行政院國家科學委員會專題研究計畫成果報告

N-烷基二苯胺光化學反應
Photochemistry of *N*-Alkyldiphenylamines

計畫編號：NSC 90-2113-M-002-031
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中文摘要

研究二苯胺衍生物及類似物在酸催化下之光化學反應。化合物 *N*-烷基（*p*-甲氧基苯基）芳香環基胺（1a-1f）在酸催化下會進行一種新型態的光重排反應，而產生一系列 1,2,4-三氫(4aH)-卡唑-3-酮之衍生物及類似物（**2a-2f**）。反應機構是經由中間體二氫卡唑質子化後，再相繼經過形式上的[1,5]、[1,3]氫轉移和甲基醚水解而完成。

關鍵詞：雜環化合物、質子化、光化學、重排反應。

Abstract

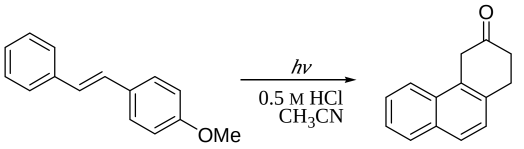
A novel photochemical transformation from *N*-alkyl(*p*-methoxyphenyl)arylamines (**1a-1f**) to 1,2,4-trihydro(4aH)-carbazol-3-ones (**2a-2f**) is reported with the assistance of protonation at the dihydrocarbazole intermediate followed by sequential formal [1,5]hydrogen, [1,3]hydrogen shifts and proton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

Keywords: heterocycles, protonation, photochemistry, rearrangement.

Introduction

Aliphatic as well as aromatic amines are photolytically sensitive, for example, *N*-methyldiphenylamines can be effectively photocyclized to *N*-methyl-carbazole.[1-5] The reactive intermediates studied by laser flash photolysis are believed to involve triplet state of *N*-methyldiphenylamine and zwitterionic dihydrocarbazole.[6]

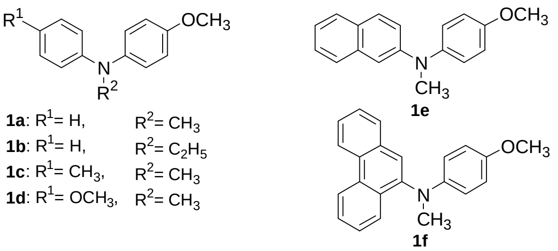
Diphenylamines can undergo many photochemical reactions which are similar to the stilbene-type system, for example, photocyclization and photoinduced electron transfer. In our previous work, we have found a novel acid-catalyzed photorearrangement of stilbenes and we would like to report here a novel photochemical transformation of **1a-1f** with the assistance of an external protic acids.



Results

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]

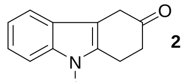
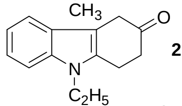
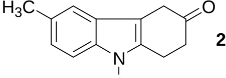
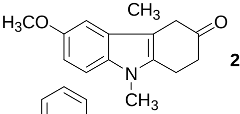
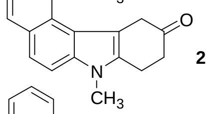
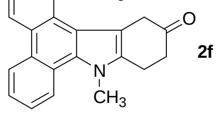
Scheme 1 Reactants of the various diaryamines



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 300nm for 20 minutes. 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) is 9-methyl-1,2,4-trihydro(4aH)-carbazol-3-one **2a** in 85% yields.[9] The minor product is *N*-methyl-3-methoxycarbazole (15% yield). Photolysis without aqueous HCl or with higher concentration of aqueous HCl (0.5M) will not lead to the isolation of the major product **2a**, because of complete protonation occurs at the amine nitrogen atom when higher acid concentration is used.

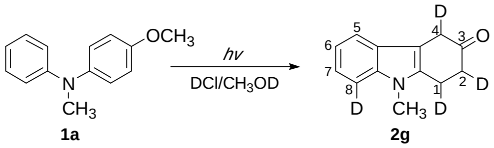
The conversions and yields for the series of *N*-alkyl(*p*-methoxyphenyl)arylamines **1a**-**1f** are summarized in Table 1 along with the structure of the products. All products (**2a**-**2f**) are supported with spectroscopic data and compound **2a** is a known compound.[10] Compound **1d** with two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

Table 1 Conversions and yields of the photo-reactions of **1a**-**1f**.

React.	*hv* time(h)	Conver(%)	Products		Yield(%)
1a	0.33	100		**2a**	85
1b	0.33	100		**2b**	84
1c	0.33	100		**2c**	72
1d	0.33	100		**2d**	96
1e	2	58		**2e**	60
1f	3	100		**2f**	50

When **1a** is irradiated in the presence of 2.5×10^{-4} M DCl in CH$_3$OD at 300nm for 20 minutes the isolated product **2g** show that the content of deuterium labeling at 1(50%), 2(73%), 4(64%) and 8(43%) positions [Eq.(1)].[11] This experiment shows the positions of protonation (position 1,4 in

DHC) and proton exchange (position 2,8 in **DHC**)in the photolysis media.

