbornene gave a single major product, which was isolated in 33% yield and recognized as 2-arylnortricyclene **5** (see Table 1 and Scheme 3).[6,7]

The result changed when the irradiation was carried out in nucleophilic, protic solvents such as alcohols. Under these conditions product **5** was accompanied by arylalkoxynorbornanes, present as three main isomers with two further components in traces, in a proportion that depended on the alcohol chosen. Thus, with methanol the yield of product **5** was reduced to 17% and the ethers became the main products. These were recognized as the following methyl ethers: 3-*endo*-aryl-2-*exo*-norbornyl (**6a**, 11%), 7-*syn*-aryl-2-*exo*-norboryl (**7a**, the main component, 30%) and 7-*anti*-aryl-2-*exo*-norbornyl (**8a**, 10%).[7] Likewise, in trifluoroethanol the corresponding ethers were by far the main products with structures **6d–8d** (**5** was reduced to 4%).[7] On the other hand, irradiation in *iso*-propanol and in *tert*-butanol gave a progressively increasing proportion of the tricyclene **5** and a lower yield of arylnorbornyl ethers. These were again three main isomers as shown by GC/MS, presumably of structure **6b–8b** and **6c–8c**, although in these cases the small amount hindered a detailed identification. A minor product in methanol (7%) and in *iso*-propanol (12%) was



**Scheme 1**

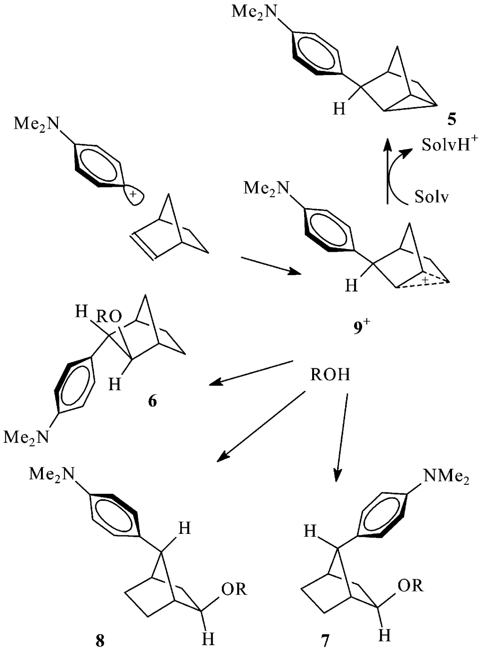


**Scheme 2**

**Table 1** Aminophenylnorbornane derivatives from the photolysis of 4-*N*,*N*-dimethylchloroaniline in the presence of 1 M norbornane

| | Products (% Yield) | | | | |
|---|---|---|---|---|---|
| Solvent | **5** | **6** | **7** | **8** | PhNMe$_2$ |
| MeCN | 33 | | | | |
| MeOH | 17 | 14 | 27 | 10 | 7 |
| *i*-PrOH | 20 | [a] | [a] | [a] | 16 |
| *t*-BuOH | 39 | [b] | [b] | [b] | 2 |
| CF$_3$CH$_2$OH | 4 | 18 | 24 | 17 | |

[a] Products **6–8**, cumulative yield 22%. [b] Cumulative yield 12%.



**a**, R=Me; **b**, R=*i*-Pr; **c**, R=*t*-Bu; **d**, R=CF$_2$CF$_3$

**Scheme 3**

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*N*,*N*-dimethylaniline. By comparison, this was the main product from the irradiation of the chloroaniline in neat acetonitrile (47%), methanol or isopropanol (90%).

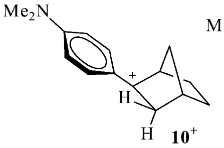
Thus, the phenyl cation is generated and effectively trapped by the alkene (only in hydrogen-donating media such as MeOH and *i*-PrOH reduction to aniline competes to a limited extent). This yields the 3-aryl-2-norbornyl cation **9**$^+$, which gives the reactions expected from a 'nonclassical' cation. In acetonitrile loss of a proton leads to nortricylene **5**. The reaction is the reverse of the generation of the 2-norbornyl cation from nortricyclene under superacidic conditions (path *d* in Scheme 1). The alternative product of deprotonation, 2-arynorbornene, has not been detected, though the unsatisfactory material balance leaves room for different paths.[6]

The result in alcohols depends on the acidity and nucleophilicity of these solvents. Thus, bulky and poorly acidic *tert*-butanol does not slow down deprotonation of the norbornyl cation and gives only a small amount of ethers (ratio **5**/ethers 3.25). With *iso*-propanol and methanol this ratio drops to 1 and 0.4. With acidic trifluoroethanol, deprotonation is effectively suppressed (ratio **5**/ethers 0.1).

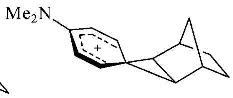
The products obtained from the reaction in alcohols are those expected from addition to cation **9**$^+$, with the nucleophile entering *exo* as generally observed in these reactions.[1,8] Further isomers such as 5-aryl-2-norbornyl ethers which would arise from different H-bonded isomers of **9**$^+$ are not among the main products, but may correspond to further isomers present in minute amounts.

The product distribution obtained is closely reminiscent of that resulting from solvolysis of 2-norbornyl derivatives, For example, the acetolysis (AcOH/AcONa) of 2-(*endo*)phenyl-3-(*exo*)tosyloxynorbornane yielded the norbornanols (R = H) **6** (23) and **7** (44) as the main products, accompanied by a minor amount of **8** (5) and some phenyltricylene (14%).[9] Neither in such thermal solvolysis nor in the present photoinduced addition were any 2-phenyl-2-norbornyl derivatives found. Thus, 2, 3-hydrogen shift leading to (classical) 2-aryl-2-norbornyl cation (**10**$^+$) has no significant role. In contrast, we previously found[3] that addition of phenyl cation to simple alkenes leads in part to rearranged benzyl derivatives through hydrogen shift from a phenonium cation (here hypothetical **11**$^+$ → **10**$^+$).

In conclusion, the above reaction offers a novel entry to the long studied 2-norbornyl cation, which occurs in solution under unprecedented mild, non acidic conditions. The product distribution obtained confirms the 'non classical' chemistry of the 2-norbornyl cation, also when formed by phenyl cation addition, different from the phenonium ion path followed with simple olefins under the same conditions.



**10**$^+$



**11**$^+$

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6 Irradiation for 2 h by external 15 W lamps, 310 nm;[3] samples were routinely Ar-flushed; omitting this slowed the reaction to 3 h, but did not change product distribution. No other volatile products are formed. Addition to the solvent and polymerization are presumed to account for the remaining material.

7 New products were analytically and spectroscopically characterized.

8 Except for the 2-*exo*-3-*exo*-aryl ethers, possibly due to steric hindering.

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