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Novel photoreaction of *N*-alkyl(*p*-methoxyphenyl)arylamines assisted by protic acids

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A novel photochemical transformation from *N*-alkyl(*p*-methoxyphenyl)arylamines (1a–1f) to 1,2,4-trihydro(4a*H*)-carbazol-3-ones (2a–2f) is reported with the assistance of protonation at the dihydrocarbazole intermediate followed by sequential formal [1,5]hydrogen, [1,3]hydrogen shifts and proton assisted hydrolysis.

Aliphatic as well as aromatic amines are photolytically sensitive, for example, *N*-methyldiphenylamines can be effectively photocyclized to *N*-methylcarbazole.[1–5]

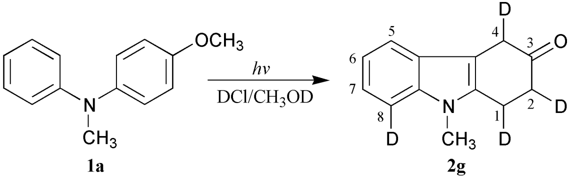
The reactive intermediates studied by laser flash photolysis are believed to involve the triplet state of *N*-methyldiphenylamine and zwitterionic dihydrocarbazole.[6]

We have prepared various *N*-methyl(*p*-methoxyphenyl)-arylamines **1a–1f** (Scheme 1) by using the coupling reaction with tris(dibenzylideneacetone)dipalladium(0) $Pd_2(dba)_3$ and imidazolium salt IprHCl (Ipr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as catalysts.[7] We would like to report here a novel photochemical transformation of **1a–1f** with the assistance of an external protic acid.

A degassed acetonitrile solution containing *N*-methyl-(*p*-methoxyphenyl)phenylamine **1a** (5×10^{-3} M) and 2.5×10^{-4} M aqueous hydrochloric acid[8] was irradiated with a Rayonet photolysis apparatus (16 × 12 W) at 300 nm for 20 min. The hydrochloric acid was removed and the solvent was evaporated to afford only two products. The major one after column chromatography (silica gel and n-hexane–ethyl acetate = 3 : 1 as eluent) was 9-methyl-1,2,4-trihydro(4a*H*)-carbazol-3-one **2a** in 85% yield.[9] The minor product was *N*-methyl-3-methoxycarbazole (15% yield). Photolysis without aqueous HCl or with a higher concentration of aqueous HCl (0.5 M) will not lead to the isolation of the major product **2a**, because complete protonation occurs at the amine nitrogen atom when a higher acid concentration is used.

The conversions and yields for the series of *N*-alkyl(*p*-methoxyphenyl)arylamines **1a–1f** are summarized in Table 1 along with the structures of the products. All products (**2a–2f**) are supported by spectroscopic data and **2a** is a known compound.[10] Compound **1d** with two methoxy groups has the highest yield (96%). Compound **1e** shows such high regioselectivity that the only isolated product is **2e**.

When **1a** is irradiated in the presence of 2.5×10^{-4} M DCl in CH_3OD at 300 nm for 20 minutes the isolated product **2g** shows deuterium labeling at positions 1(50%), 2(73%), 4(64%) and 8(43%) [eqn. (1)].[11] This experiment



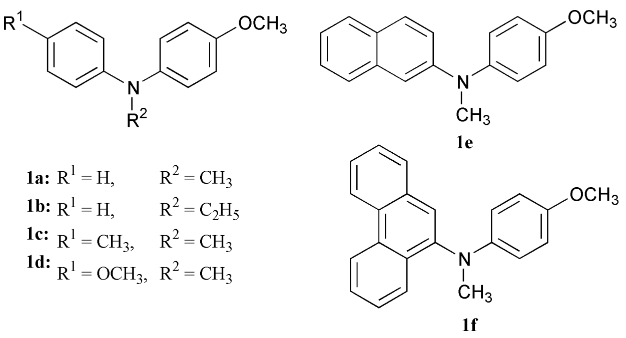
(1)

shows the positions of protonation (positions 1,4 in **DHC**) and proton exchange (positions 2,8 in **DHC**) in the photolysis media.