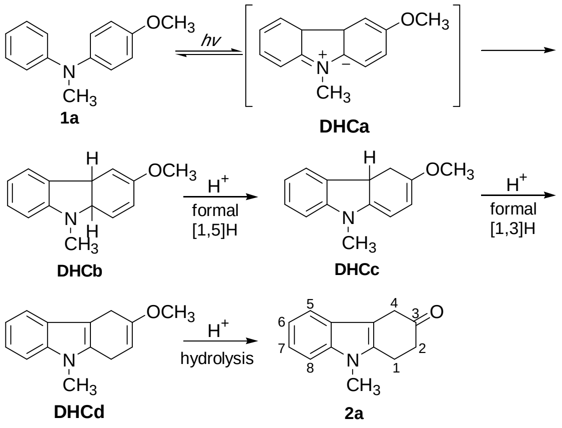


(1)

Discussion

A conceivable mechanism is summarized in Scheme 2 based on the experimental results.

Scheme 2 Mechanism for the photoreactions of the *N*-methyl-(*p*-methoxyphenyl)phenylamines **1a** to **2a** (Deuterium exchange occurs at 1,2,4 and 8 positions)

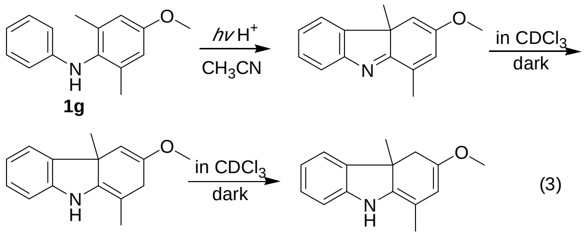


The zwitterionic dihydrocarbazole intermediate (**DHCa**) derives from a six electron cyclization in the triplet state.[6] The dihydrocarbazole intermediate (**DHCb**) is from **DHCa**.[12] Then follows a formal [1,5] hydrogen shift to afford the dihydrocarbazole (**DHCc**) and a formal [1,3] hydrogen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

In conclusion, a novel and efficient photochemical reaction is reported for a series of *N*-alkyl(*p*-methoxyphenyl)aryl-amines 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 trihydro-carbazol-3-one in a clean and efficient way.

In the presence of two ortho methyl substituents in the *p*-methoxyphenyl ring, compound **1g** and **1h**, shows different reaction products (Equation 3 and Scheme 3) as compared with the 1,2,4-trihydro(4aH)-carbazol-3-one reaction pathway.

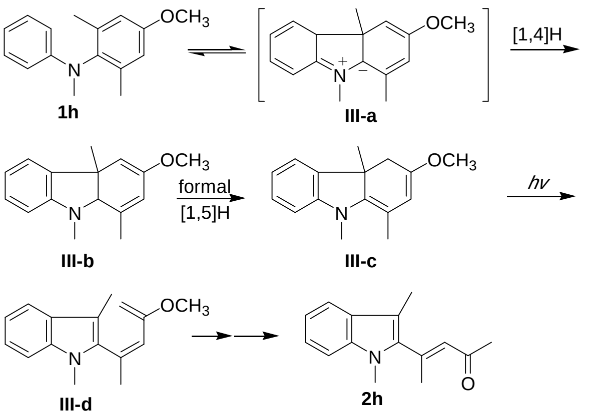


(3)

Thus the mechanism is quite different. A possible reaction mechanism for this photochemical transformation is described in Scheme 3.

The formation of dihydrocarbazole intermediates **III-a** and **III-b** is adapted from the previous studies.[6] Competitive demethane reaction leading to the formation of oxidative cyclized product and [1,5] hydrogen shift leading to the formation of intermediate **III-c** is the course of the product distribution. Then a six-electron photocycloreversion has occurred to obtain the butadienyl indole intermediate **III-d**. Followed by the acid catalyzed hydrolysis to obtaine the product **2h**. The more stable *trans*-product is derived from the *cis*-product by photochemical isomerization.

Scheme 3 Mechanism for the photoreactions of the *N*-methyl-(4-methoxy-2,6-dimethylphenyl)-phenylamines **1h** to **2h**.



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8 The aqueous HCl were prepared by dilution of the concentrated aqueous HCl in acetonitrile solution.

9 The spectral data for compound **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): = 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, $CDCl_3$): = 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/e (%): 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.

10 A. Urrutia, J. G. Rodriguez, *Tetrahedron* **1999,** *55,* 11095-11108.

11 The exchange occurs only in the presence of light. The solvent can also be D_2O containing acetonitrile. There is no deuterium exchange found in position 6 due to the low electron density.

12 K. H. Grellmann, U. Schmitt, *J. Am. Chem. Soc.* **1982**, *104*, 6267-6272.

附件：封面格式

行政院國家科學委員會補助專題研究計畫成果報告

Ｎ－烷基二苯胺光化學反應

計畫類別：□個別型計畫　　□整合型計畫
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計畫主持人：何東英 台灣大學化學系
共同主持人：
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