A conceivable mechanism based on the experimental results is summarized in Scheme 2. The zwitterionic dihydrocarbazole intermediate (**DHCa**) derives from a six electron cyclization in the triplet state.[6] The dihydrocarbazole intermediate (**DHCb**) is from **DHCa**.[12] Then follows a formal [1,5]hydrogen shift to afford the dihydrocarbazole (**DHCc**) and a formal [1,3]hydrogen shift to another dihydrocarbazole (**DHCd**). Then the acid assisted hydrolysis of **DHCd** leads to the product.

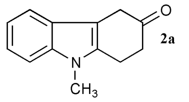
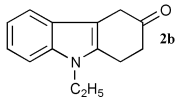
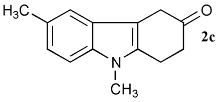
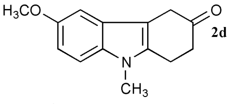
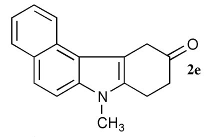
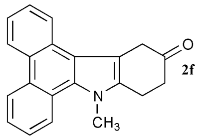
In conclusion, a novel and efficient photochemical reaction is reported for a series of *N*-alkyl(*p*-methoxyphenyl)arylamines through the protonation of the zwitterionic dihydrocarbazole intermediate followed by a series of formal [1,*n*]hydrogen shifts. Four dihydrocarbazole intermediates (**DHCa–DHCd**) are involved in the reaction.

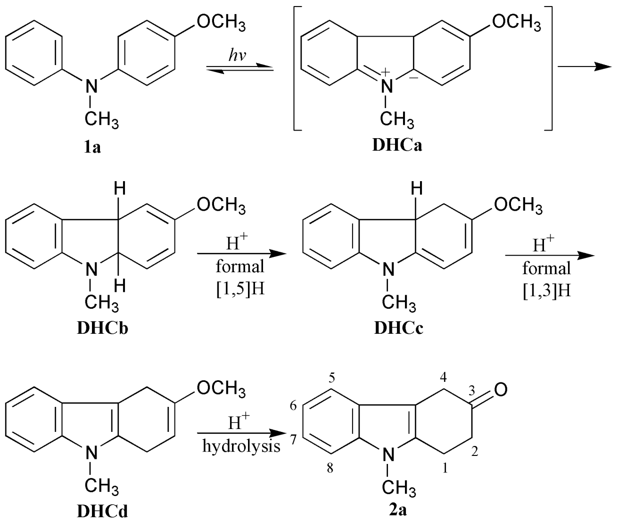
This photochemical reaction can afford new trihydrocarbazol-3-one in a clean and efficient way.



Scheme 1 Reactants of the various diarylamines.

Table 1 Conversions and yields of the photoreactions of **1a–1f**

Reactants	*hν* time (h)	Conversion (%)	Products	Yield (%)
1a	0.33	100		85
1b	0.33	100		84
1c	0.33	100		72
1d	0.33	100		96
1e	2	58		60
1f	3	100		60



Scheme 2 Mechanism for the photoreaction of the *N*-methyl-(*p*-methoxyphenyl)phenylamine **1a** to **2a** (deuterium exchange occurs at 1,2,4 and 8 positions).

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Notes and references

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8 The aqueous HCl solutions were prepared by dilution of the concentrated aqueous HCl in acetonitrile solution.
9 The spectral data for compound **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.22 (td, J = 7.4, 1.1 Hz, 1H), 7.11 (td, J = 7.4, 1.3 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 2H), 3.16 (t, J = 6.8 Hz, 2H), 2.82 (t, J = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): d = 209.53, 137.59, 133.19, 126.22, 121.59, 119.33, 117.76, 108.97, 106.09, 38.55, 36.50, 29.37, 21.62; MS (EI, 70eV) m/z (%): 199 (M^+, 92), 170 (100), 157 (8), 144 (17), 128 (10), 115 (9); HRMS ($C_{13}H_{13}NO$) estimated: 199.0997, calculated: 199.0991.
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